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Defect Levels in the Amorphous Selenium Bandgap

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Dedication

To my mother and to the memory of my father to my daughters and to my wife Nadia iv

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Contents

List of Abbreviations							
Samenvatting							
Introduction							
1	Am	orphou	us chalcogenides	11			
	1.1	Energ	y bands in amorphous semiconductors	11			
		1.1.1	The solution in the crystalline case	12			
		1.1.2	Amorphous materials	13			
		1.1.3	Electron localization	17			
	1.2	Bondi	ng in amorphous semiconductors	17			
		1.2.1	Bonding defects in amorphous semiconductors	19			
		1.2.2	Behavior of the Fermi level	27			
	1.3	Seleni	um	28			
		1.3.1	Microstructure of selenium	28			
		1.3.2	Optical properties of a-Se	30			
		1.3.3	Electronic properties	32			
2	Pho	otocon	ductivity techniques	35			
	2.1	Gener	al concepts	35			
	2.2	Steady	y-state photoconductivity	40			
		2.2.1	Effect of light intensity	41			
		2.2.2	Effect of temperature	42			
	2.3	Optica	al absorption coefficient	45			
	2.4	Transient photocurrent techniques					
		2.4.1	Time-of-flight technique	46			
		2.4.2	Transient photocurrent	50			
		2.4.3	Multiple-trapping transport model	51			

3	$Th\epsilon$	ermal transitions in the negative-U energy scheme for a-	
	\mathbf{Se}		57
	3.1	Steady-state photoconductivity	57
		3.1.1 Experimental results	57
		3.1.2 Discussion	61
	3.2	Post-transit photocurrent analysis (PTPA)	64
		3.2.1 Experimental results	66
		3.2.2 Discussion	68
	3.3	Transient photocurrent decay	73
		3.3.1 Experimental results	73
		3.3.2 Discussion	75
	3.4	Concluding discussion	75
1	Ont	ical transitions in negative-U model	77
-	4.1	Experimental conditions	78
		4.1.1 Samples	78
		4.1.2 Experimental set-ups	78
	4.2	Experimental results	80
	4.3	Discussion	83
	4.4	Conclusion	86
5	Def	ects not related to the negative-U system	87
<u> </u>		8	~ •
0	5.1	Experimental considerations	87
0	$5.1 \\ 5.2$	Experimental considerations	87 88
0	$5.1 \\ 5.2$	Experimental considerationsExperimental results5.2.1Deep levels	87 88 88
	5.1 5.2	Experimental considerationsExperimental results5.2.1Deep levels5.2.2Shallow levels	87 88 88 90
	5.1 5.2 5.3	Experimental considerationsExperimental results5.2.1Deep levels5.2.2Shallow levelsDiscussion	87 88 88 90 95
	5.1 5.2 5.3	Experimental considerations	87 88 88 90 95 95
	5.15.25.3	Experimental considerationsExperimental results5.2.1Deep levels5.2.2Shallow levelsDiscussion5.3.1Deep levels5.3.2Shallow levels	87 88 88 90 95 95 95
	5.15.25.35.4	Experimental considerations	87 88 90 95 95 97 00
6	 5.1 5.2 5.3 5.4 Tail 	Experimental considerations	 87 88 88 90 95 95 97 .00
6	 5.1 5.2 5.3 5.4 Tail 6.1 	Experimental considerations	 87 88 88 90 95 95 97 .00 03 03
6	 5.1 5.2 5.3 5.4 Tail 6.1 	Experimental considerations	87 88 88 90 95 95 97 .00 03 .03
6	 5.1 5.2 5.3 5.4 Tail 6.1 	Experimental considerations	87 88 88 90 95 95 95 97 .00 03 .03 .03
6	 5.1 5.2 5.3 5.4 Tail 6.1 	Experimental considerations	87 88 88 90 95 95 95 95 97 .00 03 .03 .03 .05 07
6	 5.1 5.2 5.3 5.4 Tail 6.1 6.2 6.3 	Experimental considerationsExperimental results5.2.1Deep levels5.2.2Shallow levelsDiscussion5.3.1Deep levels5.3.2Shallow levelsConclusion1 I-state distributions in a-Se 16.1.1Transient photocurrent method16.1.2Drift mobility method1Conclusion11 <td>87 88 88 90 95 95 95 97 .00 03 .03 .03 .03 .05 .07</td>	87 88 88 90 95 95 95 97 .00 03 .03 .03 .03 .05 .07
6	 5.1 5.2 5.3 5.4 Tail 6.1 6.2 6.3 	Experimental considerations	87 88 90 95 95 97 00 03 03 03 05 07 09
6	 5.1 5.2 5.3 5.4 Tail 6.1 6.2 6.3 Pho 	Experimental considerations Image: Constraint of the system of the s	87 88 90 95 95 97 .00 03 .03 .03 .05 .07 .09 11
6	 5.1 5.2 5.3 5.4 Tail 6.1 6.2 6.3 Photo 7.1 	Experimental considerations Image: Consideration for the second seco	87 88 90 95 95 97 .00 03 .03 .03 .03 .03 .07 .09 11 .12

viii

CONTENTS

	7.1.2	Samples illuminated with natura	al light						114
	7.1.3	Halogen lamp illumination							114
	7.1.4	Annealing effect					•		116
7.2	Discus	sion					•		116
7.3	Conclu	$sion \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots$					•		119
Summary and conclusions 12							121		
Bibliography						125			
Publica	ation I	ist							133

ix

CONTENTS

х

List of Abbreviations

Amorphous selenium
Conduction band
Constant photocurrent method
Continuous random network
Direct current
Density of states
Electron spin resonance
Kastner, Adler and Fritzsche
Light-induced electron spin resonance
Photothermal deflection spectroscopy
Post-transit photocurrent analysis
Steady-state photoconductivity
Time-of-flight
Transient photoconductivity
Tiedje and Rose and Orenstein and Kastner
Valence band

Samenvatting

De elektronische toestandsdichtheid in de bandkloof van amorf seleen (a-Se) is het onderwerp van deze thesis. Ondanks de lange voorgeschiedenis van amorf seleen als de eerste fotogeleidende halfgeleider, die onder meer werd gebruikt in fotocopiëerapparaten en als elektronische schakelaar, zijn een aantal van zijn eigenschappen nog steeds twijfelachtig en zelfs onbekend gebleven. Een kenschetsend voorbeeld van deze toestand is het feit dat, hoewel een zeer specifiek, op seleen gebaseerd model voor coördinatiedefecten met effectieve negatieve elektroncorrelatie-energie (negatieve-U) als tekstboekvoorbeeld wordt gebruikt voor dergelijke defecten in het amorfe rooster, sommige onderzoekers er nog aan twijfelen of de toestandsdichtheid van het amorfe seleen zelf wel dergelijke roosterdefecten omvat.

Het gangbare model voor de toestandsdichtheid van a-Se werd in 1988 door Abkowitz voorgesteld. Naast steile bandstaarten aan beide zijden van de bandkloof bevat het model twee ondiepe defectniveaus, zowat 0.3 eV verwijderd van de bandkanten, en twee diepe vangstcentra ongeveer in het midden van de 1.95 eV brede bandkloof en symmetrisch ten opzichte van het Fermi-niveau. Verschillende elementen van dit model moeten evenwel in vraag worden gesteld. De activeringsenergie van de driftmobiliteit van zowel gaten als elektronen werd ten onrechte gebruikt als energieafstand van de ondiepe niveaus tot de bandkanten, en van de diepe toestanden werd verondersteld dat ze met thermische overgangen overeenkomen in het negatieve-U model hoewel dat model zelf hogere energieën veronderstelt. Een nieuwe, gedetailleerde studie van de a-Se toestandsdichtheid is bijgevolg aangewezen.

Om die toestandsdichtheid van het a-Se te onderzoeken wordt in deze thesis vooral gebruik gemaakt van een aantal stationaire en transiënte fotogeleidingstechnieken. Er wordt aangetoond dat a-Se wel degelijk tot de groep van de negatieve-U materialen mag worden gerekend. Het energieschema voor verschillende ofwel thermisch ofwel optisch geïnduceerde elektronische transities die gepaard gaan met het geheel van elektrisch geladen, negatieve-U defecten kon worden afgeleid.

Voor de thermische overgangen naar het negatief geladen defect D⁻ wordt op basis van post-transit analyse van de 'time-of-flight' (TOF) transiënte fotostroom een niveau gelocaliseerd ~ 0.4 eV boven de valentieband, E_V , terwijl de temperatuursafhankelijkheid van de stationaire fotostroom tot een waarde van ~ 0.36 eV boven E_V leidt. Het verschil laat zich verklaren door een waargenomen sensitisatie van de stationaire fotostroom bij lage temperaturen. Voor de thermische overgangen naar het positief geladen D⁺ wordt anderzijds een niveau ~ 0.53 eV onder de conductiebandkant, E_C , gevonden op basis van zowel de TOF post-transit analyse als van de stationaire fotostroommetingen.

De optische absorptie door bemiddeling van de negatieve-U centra werd bestudeerd aan de hand van de constante-fotostroom-methode en van fotothermische deflectiespectroscopie. Het aan D⁺ verbonden absorptieniveau ligt ~ 1.5 eV boven E_V , en absorptie vanuit D⁻ naar E_C vraagt ~ 1.75 eV. Deze waarden plaatsen de optische transitieniveaus net voorbij de thermische niveaus naar de bandkanten toe, en suggereren dat het potentiaalprofiel van de D⁺ en D⁻ defecten slechts een kleine kromming vertoont in configuratieruimte. Het geheel van de gevonden thermische en optische transitieenergieën sluit goed aan bij het algemeen concept van de negatieve-U defecten, maar is duidelijk in tegenspraak met het hoger geciteerde Abkowitz model.

Naast de negatieve-U defecten bevat de a-Se toestandsdichtheid evenwel ook nog neutrale defecten dicht bij de bandkanten, en diepe defecten in de buurt van de het Fermi-niveau. Waar een knik in het pre-transit elektron TOF-signaal op de aanwezigheid wijst van een discreet defectniveau 0.3 eV beneden E_C , duidt een analoge knik in de transiënte fotostroom gemeten in een co-planaire elektrodegeometrie, op een corresponderend niveau 0.2 eV boven E_V . Dat beide ondiepe centra elektrisch neutraal zijn blijkt uit hun lage waarden voor de ontsnappingsfrequentie: eerder 10^{10} Hz dan de 10^{12} Hz van de geladen D^+ en D^- defecten. Een moleculaire configuratie waarbij de niet-bindende p-orbitalen van twee Se buren parallel met elkaar eerder dan loodrecht ten opzichte van elkaar georiënteerd zijn kan als oorsprong van die defecten worden aangewezen. Voor de defecttoestanden diep in de bandkloof is het niet mogelijk hun positie precies te bepalen. Hun aanwezigheid, als zowel elektronen- als gatenvangstcentrum, wordt afgeleid uit het verlies van de signaalamplitude bij repetitieve TOF metingen omwille van recombinatie met lading in de diepe vangsteentra. Het diepe elektron-vangsteentrum leidt tevens tot sensitisatie van de stationaire fotostroom bij lage temperaturen.

Tenslotte werd ook aandacht besteed aan de bandstaarten van het a-Se. Een analyse van de gatenmobiliteit in functie van temperatuur en aangelegd elektrisch veld laat toe een exponentiële toestandsverdeling met een karakteristieke energie van 25 meV voor te stellen als achtergrondsdichtheid aan de valentiebandkant van de bandkloof. Modelberekeningen voor de TOF stroomtransiënten ondersteunen die analyse. Omwille van de veldonafhankelijkheid van de elektronenmobiliteit zijn voor de conductiebandkant van de kloof enkel modelberekingen beschikbaar. Ze wijzen op een exponentiële verdeling met 20 meV als karakteristieke energie.

Samenvattend mag worden gesteld dat deze thesis het heuristische Abko-

Samenvatting

witz model heeft kunnen vervangen door een omstandig gedocumenteerd model dat zowel de geladen coördinatiedefecten van het negatieve-U systeem omvat als ondiepe neutrale toestanden veroorzaakt door afwijkende orbitaaloriëntaties, en diepe vangstcentra van nog ongewisse oorsprong.

Samenvatting

Introduction

Selenium (Se), one of the chalcogen elements (sulphur, selenium and tellurium), has been the first photoconductor discovered in 1873 [1]. W. Smith was using rods of Se as resistors to test sub-marine telegraphic cables when he discovered that its resistance depends on whether the resistor is illuminated or not. The selenium solar cell was reported in 1883 by Charles Fritts, and it was available in the market from the 1920s until the 1950s when silicon solar cells were produced. The crystalline form of selenium was used in electrical rectifiers from the 1930s to the 1960s; after this it was replaced by silicon devices. However, its more important application was in xerography [2]; this application continued until the late 1980s when organic semiconductors emerged. The photoconductivity of Se, in its amorphous form, is still attractive. Today, two imaging applications are using it: The first is its use as an avalanche photoconductor in ultrahigh sensitivity vidicon tubes (HARPICONs) [3]; the second is its use as an X-ray photoconductor in direct conversion X-ray detectors [4].

These last two applications stimulated the research work on amorphous selenium (a-Se), especially on its electronic properties. It is surprising that, despite this long history of Se usage our knowledge about it is really not sufficient to understand many of its properties. Se has two main crystalline forms, trigonal γ -Se constructed of infinite helical chains and monoclinic Se consisting of 8-fold Se rings. In the trigonal Se, holes are the more mobile carriers [5], while electron mobility is higher in the monoclinic crystal [6]. It is accepted that a-Se is constructed of random chains, in such a way that all atoms are two-fold coordinated in chains with a constant dihedral angle, but this angle is changing its sign randomly [7]. This makes a-Se a mixture of chain and ring fragments that allows both electrons and holes to attain measurable drift mobilities.

In 1988 Abkowitz [8] proposed a model for the electronic density of states in the a-Se band gap. This model consists of steep tail-state distributions in both sides of the gap, two features at about 0.3 eV from the band edges, and two deep defect bands near the mid-gap Fermi level. While the 0.3 eV features were erroneously deduced from drift mobility measurements of holes and electrons in function of temperature and field [9], the two midgap levels were deduced from xerographic residual potential data that are difficult to interpret. This makes the Abkowitz model doubtful and justifies a re-examination of the density of states (DOS) distribution in the gap of a-Se.

Another reason for investigating the a-Se DOS lies with the fact that selenium is used routinely as an example to illustrate the concept of negative effective electron correlation energy (negative-U concept) in chalcogenides [10]. However, in spite of the existence of a detailed model for the negative-U defects in a-Se [11], doubts were raised concerning the actual negative-U character of the material [12] [13]. Recently Kolobov [14] presented experimental proof, based on light-induced electronic spin resonance (LESR) for the presence of the negative-U defects in a-Se. However, this still leaves the position of the defect energy levels in the band gap unresolved. It is still relevant therefore, to probe this with other simple techniques like steady-state photoconductivity (SSPC). The negative-U centers are characterized by a strong electron-phonon coupling that leads to different transition energies for thermal and optical excitations. Consequently one needs several experimental techniques to track the different possible transitions in a negative-U system scheme. The thermally accessible levels can be seen using the timeof-flight (TOF) technique and SSPC. The optically accessible ones can be seen using the constant photocurrent method (CPM), spectral photocurrent distribution, and photo-thermal deflection spectroscopy (PDS).

Theoretical considerations predict that in negative-U systems the energetic positions of the concerned defects are situated roughly one quarter of the forbidden gap from the bands edges. For a-Se the energy gap is around 2 eV, then two defect levels will be somewhere around 0.5 eV from the edges. However the presence of these negative-U centers does not preclude the existence of other non-related defects in the a-Se lattice.

The glass transition temperature of selenium is just above room temperature, around 42 °C, which makes a-Se rather unstable and in danger of unintended crystallization. To avert this problem in technological applications, a trace of As, in the order $0.5 \ at\%$, is added to stabilize the a-Se matrix. The glass transition temperature of stabilized selenium is about 70 °C. This thesis contains a study of the electronic properties of pure and stabilized a-Se, thin films or bulk, using the above techniques in order to deal with the previously cited problems. This thesis is divided in 7 chapters as follows:

In Chapter 1 a brief review of some relevant topics concerning the physics of amorphous semiconductors is given. These topics include the band structure in amorphous semiconductors, and some new terms in comparison with crystalline materials, like mobility edge and localization. Subsequently, the specific case of chalcogenide semiconductors will be discussed. These are compounds where one (or more) of the chalcogens are an essential component. The emphasis will be on amorphous selenium and its properties, as it is the subject of this thesis.

Introduction

In Chapter 2 the photoconductivity in semiconductors will be introduced as an experimental tool to probe the electronic properties of the material. Indeed, the extra free charge carriers created by the photon absorption will contribute to the electronic transport under an applied electric field. They will interact with material defects, and at the end these extra charge carriers are injected in the external circuit or just recombine in different ways. Two different regimes can be discussed in the photocurrent. First there is the transient one and secondly the steady state. In both cases the photocurrent forms the basis of several experimental techniques, some of which will be used in this study of a-Se.

In Chapter 3 the focus will be on the T⁺ and T⁻ levels related to the negative-U model in a-Se using transient TOF, TPC and SSPC techniques. The detection of the T^+ and T^- levels will be a first step to answer the question wether a-Se is a negative-U system or not.

Chapter 4 will focus on the optical transitions involved in the negative-U model. the energetic position of the corresponding levels will be further evidence that, as other chalcogenides, a-Se is a negative-U system.

In Chapter 5 evidence for the existence of deep levels around the Fermi level, and shallow defects in the neighborhood of the band-edges will be given. These defects are not related to the charged ones involved in the negative-U model. The shallow ones are traced to a specific defect in the dihedral angle that puts lone pairs in a-Se parallel rather than perpendicular.

In Chapter 6 the tail-state distribution at both sides of the bandgap will be discussed. Experimentally, for the valence band side the variation of hole mobility in function of temperature and applied field and TPC will be used to probe the steepness of tail-state distribution. For conduction band side the only alternative for the study of the tail-state distribution are calculations.

Finally Chapter 7 presents the effect of light soaking on the DOS of a-Se. It contains the surprising observation of a photo-induced change in a-Se that is stable at room temperature, in spite of the low glass transition temperature.

Introduction

Chapter 1

Amorphous chalcogenides

This chapter gives a brief review of some relevant topics concerning the physics of amorphous semiconductors. These topics include the band structure in amorphous semiconductors, and some new terms in comparison with crystalline materials, like mobility edge and localization. Subsequently, the specific case of chalcogenide semiconductors will be discussed. These are compounds where one (or more) of the chalcogens are an essential component. The emphasis will be on amorphous selenium and its properties, as it is the subject of this thesis. More detailed information is available in the textbooks by Elliott [10] and Mott and Davis [15].

1.1 Energy bands in amorphous semiconductors

Crystalline materials consist of an arrangement of a structural unit (one or more atoms) in a three-dimensional ordered network. Using quantum mechanics theory, physicists are able to analyse electronic properties of crystalline semiconductors with their high degree of symmetry. The long-range order not only simplifies considerably mathematical calculation of the crystal system, but it forms the base to solve the Shrödinger equation for an electron in a crystal. Amorphous materials in the other hand do not exhibit this long-range order, and the existence of such materials with comparable characteristics to the crystalline ones stimulated physicists to reexamine the role of long-range order in defining the electronic properties of solids. The key point is that amorphous materials do not lose every sense of order. It was demonstrated that at short range crystalline and amorphous materials have comparable structures.

1.1.1 The solution in the crystalline case

In an isolated atom, quantum mechanics predicts that electrons can lie only in discrete possible states with discrete energy. The distribution of the electrons of this atom over these possible states obeys Pauli's exclusion principle, that one electronic state can support only two electrons, one with spin up and the other with spin down. This fact is the origin of the properties of any element. In this thesis we are dealing with elements that have eight possible states (spin taken into account) in the outermost shell. According to the number and distribution of electrons at each atom, these atoms can bond (as will be shown briefly below) to form a molecule or a solid. At this stage atomic or molecular orbitals spread to form bands of energy, where electrons can lie in a solid. The last fully occupied band is called valence band and the first allowed but unoccupied band is called the conduction band. If there is an energy gap (forbidden gap) between the top of the valence band and the bottom of the conduction band that is small (generally less than 2.5 eV), and if the Fermi level is situated in this forbidden gap the material in question is a semiconductor.

What we saw in the last paragraph is a phenomenological description of the energetic distribution of electrons in a solid. To find a mathematical description we use several approximations to reduce the problem from a manyelectron one to a single-electron problem. This is possible by taking into account the electron-electron interaction in a chosen effective one-electron potential $U(\mathbf{r})$. We can write the Shrödinger equation for an electron in a crystalline solid as follows:

$$H\Psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})\right)\Psi = E\Psi,\tag{1.1}$$

where H is the Hamiltonian, m the electron mass, E the energy eigenvalue and Ψ is the wave function.

According to Bloch's theorem the wave function of an electron in the periodic potential of a crystal is a plane wave times a function with the same periodicity as the crystal lattice:

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}).$$
(1.2)

The vector \mathbf{k} is a quantum vector defined in the reciprocal space while \mathbf{r} is characteristic of the periodic potential of the lattice. For a Given vector \mathbf{k} there are many solutions to the Shrödinger equation, with discretely spaced eigenvalues, as indicated by the index n in the above equation. The energy levels of an electron in the solid crystal are thus described by the functions

 $E_n(\mathbf{k})$. These functions are continuous in reciprocal space, with each value of n defining a band of allowed electron energies in the crystal. Collectively they are referred to as the electronic band structure of the crystal.

1.1.2 Amorphous materials

In amorphous materials the band structure problem is more complicated by the lack of long-range order. The word amorphous suggests that there is no order in the network, but in reality it turns out that the short-range order in amorphous materials is practically the same as in the corresponding crystalline materials. Using this short-range order it is possible to demonstrate that amorphous materials do have a band structure, the absence of long-range order notwithstanding.

Microstructure in amorphous materials

To describe the short-range order we use the radial distribution function (RDF) which derives its significance from the fact that it is obtained directly from diffraction experiments. This function, symbolized as J(r), is defined as the number of atoms lying at distances between r and r+dr from the center of an arbitrary origin atom. It can be written as

$$J(r) = \frac{dn}{dr} = 4\pi r^2 \rho(r), \qquad (1.3)$$

where n is the number of atoms, and $\rho(r)$ is a density function that is zero at distances less than the average of nearest-neighbors interatomic distance and equal to the average density, ρ^0 , at very large value of r where the material becomes isotropic. Between these two limits, $\rho(r)$ will exhibit an oscillatory behavior, with the peaks representing the average inter-atomic separations as shown in Fig.1.1. Correspondingly, the RDF shows oscillation about the average density parabola represented by the curve at the top in Fig.1.2. The first peak in J(r) lies at r_1 which is the distance of the first neighbors shell from the arbitrary chosen central atom. for $r < r_1$, J(r) is essentially zero.

It is important in this RDF that the area under a given peak gives the effective coordination number for that particular shell of atoms. While the first peak in the RDF is generally sharp, the second peak is broader than the first and gives the next-nearest-neighbor distance r_2 , as indicated in Fig.1.2. Given the parameters r_1 and r_2 one can immediately deduce the bonding angle θ using the formula

$$\theta = 2\sin^{-1}(\frac{r_2}{2r_1}). \tag{1.4}$$



Figure 1.1: Schematic illustration of the structural origin of certain features in the density function for an amorphous solid.

The RDF is a spatially averaged one-dimensional representation of a threedimensional structure, and it is valid only when the material is isotropic.

Using the idea of long-range disorder and short-range order (topological disorder), Zachariasen has introduced the **continuous random network**(CRN) [16]. In this model he proposed that the atomic arrangement in glass is characterized by an extended three dimensional network which lacks periodicity and symmetry. In this network each atom has a specific number of bonds to its immediate neighbors. The number of bonds of each atom follows the 8-N rule [17], whereby each atom bonds to N, respectively 8-N neighbors depending on whether its number of valence electrons N is less, respectively, 4 or more. Fig.1.3 shows an example of such CRN. This model is an idealized description of amorphous materials. Indeed, it introduces only topological disorder by allowing small variations in the bond lengths and angles, but neglects completely other kinds of disorder, like coordination defects or chemical disorder.

1.1. Energy bands



Figure 1.2: Schematic illustration showing the relationship between shortrange structural parameters: first and second-nearest neighbor bond lengths, r_1 and r_2 , and bond angle θ as deduced from the first two peaks in the RDF.



Figure 1.3: (a) Representation of a hypothetical two-dimensional crystalline oxide A_2O_3 , (b) The Zachariasen model for the amorphous form of the same compound.



Figure 1.4: Schematic representation of wavefunctions and interactions in the Weaire-Thorpe Hamiltonian.

Weaire and Thorpe model

Since the lack of periodicity and long-range order in amorphous materials makes it impossible to define a reciprocal space or to use the Bloch theorem, it is not possible to form the classical $E(\mathbf{k})$ band structure diagram. Instead we use the concept of **density of states**, that is also valid for the crystalline case. The density of states is given by the formula

$$g(E) = \frac{1}{V} \sum_{n} \delta(E - E_n), \qquad (1.5)$$

where g(E) is the DOS per unit volume and per unit energy interval, V is the volume of the system, and the summation n runs over all allowed states.

Weaire and Thorpe were the first to demonstrate the possibility of a band gap between allowed bands in a tetrahedral, fully connected network [18] like amorphous silicon or germanium. In their calculations only the short-range interactions were used in the tight binding approximation as shown in Fig.1.4 and the Hamiltonian

$$H = \sum_{\alpha i j} V_1 |\alpha i\rangle \langle \alpha j| + \sum_{\alpha \beta i} V_2 |\alpha i\rangle \langle \beta i|, \qquad (1.6)$$

where V_1 , respectively V_2 , is the strength of the intrasite, respectively intersite interaction, and the wavefunctions $|\alpha i\rangle$ and $|\beta i\rangle$ are the four sp^3 -hybridized orbitals that are localized at each atomic site. These orbitals combine as $B = \frac{1}{\sqrt{2}}(|\alpha i\rangle + |\beta i\rangle)$ to give the bonding state and as $A = \frac{1}{\sqrt{2}}(|\alpha i\rangle - |\beta i\rangle)$ to give antibonding states in the covalent network. Applying the Hamiltonian to these wavefunctions gives two ranges of permitted energies. If $V_1/V_2 < 0.5$ a bandgap $E_g = 2|V_2 - 2V_1|$ arises between bonding and antibonding states; otherwise, the two energy ranges overlap. The importance of this model lies not in its quantitative use but in the fact that it did put an end to the questioning if whether amorphous materials do or do not have a band structure, and that it showed the band structure to be mostly defined by the short-range order.

1.1.3 Electron localization

It was shown above that small deviations (fluctuations) of bond lengths and angles from the crystalline values lead to topological disorder. This disorder causes two major effects in amorphous semiconductors. The first one is tailing of permitted bands in the forbidden gap, which makes the band edges less sharp than in the crystalline case, as sketched in Fig.1.5. The second one is the localization of some of the electronic states, in the sense that an electron lying in one of these states has a wavefunction amplitude that is almost zero except in a limited space surrounding a particular lattice site; this is expressed by $\Psi \propto \exp(-\alpha r)$. It is important to point out that this is different from extended states in crystalline materials where the amplitude of the electronic wavefunction has a constant non-zero value through the crystal; in this case the wavefunction is written $\Psi \propto \exp(-i\mathbf{k}.\mathbf{r})$. This effect is known as "Anderson localization" [19].

If we have a band of width B, in the crystalline case, and a total energy range W, in the amorphous case, over which the atomic potential fluctuates (Fig.1.6), a full localization for all one-electron states of the band can be proven if W/B > C [19] where C is a model-dependent constant.

In practice disorder in amorphous semiconductors is not large enough to localize all states of the valence and conduction bands [20][21]. It has been shown that localization happens only in tail states and that there is a sharp limit between extended states and localized ones of the same band. This leads automatically to a sharp change in the carrier mobility value at energies E_v and E_c . These two energies are called mobility edges, such that we can speak also about the mobility gap in amorphous semiconductors besides the optical one that reflects the tailing of states in the forbidden gap.

1.2 Bonding in amorphous semiconductors

When atoms form stable solids, it means that they are in favorable energy configurations. In covalent semiconductors this favorable low-energy state is



Figure 1.5: (a) Parabolic DOS for a crystalline semiconductor; (b) and (c) include the smearing-out of the band edges, which is caused by topological disorder; in (c) localized states in the gap are caused by the bonding defects.



Figure 1.6: (a) Representation of potential wells for a crystalline lattice and the density of states expected for a tight-binding model.(b) Representation of the potential wells of the Anderson model and the density of states expected for a tight-binding model.

1.2. Bonding in amorphous semiconductors

achieved through the formation of covalent bonds between outer electrons from neighboring sites. Such bonding lifts the degeneracy of the atomic energy levels and produces a σ bonding orbital at lower energy and a raised anti-bonding orbital σ^* . In the solid the number of atoms is very large which causes these states to broaden into bands.

The Mott 8 - N rule mentioned earlier [17] is the rule that covalent semiconductors obey in bonding. For instence, the elements in column IV of the periodic table have an outer shell of 2s and 2p electrons. Since, in bonding, an atom strives to achieve a "complete" N=8 outer shell, the column IV element will form 4 highly directional sp^3 hybridized orbitals, pointing to the four corner of a tetrahedron, where they will link up with analogous orbitals from neighboring sites. Such bonding is assumed in the Weaire-Thorpe model, and defines the structure of semiconductors like silicon and germanium. Elements of column VI such as the chalcogens (sulphur, selenium and tellurium) have 6 electrons at the outer shell, 2 paired in an s state and 4 in the p state, 2 of the latter are of course being paired. In this case each atom makes two covalent bonds using the unpaired electrons in the p states. The paired electrons form the so-called lone-pair band that, as it will be seen, plays a crucial role in the properties of chalcogens and chalcogenides. Fig.1.7 represents the electronic structure of an isolated chalcogen atom and a solid where the s, σ and lone-pair orbitals form the valence band (VB), and the σ^* orbitals form the conduction band (CB). It is important to point out here that the lone-pairs make up the top of the valence band.

1.2.1 Bonding defects in amorphous semiconductors

In crystalline semiconductors each atom is, in the ideal case, fully coordinated to its neighbors. However for the same semiconductor in its amorphous state this is not the case. Due to the random distribution of bond lengths and angles it can happen that an atom does not find the right number of neighbors to satisfy its bonding requirement, in which case we can find an over-coordinated or under-coordinated atom. The former is characteristic for chalcogenides while the later is also found in tetrahedrally-bonded semiconductors like amorphous silicon and germanium.

It is well known that the typical defect in amorphous silicon is the dangling bond which is an sp^3 orbital that does not participate in bonding. This defect makes pure amorphous silicon not useful for any practical purposes. On the other hand, hydrogenated amorphous silicon occupies an important place in thin film transistors and solar energy cell applications. This is possible because hydrogen passivates the dangling bonds and reduces the density of states in the gap. Analogous neutral dangling bonds are not energetically



Figure 1.7: (a) Electronic configuration of an isolated chalcogen atom. (b) When chalchogen atom bonds two of the four p-state electrons will help form two bonds while the two others do not participate in bonding and form a lone pair. The bonding leads to the appearance of the σ and σ^* levels. (2 of the 8 electrons are from a neighboring atom). (c) Solid-state interaction broadens the atomic levels into bands.

favorable in chalcogenides, as will be shown below. This gives rise to a combination of charged under-coordinated and over-coordinated atoms to form the energetically most favorable defects.

As a rule, the bonding defects create localized states that, energetically, lie in the forbidden energy gap. These states play an important role in the electronic properties of amorphous semiconductors. When two electrons occupy the same defect center the correlation energy between these electrons will have to be considered. It was found that this correlation energy is positive in tetrahedrally coordinated semiconductors and negative in chalcogenides.

Positive correlation energy

In tetrahedrally coordinated semiconductors a dangling bond has one unpaired electron and sits on a three-fold coordinated site. As this site is electrically neutral, it is written as D^0 and lies at the middle of the gap at the position of the sp^3 -hybridized atomic orbital. D^0 is a paramagnetic center and can be seen by the ESR technique. When the defect accepts a second electron, it becomes a negatively charged one, written as D^- , and the energy of the level rises by an amount U (Hubbard energy) corresponding to the Colombic repulsion between the two electrons. This case is typical for

1.2. Bonding in amorphous semiconductors

positive correlation energy defects.

Negative effective correlation energy

While the prominent ESR signal in tetrahedrally coordinated amorphous semiconductor is an efficient tool to probe the defects density in these materials, no equilibrium ESR signal has been detected in most of the chalcogenides 1 [22] [23]. This does not only mean that we lost a tool to probe the defects in chalcogenides, but it also gives rise to a fundamental question as to why these materials do not show any spin resonance? A first explanation was given by Anderson [24]. Since the absence of an ESR signal at dark equilibrium, means that no significant amount of unpaired electrons are present in the material, he proposed that strong electron-phonon coupling in the chalcogenides allowed doubly occupied sites to lower their energy below that of the singly occupied ones. Such polaronic deformation of the lattice is facilitated by the two-fold coordination of the chalcogen atoms in the lattice which makes the network very flexible. This flexibility is the key to explain the lack of neutral dangling bonds D^0 , and thus unpaired electrons. Street and Mott [25] filled in this idea as follows: The dangling bond in chalcogenides is doubly occupied and is therefore a negatively charged defect D^- . Charge neutrality requires that D^{-} should be compensated by another defect having the same density and the opposite charge state D^+ .

The harmonic lattice potential has a minimum at configuration coordinate q = 0 and can be written as

$$V = \frac{Cq^2}{2},\tag{1.7}$$

where C is a constant. The lattice deformation due to electron-phonon interaction can be written as

$$E_p = -\lambda q(n_{\uparrow} + n_{\downarrow}), \qquad (1.8)$$

where λ is the electron-phonon coupling strength, and n_{\uparrow} and n_{\downarrow} are the site occupation number for an electron with spin up or down. E_p is a negative quantity and thus can allow lower energy at configuration coordinate $q \neq 0$.

If two electrons are at the same defect the energy of the system will rise by the Coulombic positive repulsion energy (Hubbard energy) $U = e^2/4\pi\epsilon r$, where ϵ is the dielectric function and r the distance between electrons. In negative-U systems this Hubbard energy is more than compensated by the electron-phonon interaction if the constant λ is large enough as it is shown in Fig.1.8 which illustrates how the reaction $2D^0 \longrightarrow D^- + D^+$ is exothermic.

¹However ESR signals are seen in the germanium sulfides.



Figure 1.8: Configuration-coordinate diagram of a D^+D^- pair. Exchange of an electron between two D^0 centers to give a D^+D^- pair at the same configuration costs the Hubbard energy U. The D^+D^- centers subsequently relax to a different configuration and the overall energy is lowered by the effective correlation energy U_{eff} [10].

Indeed Anderson calculated the effective Hubbard energy, shown in Fig.1.8, and found it as

$$U_{eff} = U - \frac{2\lambda^2}{\hbar\omega}.$$
(1.9)

where ω is a phonon frequency. This effective energy will be negative if $U < 2\lambda^2/\hbar\omega$. This is possible if the lattice is flexible enough to make λ sufficiently large. As mentioned above the low coordination number makes chalcogenides more flexible than other semiconductors and this gives a large polaronic effect.

Kastner, Adler and Fritzsche (KAF) [11] offered a detailed proposal for the bonding configurations in the elemental semiconductor selenium that gives rise to the defects in question, and they show that a negative effective correlation energy is expected. In their paper, and as shown in Fig.1.9, they use the notation C_n^l for the D^0, D^+ and D^- whereby the superscript l refers to the charge at an atom and the subscript n to its coordination number. In this thesis both notations will be used.

Fig.1.9, shows different possible bonding configurations for group VI elements (S, Se, Te). At the configuration sketches, straight lines refer to bonding (σ) orbitals, open circles represent electrons in LP orbitals and asterisks represent electrons in antibonding (σ^*) orbitals. The arrows represent



Figure 1.9: Structure and energies of simple bonding configurations of group VI elements. Straight lines represent bonds, small circles lone-pair (LP) electrons and asterisk the antibonding electrons. Arrows represent electrons with spin. The zero energy is the energy of LP [11].

electrons with spin up or down. With the energy of a LP taken as zero, the energy per electron of a σ orbital is $-E_b$ while the energy per electron in a σ^* is $E_b + \Delta$, where $\Delta > 0$ because the antibonding states are always pushed up more than the bonding states are pushed down. In all cases if an electron is added to a Se atom it would be placed in a linear combination of σ^* orbitals with a correlation energy U_{σ^*} which is smaller than the correlation energy U_{LP} if the added electron is placed on a lone-pair [11]. It is assumed that E_b is much larger than Δ , U_{σ^*} and U_{LP} .

In the KAF notation a doubly coordinated Se atom would be written C_2^0 and has an energy of $-2E_b$. The neutral three-fold coordinated atom C_3^0 has an energy of $-2E_b + \Delta$ but it is not stable as we will see below and the neutral singly coordinated atom has an energy of $-E_b$. As it can be seen, the neutral dangling bond costs a full bond energy $-E_b$ with respect to normal C_2^0 while the C_3^0 configuration costs much less. Consequently, the neutral dangling bond is energetically unfavorable. In other words, in a



Figure 1.10: Visualisation of the three-fold coordinated D^+ and singly coordinated D^- defect centers (Valence Alternation Pair) by the exchange of an electron between two D^0 centers [10].

situation where disorder disrupts the normal C_2^0 bonding, the C_3^0 appears to be the most likely defect configuration. However this C_3^0 configuration is unstable. A charge transfer from one C_3^0 configuration to another one by the reaction $2C_3^0 \longrightarrow C_3^+ + C_3^-$ would costs an energy $U_{\sigma*}$ according to the scheme of Fig.1.9, but by breaking one of the three bonds, C_3^- spontaneously becomes an ordinary C_2^0 while converting a nearest-neighbor C_2^0 site into a singly coordinated selenium atom with the extra electron, C_1^- . The reaction $C_3^- + C_2^0 \longrightarrow C_2^0 + C_1^-$ is exothermic if $2\Delta - (U_{LP} - U_{\sigma*}) > 0$. The sum of the two last reactions is $2C_3^0 \longrightarrow C_3^+ + C_1^-$, and in this way the system lowers its energy by transferring two σ and two σ^* electrons into LP states of one singly-coordinated and one two-fold coordinated chalcogen. Because the creation of the two charged centers $C_3^+C_1^-$ is linked, they are known as Valence Alternation Pairs, (VAP). A VAP creation mechanism is illustrated in Fig.1.10. It uses the neutral dangling bond as a precursor as suggested by Street and Mott [25], contrary to the KAF proposal mentioned above where the neutral three-fold coordinated defect is the precursor. In either case the charged centers that are created in the network lead to localized states in the forbidden gap that will be the subject of the next paragraph.

Energy levels of charged defects

The lattice deformation that causes the negative effective correlation energy causes charged defects to be characterized by different transitions energies from and to the bands depending on the electron occupation of these defects. Taking into consideration that phonons can supply the necessary momentum

1.2. Bonding in amorphous semiconductors

to accommodate the lattice deformation and photons cannot, there will be a difference between energies of optical and thermal transitions. To understand the different transitions involved in a negative-U system we can use the Fig.1.11, where the the different possible transitions to and from D^+ and D^- defects are shown together with an energy-configuration diagram for the D^+ defect.

The levels A^+ and A^- correspond to the charged defects at their equilibrium configuration q_0 , these two levels are related to the optical transitions (1 and 1') from the valence band to A^+ and from A^- to the conduction band respectively. The levels T and O represent thermal and optical transitions involving the defects in their excited, electrically neutral states at changed configuration q_n . Transitions 4 and 5 are thermal transitions between the valence respectively conduction band and the D^+ defect, bringing this defect back to its its $D^{(+)0}$ configuration; the transition 4' and 5' are the similar ones between the conduction respectively valence band and the D^- defect. Transitions 2 and 3 correspond to photoluminescence and photoinduced absorption respectively. In these transitions the D^0 defect for instance, a neutral dangling bond, appears only as excited state of the charged defects.

The energy difference between $T^{+(-)}$ and $A^{+(-)}$ is $W^{+(-)}$, that is also the energetic difference between $T^{+(-)}$ and $O^{+(-)}$ in the symmetric models used in [11][25]. The energies E_1 and E_2 are defined by the equations:

$$D^{+} + e + (E_{1}) \longrightarrow D^{0}$$
$$D^{0} + e + (E_{2}) \longrightarrow D^{-}$$
$$U_{eff} = E_{2} - E_{1} < 0$$

Then the transitions involved in the negative-U model can be summarized in this set of equations :

Thermal transitions

$$(4)D^{+} + e_{VB} + (E_{1}) \longrightarrow D^{0}$$

$$(5)D^{0} + (E_{g} - E_{1}) \longrightarrow D^{+} + e_{CB}$$

$$(5')D^{0} + e_{VB} + (E_{2}) \longrightarrow D^{-}$$

$$(4')D^{-} + (E_{g} - E_{1}) \longrightarrow D^{0} + e_{CB}$$

$$(1.10)$$

Optical transitions



Figure 1.11: Energy level diagram for charged defects D^+ and D^- with the different possible transitions represented. The right-hand part of the figure is the energy-configuration diagram for the D^+ defect.

$$(1)D^{+} + e_{VB} + (E_{1} + W^{+}) \longrightarrow D^{0}$$

$$(3)D^{0} + (E_{g} - E_{1} + W^{+}) \longrightarrow D^{+} + e_{CB}$$

$$(3')D^{0} + e_{VB} + (E_{2} + W^{-}) \longrightarrow D^{-}$$

$$(1')D^{-} + (E_{g} - E_{2} + W^{-}) \longrightarrow D^{0} + e_{CB}$$

$$(1.11)$$

These predicted energy levels in the negative-U systems have been found to agree with experimental results for chalcogenides like As_2Se_3 and As_2Te_3 [27], [28]. The negative-U model was in fact able to explain some of defect levels measured on chalcogenides well before its appearance, like the distinct recombination levels deduced from steady-state photoconductivity and corresponding to the T levels [26]. The model also explains the Stokes shift of photoluminescence in chalcogenides (energy difference between transitions 1 and 2 in Fig.1.11).

In the earlier papers dealing with this model the energetic distances W^+ from A^+ to T^+ and from T^+ to O^+ are taken to be equal and also equal to W^- the equivalent energetic distance A^- to T^- and from T^- to O^- .
1.2. Bonding in amorphous semiconductors

This assumption has no physical ground as can be seen in the comparison of experimental and theoretical results given in [27].

Over the three decades since the negative-U energy-level scheme was proposed it has found support in a wide range of experimental results (see for example [27] [28]). Nevertheless, some dissenting voices have been heard. Based on theoretical calculations, Vanderbilt and Joannopoulos [13] concluded that a-Se is a positive correlation energy system. In this calculation a superlattice containing the charged defects in question was used. The superlattice is constructed of supercells of 12 atoms, each containing 2 C_1^0 centers in one calculation or C_3^+ and C_1^- centers in the next one. The effective energy $U_{eff} = U(C_3^+C_1^-) - U(2C_1^0)$ was found to be positive. The problem with this study is that the superlattice is unrealistically small to represent a-Se, and that 25% of defect sites is unrealistically high. Tanaka [29] on the other hand has questioned the presence of charged defects in chalcogenides on the basis of optical absorption measurements on highly purified As_2S_3 samples. However, the lack of extra optical absorption at the energy levels predicted by the negative-U model is not a sufficient argument to doubt the validity of this model in chalcogenides [12]. Indeed, absorption by the wide band tails generated in As_2S_3 by homopolar As - As bonds can easily mask absorption by underlying charged defects.

1.2.2 Behavior of the Fermi level

Serious efforts have been made in the past to dope the chalcogenide semiconductors [30], all without success. Nevertheless, it was reported that it is possible to make certain germanium selenides n-type by doping (the better word will be alloying in this case) with about 10% of Bi or Pb [31], [32]. The fact that the Fermi level stays pinned in the neighborhood of midgap, a characteristic property of the chalcogenides, was argued by Adler [33] as follows:

Consider that we have a semiconductor with valence and conduction band edges, E_v and E_c , and an empty defect giving rise to localized states in the gap at energy T_0 .Extra carriers are then introduced in the system. For a material with a positive correlation energy the doubly occupied states are higher in energy than the singly occupied states. As electrons are injected into the system they populate the unoccupied states at energy T_0 . Consequently, the Fermi level shifts gradually in the band around T_0 due to the average chemical potential at which the additional electron would be located (Fig.1.12).a. When the number of electrons per defect n becomes 1, where $n = N/N_0$ and N is the total number of electrons associated with the defect states and N_0 is the total number of defects [33] (this means that all defects are singly occupied), all other injected electrons would have to create doubly occupied states at higher energy $T_0 + U$. At this condition the Fermi level jumps discontinuously from the T_0 into the $T_0 + U$ band, and rises gradually in this band until n = 2, as shown in the part a of the lower frames in the same figure. All states are then doubly occupied.

In the case of negative correlation energy systems, the results are totally different. The doubly occupied state has the lower energy position in the gap such that, as electrons are injected into the system, they first populate an unoccupied state giving rise to a singly occupied level (an unoccupied state + e), and then this singly occupied level becomes doubly occupied one by being populated by the next injected electron. (a doubly occupied state = a singly occupied state + e). Thus this level falls in energy band at $T_0 - U$, as shown in Fig.1.12.b. The number of doubly occupied states is proportional to the number of electrons introduced into the system. Since this band of defect levels is always full, we conclude that in this system the Fermi level will be pinned midway between the energies T_0 and $T_0 - U$ over the whole range of occupation number n, as shown in part b of the lower half of Fig.1.12.

1.3 Selenium

As mentioned in the introduction, Se is the oldest semiconductor that physicists have deal with. Its golden age coincided with its application in reprography in Xerox machines, but its economic importance decreased drastically after introduction of silicon and organic semiconductors in this application. The new usage of Se as an X-ray-sensitive material in digital X-ray imaging detectors has brought renewed interest, while also reminding us that our knowledge about a-Se is poor. Here we summarize some of its characteristics.

1.3.1 Microstructure of selenium

Selenium has five crystalline states [30], the more important of which are the hexagonal and monoclinic ones.

Hexagonal Se which is always referred to as Se_{γ} , is the most stable form of selenium. The crystal is made up of parallel helical chains, as shown in Fig.1.13, where every atom has two nearest neighbors from the same chain situated at a distance 2.30 Å -2.37 Å and four neighbors from the other chains situated at a distance 3.42 Å - 3.48 Å. While the interaction between chains is of the Van der Waals type, the atoms are covalently bonded within the same chain. The hexagonal unit cell contains three atoms and the lattice parameters at 18 °C are a = 4.3544 Å, c=4.9496 Å, c/a=1.1367 [30]; the



Figure 1.12: Density of quasiparticle states for a semiconductor with localized states in the gap relating to a single defect at T_0 , and the Fermi energy as a function of electronic density, $n = N/N_0$ at a low but finite temperature: (a) positive correlation energy; (b) negative correlation energy. States occupied at T = 0 are shaded. Optical transitions connecting localized and band states are indicated by arrows. (From D. Adler et al. [33]).



Figure 1.13: The hexagonal selenium (left part of the figure) and monoclinic selenium phase β (right part)[30]

bond angle is $(103.7 \pm 0.2)^{\circ}$.

Monoclinic selenium has two forms, labeled α and β . The Se_{α} consists of 8-atom non planar rings as shown in Fig.1.13. The selenium atoms are situated at the corners of two superposed squares, one of them is rotated by 45° and shifted along the normal to the plane. The lattice parameters are : a = 9.054 Å, b = 9.083 Å, c = 11.601 Å and $\beta = 90.49^{\circ}$. The Se dihedral angle is alternating in sign in the same ring and equals $(105.7 \pm 1.6)^{\circ}$ which is close to its Se_{γ} value of $(101.3 \pm 3.2)^{\circ}$. The values of angles given here are averaged [30]. The Se_{β} differs from the Se_{α} in the packing of the rings.

The microstructure of a-Se is less well defined. It was assumed that a-Se consists of a mixture of rings and chains, with no definite ratio [34] [35], and with the rings having either 6 or 8 atoms. On a basis of infrared spectroscopy Lucovsky [7] proposed that a-Se consists of units made of segments of chains linked to fragments of rings. The chain segments are characterized by a succession of dihedral angles of the same sign (positive or negative) while the ring fragments are characterized by an alternation of dihedral angle signs. Fig.1.14 shows a schematic representation of such units.

It is important to point out here that the glass transition temperature of Se is just above 40 °C, which puts a-Se at room temperature in perpetual danger of crystallization [30]. This effect was well noticed in the course of this work.

1.3.2 Optical properties of a-Se

The optical gap of Se is $E_g \sim 2$ eV [36][37], and the Urbach tail of a-Se, i.e. the exponentially varying values of the optical absorption coefficient at

1.3. Selenium



Figure 1.14: Local molecular order in a selenium chain in which there are segments characterized by repetition of the dihedral angle, "chain-like" in the sense of trigonal Se, and segments characterized by alternating dihedral anhles, "ring-like" in the sens of the Se₈ ring [7].

low values of the absorption, has a characteristic width about 60 meV at room temperature, whether as thin evaporated film or in bulk, [37]. a-Se was thought to differ from other chalcogenides by the fact that its optical absorption at high photon energies shows a linear rather than a power-law behavior [38]. However, calculations of optical transitions in chalcogenides, based on a constant dipole matrix element instead of the constant momentum matrix element [39] showed that optical absorption of a-Se at high photon energies fits the same power law $(\alpha E)^1/2 \propto E - E_g$ as other chalcogenides. The energy gap of a-Se is temperature dependent. It changes between 1.95 eV at room temperature and more than 2.1 eV at liquid nitrogen temperature[37].

The photodarkening effect, which is a decrease in energy gap of the material caused by photon irradiation, was observed in a-Se [40] at low temperature (less than 77 K), but bleaches out at higher temperature. As with all photoinduced changes in chalcogenides, there is more than one model that tries to explain the effect. Nagels [40] interpreted the photodarkening in a-Se as due to the formation of intrinsic defect states originating from dihedral angle distortions, a model first introduced by Wong et al. [41]. The same model was used by Koughia et al. to interpret an observed shallow defect level, as it will be seen in later chapters [42].

In selenium the quantum efficiency of carrier generation (η) , i.e. the number of electron-hole pairs created per absorbed photon and participating in the photocurrent, is a function of the photon energy and applied field. This effect will be discussed in Chapter 4 which deals with the optical transition involved in the negative-U model.

1.3.3 Electronic properties

As is the case for other chalcogenides, holes are the more mobile charge carriers in a-Se [43][9]. Their mobility is around thirty times the electronic one. At low temperature, the hole mobility is dependent on the applied electric-field while the electronic one is field-independent [9]. It is well known that the DOS is the key to understand the electrical transport properties of amorphous materials. However, for a-Se the DOS model proposed by Abkowitz [8], shown in Fig.1.15, has serious deficiencies as will be discussed later. It is required, therefore, that a more firmly-based specification of the a-Se DOS be elaborated.

It may be remarked that a very specific model for the negative-U centers is available for a-Se [11], but with the experimental positioning of the defect levels in the bandgap not yet resolved, while the reverse situation holds for other chalcogenides. For instance: Negative-U energy levels are well established for As_2Se_3 [28] [27], but the actual atomic configurations of the charged defects remain in doubt [44]. Elliott [10] has mentioned that several parameters make Se an anomalous material in a number of ways. One of these parameters is the Se dielectric constant which is approximately half the value of other chalcogenides. Consequently, the repulsive energy between two electrons on the same defect site is high, and its compensation is less probable, thus conceivably making double occupancy less likely. The lack of ESR signal could then be interpreted through the sensitivity of a-Se for unwanted additives like chlorine or oxygen that might compensate the defects [10]. It is clear from the above that defining the DOS of a-Se and answering the question whether it is a negative- or positive-U system are related problems. Experimentally we can detect the defect levels in the gap of a-Se by the photoconductivity techniques that will be discussed in the next chapter.



Figure 1.15: Density of states diagram for a-Se deduced from time resolved analysis of xerographic potentials on undoped and doped a-Se combined with transient photoconductivity data. (From M. Abkowitz [8]).

Chapter 2

Photoconductivity techniques

In this chapter the photoconductivity in semiconductors will be introduced, i.e the increase of the conductivity under optical excitation, as an experimental tool to probe the electronic properties of the material. Indeed, the extra free charge carriers created by the photon absorption will contribute to the electronic transport under an applied electric field. They will interact with material defects, and at the end these extra charge carriers are injected in the external circuit or just recombine in different ways. Two different regimes can be discussed in the photocurrent. First there is the transient one and secondly the steady state. In both cases the photocurrent forms the basis of several experimental techniques, part of which have been used in this study of a-Se.

2.1 General concepts

When the appropriate light strikes a semiconductor, it generates free charge carriers. The total free-electron and free-hole concentrations n and p are given by :

$$n = n_0 + \Delta n,$$

$$p = p_0 + \Delta p,$$
(2.1)

where n_0 and p_0 are the thermal equilibrium concentrations and Δn and Δp are the extra free carrier concentrations generated by the light. Then the photoconductivity is given by :

$$\Delta \sigma = e(\mu_n \Delta n + \mu_p \Delta p), \qquad (2.2)$$

where μ_n and μ_p are the electron and hole mobility and e is the electron charge. Technically there are several ways to prepare a sample for photocon-



Figure 2.1: Basic arrangements for photoconductivity measurements on a: (a) gap cell sample, I_d is the dark current and I_{ph} is the photocurrent, (b) sandwich cell sample with n and p are the total free charge carrier densities, n_0 and p_0 are free carrier densities in the dark, and Δn and Δp are the excess free charge carrier densities.

ductivity measurements such as shown in Fig. 2.1. The generation rate G is defined as the number per unit volume per second of free electrons and holes produced by the light, and is given as [15]:

$$G = \eta \{ \frac{I_0(1-R)(1-\exp(-\alpha d))}{d} \},$$
(2.3)

where d is the sample thickness, R is the reflectivity, α is the absorption coefficient, I_0 is the incident photon flux density, and η is the quantum efficiency for photogeneration (number of free charge carrier per photon). The quantity between brackets is the number of photons absorbed by the sample per unit surface.

Free charge carriers contribute to the electrical conductivity of the material, and are subject to trapping and recombination. Fig.2.2 illustrates different possible effects that a charge carrier can undergo while it is moving through the sample under the effect of an electric field. In this figure free carrier generation by raising an electron from VB to CB, leaving behind it a free hole, is illustrated by the transition (a). A free electron can also be generated by raising an electron from a defect to the CB transition (b), and a hole can be generated by raising an electron from VB to a defect level (c).

2.1. General concepts



Figure 2.2: Major transitions and phenomena associated with amorphous semiconductors (a) direct absorption (b) and (c) absorption through localized states, (d) and (e) capture and recombination, (f) trapping and release.

An electron can be captured from the CB in a deep defect level (d) and a hole can be captured from the VB in a deep defect level transition (e), with the combination of transitions (d) and (e) being equivalent to recombination at the defect level. An electron captured from the CB in a shallow defect level can be thermally re-emitted to the CB and similarly for holes and the VB (f).

The capture process can be described as follows: If the concentration of free electrons in the CB is n and the density of defects is N, then the rate of capture C_r is given by:

$$C_r = \beta n N, \tag{2.4}$$

where β is a capture coefficient given by the equation

$$\beta = vS, \tag{2.5}$$

with S is a capture cross section and v a thermal velocity.

Once an electron is captured at a defect there are two possibilities:

• It recombines with a hole that is captured by the same defect. A captured hole can recombine with an electron in the same way. In this case

the defect is called a recombination center. This recombination process is called indirect recombination, in contrast to the direct recombination where an electron falls directly from the CB to the VB.

• It can be thermally excited to the CB to participate again in the electronic transport and in this case the defect is called a trap. The phenomena of capturing in a trap (trapping) and release from it (detrapping) play an important role in the electronic transport in amorphous semiconductors. Indeed, a charge carrier moves through the semiconductor in the extended states in the lapse of time between the last detrapping and the next trapping event, which means the charge carrier is free when moving.

Whether a center (defect level) is to be considered as trapping center or a recombination center depends on the probability for the charge carrier (electron) to be thermally ejected to the conduction band or to recombine with the opposite charge carrier. If the recombination probability is larger than the release probability, the defect is a recombination center. A center acts as a trap under specific conditions and as a recombination center under other conditions; the delimitation between the two is defined by the quasi-Fermi levels, which will be discussed later.

If attention is restricted to the recombination at a density of recombination centers N with capture coefficient β , the average time the carrier (in this case the electron) is free before recombination is given by the equation:

$$\tau = \frac{1}{\beta N}.\tag{2.6}$$

Combining this equation with Eq.2.4 gives that the capture rate C_r , which becomes in this case a recombination rate, is equal to n/τ . In the steady state regime the density of free electrons n is constant, which means that the rate of generation is equal to the rate of recombination and this happen when [45]:

$$n = G\tau. \tag{2.7}$$

When a semiconductor is in a thermal equilibrium the occupation probability of a state at energy E is given by the Fermi-Dirac distribution:

$$f(E) = \frac{1}{1 + \exp(\frac{E - E_{F0}}{kT})},$$
(2.8)

where E_{F0} is the equilibrium Fermi level, k the Boltzmann constant and T the temperature. The free electron and hole densities at thermal equilibrium

2.1. General concepts



Figure 2.3: Occupation function before (solid line) and after (dashes) illumination.

can be approximated by:

$$n_0 = N_c \exp(-\frac{E_c - E_{F0}}{kT}), \qquad (2.9)$$

$$p_0 = N_v \exp(-\frac{E_{F0} - E_v}{kT}), \qquad (2.10)$$

where N_c and N_v are the effective density of states in the CB and VB respectively.

Under illumination the thermal equilibrium of the semiconductor is broken by the generated electron-hole pairs. Some electrons are pumped up to occupy traps above the equilibrium Fermi level E_{F0} , leaving behind some empty states below E_{F0} as shown in Fig.2.3. The occupation probability and concentrations are no longer described by the equilibrium Fermi level. Instead we use two quasi-Fermi levels, one for holes and a second one for electrons [10], also called *steady-state Fermi levels*. The free-carrier concentrations of electrons, respectively holes at the CB and VB are then given by:

$$n = N_c \exp(-\frac{E_c - E_{Fn}}{kT}), \qquad (2.11)$$

$$p = N_v \exp(-\frac{E_{Fp} - E_v}{kT}).$$
(2.12)



Figure 2.4: Schematic time development of the excess carrier concentration Δn in response to a period of illumination.

When the semiconductor is irradiated the electron quasi-Fermi level is above the equilibrium Fermi level E_{F0} , while the other one is below it. The energetic distance between a quasi-Fermi level and the equilibrium one is proportional to the light intensity and inversely proportional to the temperature. When the irradiation is stopped the two quasi-Fermi levels collapse to the equilibrium E_{F0} . It may be noted that the occupancy function involving the quasi-Fermi levels has similar form as the equilibrium Fermi-Dirac distribution function.

It is customary to define demarcation levels between the shallower energy levels that will trap and re-emit carriers and the deeper levels where a trapped carrier has a higher probability of recombining with a carrier of the opposite sign, rather than being re-emited. To first approximation, these demarcation levels can be identified with the quasi-Fermi levels. The states lying between the two demarcation levels are taken as recombination centers. When the concentration of free charge carriers n and p is increased, the two demarcation levels are separated further giving rise to more recombination of carriers.

2.2 Steady-state photoconductivity

After illuminating the sample, the photocurrent will build up to a steadystate value, as sketched in Fig.2.4 Using Eq.2.2 and Eq.2.7 one can write:

2.2. Steady-state photoconductivity

$$\Delta \sigma = eG(\mu_n \tau_n + \mu_p \tau_p), \qquad (2.13)$$

where τ_n and τ_p are the average lifetimes of electrons and holes respectively. If one term in the last equation is much larger than the other one, which is the case in chalcogenides where the hole term dominates, then the photoconductivity can be written as:

$$\Delta \sigma = e G \mu_p \tau_p. \tag{2.14}$$

When it can be assumed that the absorption is uniform through the semiconductor, and that reflectivity is small enough to be neglected, then the photogeneration rate can be written as $G = \eta \alpha I_0$ and the steady-state photoconductivity becomes:

$$\Delta \sigma = e \mu_p \tau_p \eta \alpha I_0. \tag{2.15}$$

In this equation the two parameters α and η represent the effect of photogeneration on the photoconductivity while the two parameters μ_p and τ_p represents the effect of transport.

2.2.1 Effect of light intensity

It was experimentally observed that in chalcogenides the photocurrent at small light excitation intensities, I_0 , and/or high temperatures, grows linearly with I_0 , while at high light intensities and/or low temperatures the photocurrent is proportional to the square root of I_0 . This can be summarized in the following equation:

$$I_{ph} \propto I^{\gamma} : 1 \ge \gamma \ge 0.5. \tag{2.16}$$

The current dependence on light intensity (called Lux-Ampère characteristics) has been widely studied [26][46][47], and was found to have a close relationship with the type of recombination involved in the process. Information about the DOS can also be deduced as we will see later.

Weiser [46] proposed a model to explain the Lux-Ampère characteristics in chalcogenides. Consider a semiconductor where the electrical transport is dominated by one type of carrier, and with only one type of recombination center. Under optical excitation an extra density of holes Δp is generated with generation rate G. If the material is assumed to be intrinsic such as $n_0 = p_0$ and that $\Delta n = \Delta p$, the rate of change of the excess carriers Δp is given by:

Chapter 2. Photoconductivity techniques

$$\frac{d(\Delta p)}{dt} = G - \left[\beta N_r(p_0 + \Delta p) - \beta p_0^2\right],\tag{2.17}$$

where N_r is the concentration of the recombination centers. In steady-state, $d(\Delta p)/dt = 0$, and under the conditions mentioned above (an intrinsic semiconductor with one type of recombination centers) $N_r = p_0 + \Delta p$, giving:

$$G = \beta (\Delta p^2 + 2p_0 \Delta p). \tag{2.18}$$

At low intensity $\Delta p \ll p_0$, meaning that thermally excited carriers p_0 are dominant, Eq.2.18 becomes

$$\Delta p = \frac{G}{2\beta p_0},\tag{2.19}$$

from where we can write:

$$I_{ph} \propto \sigma_{ph} \propto \Delta p \propto G \propto I_0 \tag{2.20}$$

In this case the recombination type is referred to as *monomolecular*.

At high light intensity $\Delta p \gg p_0$, the thermally excited carriers can be neglected and the Eq.2.18 becomes:

$$\Delta p = \left(\frac{G}{\beta}\right)^{\frac{1}{2}}.\tag{2.21}$$

It can then be written :

$$I_{ph} \propto \sigma_{ph} \propto \Delta p \propto (\frac{G}{\beta})^{\frac{1}{2}} \propto (I_0^{\frac{1}{2}}), \qquad (2.22)$$

in which case the recombination type is referred to as *bimolecular*.

It is now established that by changing light intensity the recombination changes from one regime to another (changes of γ between 1 and 0.5). Intermediate values of γ between 1 and 0.5 indicate that photo-excited carriers have approximately the same density as the thermally excited ones.

2.2.2 Effect of temperature

Experimentally it was seen that in traditional chalcogenide semiconductors, like As₂Se₃, photoconductivity in function of temperature has a maximum at temperature $T = T_m$ separating two regimes:

• at temperatures $T > T_m$ the photocurrent I_{ph} is generally lower than the dark current I_d . In this range I_{ph} increases exponentially with



Figure 2.5: Temperature dependence of steady-state dark I_d and photocurrent I_{ph} in bulk a-As₂Se₃ gap cell at different light intensities [48].

1/T and changes linearly with light intensity I_0 , (the monomolecular regime).

• at temperatures $T < T_m$ the photocurrent I_{ph} is higher than the dark current I_d , it decreases exponentially with 1/T, and varies as the square root of the light intensity I_0 (bimolecular regime).

The temperature T_m , corresponding to the photocurrent maximum, moves to lower temperatures with decreasing light intensity, and this can be explained by the fact that an increase in temperature reduces the energetic distance between the quasi-Fermi levels, analogous to the effect of decreasing light intensity. These effects are observed in Fig.2.5.

A four-level model has been proposed to explain this behavior of photoconductivity in chalcogenides [26][49]. Consider a semiconductor with two sets of trapping levels, one located above the equilibrium Fermi level E_{F0} at energy E_1 and the other one below E_{F0} at energy E_2 , as shown in Fig.2.6. These two sets of trapping levels and the band edges E_C and E_V form the four levels. Since chalcogenides are intrinsically p-type semiconductors, the equilibrium Fermi level will be a bit below the middle of the gap, as indicated in Fig.2.6.



Figure 2.6: Schematic description of the four levels model.

In the references [26][49] the free and trapped carrier densities under optical excitation are obtained by solving the rate equations for the changes in occupation of the four levels in terms of the transition rates of charge carriers (electrons and holes) into and out of a particular level. The photocurrent deduced in the the 4-level model does show the two ranges of interest indicated above:

• The range corresponding to low light level and characterized by the fact that $p_0 \gg \Delta p$. In this range the photocurrent increases linearly with the generation rate G (monomolecular regime), and increases exponentially with 1/T with activation $\Delta E_m/k$ [49]. In this regime the extra steady state density of holes (to which the photocurrent is proportional) is given by:

$$\Delta p = \left(\frac{G}{vSN_t}\right) \exp\left(+\frac{\Delta E_m}{kT}\right),\tag{2.23}$$

where v is thermal velocity, N_t the density traps and S is the hole capture cross section for the trap. ΔE_m is defined differently in the calculations of Simmons [49] and those of Main [26]. While Main calculates the result as $\Delta E_m = \frac{1}{2}(E_1 - E_2)$, Simmons uses $\Delta E_m = E_{\sigma} - (E_2 - E_v)$,

2.3. Optical absorption coefficient

where E_{σ} is the activation energy of the thermally activated dark current which, to first approximation, equals E_F . Since E_F itself lies roughly in mid-gap, the difference in the results in not significant.

• The range corresponding to high light level and characterized by the fact that $\Delta p \gg p_0$. In this range the photocurrent increases as the square root of the generation rate G (bimolecular regime), is decreasing exponentially with increasing 1/T, and has an activation energy $\Delta E_b/k$. The density of photoexcited holes is given in this case by:

$$\Delta p = \left(\frac{GN_0}{vSN_t}\right)^{\frac{1}{2}} \exp\left(-\frac{\Delta E_b}{kT}\right),\tag{2.24}$$

where N_0 is the density of states at the band edges E_c and E_v , and $\Delta E_b = \frac{1}{2}(E_2 - E_v)$.

The experimental observations are in agreement with this model. The set of two localized states are located experimentally by measuring the three parameters E_{σ} , ΔE_m and ΔE_b , which define the energetic positions E_1 and E_2 of Fig.2.6. It was mentioned earlier that this set of localized states is congruent with the charged defect levels of the negative-U model in chalcogenides.

It is important to note here that this does not mean that other possible defect levels do not exist in the material. Moreover this image is idealized because every set of traps in amorphous semiconductors is spread out around a mean energy, and the band edges are "smeared out" by tailing.

2.3 Optical absorption coefficient

The optical absorption coefficient is tightly related to the DOS in the subgap energy range of a semiconductor, and SSPC can be used in a number of ways to measure this optical absorption coefficient. If the optical flux I_0 is written as $I_0 = I/h\nu$ then the photoconductivity will be written as:

$$\Delta\sigma(E) = e\mu_p \tau(I/h\nu)(1-R)\eta\alpha(E). \tag{2.25}$$

If the parameters η , R and μ are energy-independent, a direct determination of $\alpha(E)$ from $\Delta\sigma(E)$ can be made by measuring $\Delta\sigma$ as a function of photon energy using the SSPC experimental setup. Of course, care should be taken to fulfill the validity conditions of Eq.2.25, i.e the maximum photonenergy used is less than the energy gap of the semiconductor. Any feature in the DOS, lying in the experimental energy range, will be reflected in this absorption spectrum. However, in a-Se η is energy-dependent, and thus α cannot be measured directly, but the photocurrent spectral response, that is the photocurrent at different wavelengths for the same number of photons, can be used for the same goal.

The constant photocurrent method (CPM) was proposed by Vanecek and co-workers [50][51] to measure α as a function of energy. In CPM the photocurrent is kept constant by continuous adjustment of the light intensity Iwhile the photon energy is scanned across the spectrum, which means that the positions of the quasi-Fermi levels are immobile and thus the free carrier lifetime τ is constant. The required light intensity in this case is inversely proportional to the number of photogenerated free charge carriers. For a-Se and using the Eq.2.25 with the assumption that R and μ are energy independent the parameter $\alpha \eta$ can be measured, and information about the DOS can be drawn from that.

In both above techniques, a convolution of the two sides of the bandgap DOS is probed, just as is the case with standard optical spectroscopy. Resolved features close to the band edge may, therefore, point to defects in either VB or CB tail.

2.4 Transient photocurrent techniques

The study of transient aspects of photoconductivity can relate to either the build-up or relaxation of steady-state photocurrents, or to a material's response to pulsed excitation. The SSPC turn-on transient reflects the interplay between generation and recombination of carriers. This interplay can lead to a current overshoot as has been seen seen with some low-temperature results. A special focus in this work will be on the transient photocurrents after a pulsed laser flash, involving both the traditional transient photoconductivity (TPC) and time-of-flight (TOF) techniques. The transient photocurrents can be interpreted in terms of a multiple-trapping (MT) model.

2.4.1 Time-of-flight technique

The TOF technique involves the creation and drift of a thin layer of excess charge carriers (holes or electrons) through the thickness of a sandwichcell configuration of a semiconductor sample. It was first used by Spear to measure the drift mobility of carriers in a-Se [52], where a short pulse of high-energy electrons was used to create the layer of excess charge carriers just beneath the top contact. It was adapted from the original technique by Haynes and Shockley [53] who measured the drift mobility in long crystalline rods of semiconductors. Nowadays the creation of the excess charge carriers is achieved through the use of a short laser flash (nanoseconds and less). The fact that in the TOF technique only one type of charge carriers can be drifted at a time, depending on the applied field, gives to it a special importance because it provides the opportunity to separately probe the DOS at the CB side as well as the VB side. While the excess charge carriers are drifted through the sample, they interact with the trap and recombination centers in the band gap. This interaction creates a relationship between the transient current in this technique and the DOS of the material, and thus the opportunity to probe the electronic properties of the material studied. When most of the excess carriers leave the sample at the back contact, the transient photocurrent drops abruptly, but a measurable current can still be seen due to carrier release from deep traps. This "post-transit" current makes it possible to study those deep traps.

Physical validity conditions

- In order to be able to see a transit time t_T , which corresponds to the arrival of a representative part of the excess charge carriers at the back contact, the dielectric relaxation time τ_e of the semiconductor should be much larger than the transit time $\tau_e \gg t_T$. Thus, the highly resistive semiconductors are suitable for this purpose because $\tau_e = \rho \epsilon_0 \epsilon_r$, where ρ is the semiconductor resistivity, ϵ_r is its relative permittivity and ϵ_0 the dielectric constant. The low dark current is a result of the above conditions and it makes the photocurrent more distinguishable and measurable. It was shown that the influence of the dielectric relaxation time on the post-transit photocurrent is minimal [54][55].
- To obtain a representative drift mobility, excess charge carriers must be drifted across the sample with a constant drift velocity, (v_d) . This requires a uniform applied electric field F_a which is achieved by applying a pulsed voltage V_a to the sample before triggering the laser flash [52]. The creation and drifting of an excess carrier layer through the sample perturbs the uniformity of the applied field. However, it is possible to minimize this uniformity perturbation by making the total created excess charge much less than the equilibrium charge CV_a on the sample capacitance. Indeed, at time $t < t_T$ the system can be described as two capacitors in series, as shown in Fig.2.7, the upper one with charge Q' - Ne, where N is the number of excited carriers, under a field $F_1(x)$ and the lower one with charge Q' under a field $F_2(x)$, these two electric fields are given by the following equations:



Figure 2.7: Schematic representation of the TOF experiment. The layer of excess carriers Ne with a drift velocity v_d perturbs the applied field $F_a = Va/d$, resulting in fields F_1 and F_2 . The excess carriers are created in a thin layer δ under the top contact.

$$F_1(x) = F_a - \frac{Ne}{\epsilon A}(1 - \frac{x}{d}),$$
 (2.26)

$$F_2(x) = F_a + \frac{Ne}{\epsilon A} \frac{x}{d}, \qquad (2.27)$$

where A is the surface of the capacitor (contact) and d the thickness. If the total excess carrier charge is small enough with respect to the equilibrium capacitor charge $Ne \ll Q = CV_a$, the field will be considered as constant $F_1 \simeq F_2 \simeq F_a$.

• In the ideal case the distribution of the created excess carrier layer should be a delta function, $G\delta(x)\delta(t)$. The laser flash, on the order of nanoseconds in length fulfills the condition of the very short distribution in time, while an appropriate wavelength of the laser flash, strongly absorbed in the material, ensures the narrow distribution in space. Indeed, if this is not the case the laser flash will be absorbed throughout the semiconductor which causes a spread in the arrival time of the carriers at the back contact and a large uncertainty on the measured transit time. Care has to be taken as well to avoid the absorption at very shallow depth in the semiconductor where the excess charges can recombine in the highly defective surface layer. No useful transient TOF photocurrent is obtained in that case.



Figure 2.8: Diagram showing the essential components of a TOF setup.

- The lifetime, that is the average time that an electron or hole stays at extended states or being shallowly trapped (the trap is shallow enough to allow a fast re-emission of the trapped carrier to the extended states as it will be seen later in this chapter), τ_d should be higher or at least of the order of the transit time t_T . In other words, significant deep trapping should only occur at times $t \geq t_T$. If this is not the case, i.e. $\tau_d \ll t_T$, the transient current will only reflect the deep trapping.
- Since the transient TOF current is a primary photocurrent, that is the photocurrent flowing between two blocking contacts, it is important to be sure that the contacts in the sample are blocking. Indeed an injection of carriers through the contacts into the semiconductor disturbs the measurement of the primary current. For a-Se, evaporated aluminium or gold contacts, as used for all the samples used in this study, prove to be sufficiently blocking. There is also the possibility of depositing very thin insulator layers before the deposition of contacts or to use p-i-n junctions in reverse bias with very thin p and n layers, the latter technique being used for a-Si:H. It is also preferable to make the back contact less resistive than the top contact to avoid charge accumulation at the back of the sample, which could distort the measured signal.

The experimental setup

The Fig.2.8 shows a schematic representation of the TOF setup; more details can be found in [56]. A voltage pulse V_a , of up to 10 ms in length is applied to the sample using an HP214B pulse generator. For times larger than 10 ms a DC voltage source is used. The pulse generator, which is characterized by a fast rise time, is connected to the samples by coaxial cables across a 50 Ω parallel resistor to avoid reflection in the cables that are kept as short as possible.

A time delay generator triggers a VSL-337 nitrogen laser, via a 20 m long coaxial cable, 80 μ s after the start of the voltage pulse. The laser pulses are 3 ns long, have an energy of 120 μ J, and a wavelength of 337 nm. The laser pumps a dye cell with Coumarin 440 A dissolved in ethanol that gives by fluorescence a 440 nm wavelength light pulse of 5 ns duration. The intensity of this light pulse can be, if necessary, reduced by neutral density filters. To avoid disturbance to the electrical circuit, the laser source is placed in a copper box that it-self is in an aluminium enclosure, both of them acting as Faraday cages. This light pulse is highly absorbed in a-Se and can create a suitable layer of excess carriers for TOF experiments.

An IWATSU-8123 digitizing oscilloscope is used to record the currents, measured repeatedly on different time scales to extend the range and keep sufficient resolution (on logarithmic scale). At first the voltage pulse is applied, followed, after 80 μ s to avoid distortion of the signal by the RC time constant of the measuring circuit (sample included), by a light pulse and the total current is measured. Next the voltage pulse is repeated and the dark current recorded. The desired photocurrent is the result of subtracting the dark current from the total current. The measured quantity is the voltage drop across a variable load resistor R placed across the scope input. Actually a 50 Ω resistor is used at short time scales, and this resistor is increased stepwise till 500 K Ω to measure lower and lower photocurrents at longer times. The total transient TOF photocurrent signal consists of the overlap of all photocurrents measured at successive time scales [56]. It is important to point out that the RC constant of the circuit should be sufficiently small. A proper balance between the contact area, thickness of the sample, and its dielectric constant will keep the sample capacitance low.

The sample is mounted in a cryostat that can be evacuated during measurements, and where the temperature of the sample can be kept constant at a chosen value between 150 K and 400 K, through a combination of cooling and heating. The former is done with a cold finger immersed in liquid nitrogen, and the latter is done with an electrical filament wound around the top of the copper rod that forms the cold finger. The temperature regulation within 0.5 K is achieved by controlling the current through the filament.

2.4.2 Transient photocurrent

In the standard TPC, a coplanar sample configuration (gap cell) is used, thus both electrons and holes participate in the measured current. A DC voltage V is applied to the sample, followed by a light flash that creates extra charge carriers distributed in the bulk of the sample within a depth depending on

2.4. Transient photocurrent techniques

the wavelength used. It is preferable to avoid highly absorbed light and thus strong absorption at the surface of the sample since this is highly defective and does not reflect the bulk properties of the studied material. Under the influence of the applied field the extra charges (electrons and holes) move through the sample until their eventual disappearance through recombination, but before this happens they will have been immobilized a number of times by various traps that are present in the semiconductor. Through these interactions, the measured photocurrent contains information about the DOS of the material. Experimentally the same setup described above for TOF technique is used.

2.4.3 Multiple-trapping transport model

As described above, when a distribution of excess charge carriers is generated in an amorphous semiconductor, the carriers will eventually leave the sample or recombine. In between these two events, creation and leaving or recombination, it is assumed that the carriers move in the extended states and can be trapped once or several times in traps lying at different energies in the band gap of the semiconductor, from where they will be thermally re-emitted to the extended states. The time that each carrier spends in a trap depends on the energy position of this trap according to $t = \nu^{-1} exp(E_t/kT)$ where ν is the attempt-to-escape frequency, E_t is the energy of the trap, k the Boltzmann constant and T the temperature. These effects are illustrated for an electron in the Fig.2.9. Such transport mechanism is called the multiple-trapping transport model, or trap-limited band transport, and can be used to interpret experimental results of different transient photoconductivity techniques such as TOF and TPC. This mechanism of transport is dominant in amorphous semiconductors at relatively high temperatures (above 150 K) but it is less dominant at low temperatures, where other transport mechanisms like hopping between localized states dominate.

The equations that describe MT are written for a system with M trapping levels as:

$$\frac{\partial n}{\partial t} + \frac{\partial f_n}{\partial x} = G(x, t) + \sum_{i=1}^M r_i n_i - n \sum_{i=1}^M \omega_i, \qquad (2.28)$$

$$\frac{\partial n_i}{\partial t} = n\omega_i - r_i n_i, \qquad (2.29)$$

where n is the density of free carriers, n_i is the density of carriers trapped at an energy level E_i , r_i is the release rate from traps situated at E_i , ω_i is the capture rate (probability per unit time) in traps at E_i , G(x,t) is the



Figure 2.9: Schematic representation of trap-limited band transport.

generation rate of excess carriers and f_n is the flux of free carriers. If the diffusion is negligible, as is always the case for amorphous semiconductors, the free carrier flux is $f_n = n\mu_0 F$, with μ_0 the trap-free drift mobility and F the applied field. These equations are a form of continuity equation.

To use this set of linear differential equations to analyse experimental data, the different parameters of the actual sample can be discretized as follows: The density of states g(E) is described as a discrete distribution of M traps situated at regular intervals ΔE below the conduction band edge E_C and above the valence band edge E_V such that $E_i = i\Delta E$; in both cases the origin of the energy scale is taken at the band edge, and its positive direction is towards the gap. The density of states corresponding to energy E_i is $N_i = g(E_i)\Delta E$. The capture rate is given by $\omega_i = N_i S v$ with S the capture cross section and v a thermal carrier velocity. The capture cross section is commonly considered to be energy-independent while the release rate is temperature activated:

$$r_i = \nu \exp(\frac{-E_i}{kT}). \tag{2.30}$$

This assumption obviously has implications for the parameter values (such as, e.g., the slope of the band tail) and does signify that only an effective DOS will result from the analysis. Alternatively, a continuous distribution



Figure 2.10: The thermalization process for electrons as a function of time. The trapped charge is represented by the shadded area. (a) Immediate charge trapping after photocreation; (b) E^* sinks deeper in the gap as time goes on; (c) carrier distribution for $T > T_C$.

can replace the summation over discrete levels of Eq.2.28 as demonstrated by Arkhipov et al [57]. A simplified analysis of transient currents in MT context was worked out by Tiedje and Rose [58] and Orenstein and Kastner [59] (TROK). They used, implicitly or explicitly, the thermalization concept that allows the distinction between thermalized states and non-thermalized ones. For an amorphous semiconductor with a DOS that has an exponential shape $g(E) = g(E_c = 0) \exp(-E/kT_c)$, where kT_c is the characteristic width of the conduction band tail (a similar analysis can be done with holes, the more mobile carriers in chalcogenides), and assuming that the transport is a statistical process with an energy-independent capture cross section S. With energy-independent capture, the initial distribution of trapped carriers is proportional to the DOS. As time goes on, the shallowly trapped carriers are thermally re-emitted to the extended states while deeper trapped carriers have to wait longer, in function of the trap depth, to be released; at the same time the trapping of previously released carriers remains random and thus trapped carriers accumulate at the deeper states. The thermalization energy, that is the limit between shallow and deep states at any moment, is defined as the energy where the release time $r^{-1}(E^*)$ is equal to the time elapsed after the laser pulse, $t = \nu_0^{-1} \exp(E^*/kT)$, and thus the expression :

$$E^*(t) = kT \ln(\nu_0 t).$$
(2.31)

All the states above $E^*(t)$ are in quasi-thermal equilibrium with the extended states (valence band in the case of holes) while the states below the $E^*(t)$ are not as shown in Fig.2.10. For temperatures $T < T_C$ the concentration of occupied states exhibits a sharp peak at $E^*(t)$ that, progressively, moves to greater depths as time elapses. The concept of thermalization can be extended to non-exponential DOS [60]. In the case where $T_c < T$ the density of trapped carriers does not show the same sharp peak at E^* as shown in Fig.2.10.c.

Since the time spent by a carrier in a trap at energy E_i is an exponential function of this energy, differences in energetic positions of traps lead to big differences in the transit time for individual carriers depending on which trap or traps they visited before completing their transit. Thus the original thin layer of excess carriers has become spread out at the arrival to the back contact in a TOF experiment (much more than the spread that would be caused by diffusion in a trap-free semiconductor). In this case the transport is called dispersive.

The trap-free mobility is reduced in amorphous materials by the time that carriers spend in traps and thus the drift mobility is

$$\mu_d = \mu_0 \frac{\tau_f}{\tau_f + \tau_t},\tag{2.32}$$

where the subscript f refers to a free and the subscript t refers to a trapped carrier. The last equation can be written in function of trapped and free carrier densities, and taking in account that trapped carriers largely outnumber the free ones in amorphous semiconductors, as follows:

$$\mu_d = \mu_0 \frac{n_f}{n_f + n_t} \simeq \mu_0 \frac{n_f}{n_t}.$$
 (2.33)

Interpretation of TOF transient currents

Within the conditions of validity of a TOF experiment the generation rate G can be written as $G(x,t) = G_0 \delta x \delta t$. By using the appropriate boundary conditions the set of Eq.2.28 and 2.29 can be solved for n(x,t) and $n_i(x,t)$ via inverse Laplace transforms. In the TROK approximation and for $T < T_c$ the mobility can be treated as a two-level problem, the first one at the band edge (E = 0) where n_f is defined, and the second one at the time dependent energy E^* (Eq.2.31) where the maximum of the trapped carriers density n_t is located. Like all other quantities, n_f is time-dependent and for an exponential DOS, it decreases with time as $t^{\alpha-1}$, where α is defined as the dispersion parameter and given by $\alpha = T/T_c$. From Eq.2.33 it follows that μ_d is also time dependent and that a carrier crosses the sample with a time-dependent

2.4. Transient photocurrent techniques

average drift speed $v_d(t) = \mu_d(t)F$. The transit time t_T corresponds to the time that carriers having the above average drift speed need to reach the back contact, and thus:

$$d = \int_0^{t_T} \mu_d(t) F dt.$$
 (2.34)

The above power-law decay of transient TOF photocurrent $I \sim n_f$ only lasts until the transit time t_T :

$$I(t < t_T) \sim t^{-(1-\alpha)};$$
 (2.35)

at longer times, the photocurrent decreases according to the steeper powerlaw:

$$I(t > t_T) \sim t^{-(1+\alpha)}.$$
 (2.36)

According to the TROK model, the parameter α is the same for the two power laws. However in experimental results it was noticed that it is not the case and that it has two values α_1 for the first power law and α_2 for the second, and that they obey different temperature dependencies. This can be attributed to the failure of the simplified exponential distribution of tail states. The pre-transit photocurrent decay is due to the decrease in density of free carriers associated with the progressive thermalization and random trapping, while the steeper decay in the photocurrent at the post-transit region is due to extraction of carriers from the sample through the back contact.

It follows from Eq.2.34 and the assumption of an exponential DOS that t_T has a non-linear dependence on field and sample thickness of the form:

$$t_T \sim \left(\frac{d}{F}\right)^{\frac{1}{\alpha}}.\tag{2.37}$$

Also the TOF drift mobility that is calculated from t_T by the formula

$$\mu_d = \frac{d^2}{t_T V_a},\tag{2.38}$$

will therefore have a non-linear dependence on field and sample thickness. These relationships should be used to estimate the parameter α , rather than the power law of the pre-transit current of the TOF signal because in the former data as a function of both temperature and field are used, while in the latter data are in function of temperature only.

Experimentally, it was further found that, to first approximation, the drift mobility at fixed field is thermally activated according to the equation:

$$\mu_d \propto \exp(\frac{-E_a}{kT}),\tag{2.39}$$

where the activation energy E_a corresponds to the deepest energy level that a trapped carrier can be released from on average at the transit time t_T . It is also reported that this activation energy is field dependent, the higher field giving the lower activation energy. This is caused by the higher velocity of free carriers under the higher field, leading to fewer trapping events during the carrier transit, thus preventing the demarcation level from reaching the same energetic depth as for the lower field [61][62]. Michiel et al. reported that the activation energy becomes field-independent when the distribution of states is too steep or when the DOS contains a sharp feature that dominates the transport [63].

Interpretation of TPC transients

The analysis of standard TPC experimental data sets in the MT formalism follows closely the above analysis for the TOF signals. Although TPC uses the gap-cell geometry while TOF makes use of sandwich cells, pulsed optical excitation is employed in both instances to create a reservoir of free carriers at t=0. Those carriers then thermalize in and drift through the sample. In fact both pre-transit TOF analysis and TPC give the same $t^{-(1-\alpha)}$ power law for the exponential DOS. With respect to the TPC signal, a further development has been the study of the current behavior when a sharp feature is superimposed on the exponential DOS [64] [65]. Such feature produces a kink in the current trace; from its temperature dependence the energy position of the feature can be deduced.

The pre-transit current in a TOF experiment on a thick sample can be treated as the standard photocurrent decay in a gap cell configuration sample, and it can show the same behavior described above.

Chapter 3

Thermal transitions in the negative-U energy scheme for a-Se

As was mentioned in Chapter 1, the thermally accessible localized state levels T^+ and T^- can be detected using either transient or steady-state photoconductivity techniques. This chapter will deal with these levels related to the negative-U model in a-Se using TOF, TPC and SSPC techniques. The detection of the T^+ and T^- levels will be a first step to answer the question whether a-Se is a negative-U system or not.

3.1 Steady-state photoconductivity

Often steady-state photoconductivity is the simplest technique to probe the recombination levels in the gap of chalcogenide amorphous semiconductors. However, for a-Se the situation is more complicated since the range of temperatures where we can see the change of recombination mode from bimolecular to mono-molecular is narrow. Indeed, as it was mentioned above, the glass transition temperature of a-Se is around 42 °C. Another problem in this sense is that a-Se is a highly sensitive photoconductor, and thus it is difficult to measure photocurrents lower in magnitude than the dark current.

3.1.1 Experimental results

Experimental conditions

DC conductivity measurements were carried out in a 5×10^{-3} Pa atmosphere by means of a Keithley 428 current amplifier and an Agilent 3440a millivoltmeter, with a suitable applied voltage for every sample. For measuring the steady-state photoconductivity (SSPC), a 15 mW He-Ne laser (632.8 nm) or an infra-red light emitting diode (LED), 890 nm, 1.7 mW/cm^2 at 50 mA were used as monochromatic light sources. Calibrated neutral density filters served to modify the light intensity.

a-Se films with thickness varying from 1 to 20 μm were evaporated in a vacuum background of 10^{-2} Pa from 99.995% pure Se (Alfa Aesar) onto high-resistivity Corning 7059 glass substrates. For the measurements, either gap-cell or sandwich-cell configurations were used. Gap cells had evaporated gold electrodes on top of the films with active areas of 0.5 mm × 10 mm. Aluminium electrodes were used for one bulk sample. The substrate temperature was not regulated during the evaporations, but X-ray examination of several films proved that they were fully amorphous. A further set of samples deposited on either glass or aluminium substrates and with Au and Pt top contacts was provided by Prof. Kasap (University of Saskatchewan). Their thickness ranged from 8 to 300 μ m. From this set, a 265 μ m thick sandwich sample deposited on aluminium and provided with top gold contact, was used for the steady-state measurements.

During SSPC measurements, the sample is placed on a metal support in the vacuum chamber. The sample temperature is controlled to better than 0.5 K by a combination of liquid nitrogen cooling and regulated electrical heating of the sample support.

Results

Fig.3.1 shows data sets for the temperature dependence of the steady-state photo- and dark currents as follows:

• The 265 μ m thick a-Se sandwich cell, when illuminated at 890 nm with the LED is shown in Fig.3.1.a. The change-over from rising currents with rising inverse temperature at the high-temperature end to decreasing currents at the low-temperature end corresponds to the traditional pattern observed in numerous chalcogenide glasses [28][26][30]. At the higher temperatures, i.e. at high concentrations of thermally generated carriers, monomolecular recombination controls the magnitude of the photocurrent [26] and the activation energy, ΔE_m , of the photocurrent in that range indicates the position above the material's Fermi level of a donor-like recombination center. At the low-temperature side, the optically generated carriers will dominate the conductivity, the recombination will be mostly bimolecular, and the photocurrent activation energy in this region, ΔE_b , can be linked to an acceptor-like recombination center located $2\Delta E_b$ above the valence band mobility edge [26].



Figure 3.1: (a) Temperature dependence of the steady-state photocurrent for four intensities of 890 nm illumination, with 100 V applied across a 265 μ m thick a-Se sandwich cell. Reference light intensity is $I_0 = 4 \times 10^{16}$ photons $cm^{-2}s^{-1}$. The full symbols indicate the level of the underlying dark current. (b) Temperature dependence of dark current I_d (full symbols) and steady-state photocurrents at 470 nm illumination for an a-Se film with three different light intensities: $I_0 = 2 \times 10^{13}$ photons $cm^{-2}s^{-1}$ (o), $5 \times 10^{-2}I_0$ (\triangle) and $3.8 \times 10^{-3}I_0$ (\diamond). 50 V was applied across a 0.5 mm gap. (c) Dark and photocurrents from an a-Se bulk sample illuminated at 632 nm with $I_0 =$ 5×10^{17} photons $cm^{-2}s^{-1}$ and with 100 V applied across a 0.5 mm gap.

From Fig.3.1.a, $\Delta E_m = (0.50 + 0.02)$ eV can be determined with good precision, but the temperature range available below the photocurrent maximum is too limited to permit the determination of ΔE_b with similar precision. Consequently, the value of ΔE_b has to be deduced from other measurements where a larger temperature range is available.

The dark conductivity data shown in Fig.3.1.a testify to the presence of two different conduction mechanisms in the sample. For $10^3/T < 3.2$ K^{-1} , an activation energy of 0.92 eV is observed, in general agreement with results from other samples and with reported literature values in the 0.9 to 1.0 eV range. To first approximation this energy reflects the energetic distance $E_F - E_V$ between the valence band mobility edge and the Fermi level (holes being the mobile carriers in the chalcogenides), and indicates that band transport dominates. At lower temperatures a hopping current component is dominant with the approximate activation energy of 0.25 eV reflecting injection across the aluminium oxide barrier at the bottom contact of the sample. Depending on the individual sample, the magnitude of this injected current can vary widely, but the activation energy remains the same.

- The open symbols in 3.1.b show the temperature dependence of the photocurrent in an a-Se gap cell in a $logI_{ph}$ versus $10^3/T$ diagram for three different light intensities: I, $1, 5 \times 10^{-2}$ I and 3.8×10^{-3} I, where $I = 2 \times 10^{13} \ photons/cm^2s$ represents the full light intensity at 470 nm (2.64 eV) illumination. At low temperatures and high light intensities, i.e. when the photocurrent is larger than the dark current, a bimolecular recombination regime leads to an exponentially decreasing I_{ph} with 1/T. Activation energy value, ΔE_b of 0.13 eV is found. More results not presented in this thesis, but to be found in [66], have given a ΔE_b value of 0.17 eV.
- Similar temperature dependencies of the photocurrent are found in bulk stabilized a-Se samples. However, the transition between the monoand bimolecular recombination regimes is now more spread out in temperature since successively deeper-lying layers of the bulk sample will be subject to increasingly lower illumination intensities. The optically excited free carrier density will thus vary through the sample while the thermally excited, dark, density remains constant. Fig.3.1.c shows an example of such transition. A He-Ne laser (632.8 nm) was substituted for the 470 nm excitation used above in order to moderate the variation in optical excitation density. While the ΔE_b slope (~ 0.28 eV) is readily available, and the transition to a different regime is seen, no

3.1. Steady-state photoconductivity

clear monomolecular recombination regime is observed.

Taking in account all the obtained results mentioned above a value of $\Delta E_b = 0.18 \pm 0.03$ eV can be calculated for the bimolecular regime. The recombination centers, discussed above and located at $E_V + 2\Delta E_b$ and $E_F + E_m$, have been identified in the literature as the thermally accessible levels of the negative-U energy diagram [27][67]. Steady-state photoconductivity, of course, reflects the equilibrium between optical excitation and thermal recombination of charge carriers.

The change in recombination mechanism that is signaled by the changing value of the photocurrent activation energy, also can be seen from the light intensity dependence of the photoconductivity in chalcogenides. This dependence has been determined at different temperatures for several a-Se gap cells. Fig.3.2 shows the photoconductivity induced by the 470 nm illumination as a function of photon flux over two orders of magnitude at two different temperatures. For both film and bulk samples the photocurrent, I_{ph} , grows with light intensity, hence photocarrier generation rate G, according to $Iph \propto G^{\gamma}$ with $\gamma = 0.5$ at the lower temperature (297 K), while at the higher temperature $\gamma \approx 0.66$ is found. The value $\gamma = 0.5$ signifies bimolecular recombination behavior [26]. Since $\gamma = 1$ would be required for a fully monomolecular one, a value of $\gamma \approx 0.66$ indicates that the higher temperature lies in the transition region between the two recombination regimes. In fact, the data in Fig.3.1.b and c confirm that the transition to monomolecular behavior has only started. Nevertheless, the results in Fig.3.2 provide further evidence that the change-over in the recombination process, that has become a hallmark of the arsenic chalcogenide semiconductors and their negative-U centers, can also be resolved in a-Se samples. Examining the light-intensity dependence of the photocurrents in Fig.3.1.a, we find a value of $\gamma = 0.95$ in the high-temperature region, in agreement with the notion of monomolecular recombination. However, the value of γ does not change as the temperature is lowered. This fact, conceivably, relates to a photo-sensitization effect that will be discussed in a later chapter.

3.1.2 Discussion

Electrical conduction in a-Se is mainly due to holes, which means that the dark current activation energy E_{σ} corresponds, to first approximation, to the energy distance between the Fermi level, E_F , and the valence band mobility edge, E_V . In the analysis of the photocurrent temperature dependence as worked out for chalcogenide materials by Main and Owen [26], Simmons and Taylor [49] or Okamoto et al. [67], and as described in Chapter 2, these E_F



Figure 3.2: The dependence of the photocurrent on the light intensity, at two temperatures, for a-Se film (open symbols) and bulk (full symbols) samples.

and E_V levels serve as references for the energy positions of the recombination centers that dominate in either the monomolecular or the bimolecular recombination regime. At high temperatures and low illumination intensities, the photocurrent defines the energy location in the gap of a discrete donor-like recombination center as $E_1 = E_V + E_F + \Delta E_m$. The high-temperature photocurrent in turn locates an acceptor-like recombination center at the energy $E_2 = E_V + 2\Delta E_b$. In chalcogenides these centers can be identified with the negative-U centers, i.e. the charged defects with negative effective electron correlation energy [15][10]. In selenium, these are thought to be a three-fold coordinated positively charged selenium atom C_3^+ and singly coordinated negatively charged one C_1^- .

Applying the above relationships to our steady-state photoconductivity results for a-Se, the energy values deduced are $E_2 - E_V = (0.36 \pm 0.06)$ eV and $E_1 - E_V = (1.42 \pm 0.02)$ eV for the thermal transitions involving negative-U defects. With respect to the conduction band, the E_1 level finds itself at $E_C - E_1 = (0.53 \pm 0.02)$ eV if the accepted gap value of Eg = 1.95eV is used. The 0.36/0.53 eV set of levels, thus obtained with respect to the bands are closer to the theoretical values of $Eg/4 \approx 0.5 \ eV$ than to the earlier 0.26/0.35 eV set proposed in [8] and shown in Fig.1.15. These earlier
3.1. Steady-state photoconductivity

values are in fact based on a misinterpretation of the original TOF data sets of Kasap and Juhasz [9]. Indeed, in analogy to the pioneering work on TOF in chalcogenides by Marshall and Owen [68], it was assumed in [8] that the activation energy of the drift mobility corresponds to the energy position in the bandgap of a prominent trapping center. Marshall [69] has since shown that such interpretation is unwarranted, and that a field dependence of the drift mobility as seen for a-Se does actually signal a broad featureless distribution of traps in the relevant energy range.

As can be seen in Fig.3.1, experimental conditions affect the results considerably. One of these experimental factors is the use of short-wavelength light in a gap-cell configuration which allows surface states to play a role in the recombination, while longer wavelengths, as used with the sandwich cell configuration, permit to reduce the influence of these surface states and make the illumination more homogenous through the sample bulk. A clear limitation is the restricted temperature range over which SSPC measurements can be made on the high temperature side of the photoconductivity maxima. The low glass transition temperature of a-Se is responsible for that limit. It is important to mention that the nice monomolecular recombination regime seen in Fig.3.1.a is measured above glass-transition temperature, and with infrared light excitation in a very thick sandwich sample. Care was taken to measure at temperatures above the glass transition temperature for brief periods only to avoid any unwanted crystallization of the material. Nevertheless, in spite of this limitation, it was possible to see the change from one regime to the other in all measured samples. This sensitivity to experimental conditions does explain the scatter in data deduced from measurements on different samples, as shown by the set selected for Fig.3.1.

Results deduced in this work are totally different from a set of steadystate photocurrent measurements that resolved a linear dependence of the photocurrent on the light intensity for all temperatures and wavelengths [70]. However, the latter should not be trusted because the data were obtained with 60 nm thin films deposited on glass. Although the substrate is not mentioned in [70], contemporary papers by the same group [71] indicate the use of glass substrates, and the resulting dark current activation energy of $0.7 \ eV$ clearly refers to Na ionic conductivity in the substrate [72] rather than the a-Se film on top.

At temperatures below the ones discusses in this section, a defect level situated just above the Fermi level can causes a sensitization effect, which leads to an increase in photocurrent at lower temperature (with maximum around -20 °C) As will be seen in later chapter, this photocurrent feature can affect the photocurrent slope in the bimolecular recombination regime.

The two defect levels that were identified above, can be probed by other

techniques as well. Among them are the transient photocurrent techniques that will be dealt with in the next sections.

3.2 Post-transit photocurrent analysis (PTPA)

As described in chapter two, the transient TOF current consists of three parts: The first part corresponds to times $t < t_T$ and shows a decaying power law, the second part at times just after t_T decays with a steeper power law, and the third part, the so-called post-transit photocurrent, corresponds to times $t \gg t_T$. While some knowledge about the tail states can be deduced from the TOF transit time, later parts of the current transient contain information about the gap states. Indeed, when $t \gg t_T$, the charge carriers contributing in the post-transient current are mainly those re-emitted from deep states according to the release time approximation

$$t = \nu^{-1} exp(E/kT).$$
 (3.1)

The post-transit photocurrent I(t) will then be proportional to the number of carriers released at time t from the density of states g(E) at the corresponding energy level. Assuming equal capture probability into all states, the posttransit current I(t) is directly related to the density of gap states g(E) [73] through the relation

$$g(E) = \frac{2g(0)}{Q_0 t_0 \nu} t I(t), \qquad (3.2)$$

where Q_0 is the total charge participating in the transient photocurrent, t_0 is the free-carrier transit time i.e., the carrier crosses the sample without being trapped, and g(0) is the DOS at mobility edge. Q_0 can be estimated from the time domain integral of I(t). Since in Eq.3.2 several parameters cannot be measured, calculation of absolute values of g(E) is difficult. Nevertheless, estimations of g(E) can be made by assuming generally accepted values for the parameters t_0 and g(0).

It is important to note here that contrary to the conditions required for measuring the transit time, where a small excess charge compared to the total charge of the capacitance is required, this is not the case for the posttransit current. Therefore, the PTPA can be achieved with photocurrents measured under high light intensities as well as low ones [74].



Figure 3.3: (a) TOF electron transient photocurrent from a 4 μm thick sample at different temperatures(b) TOF hole transient photocurrent from 7 μm thick sample at different temperatures, the current traces are offset for clarity.

3.2.1 Experimental results

Fig.3.3.a shows TOF photocurrent transients for electrons as obtained from 4 μ m thick sample under various temperatures while Fig.3.3.b shows TOF photocurrent transients for holes form a ~7 μ m thick a-Se sample at 0 and -20 °C under applied voltage of 5 V. The TOF transit time t_T can readily be deduced from the first change of slope of the current traces. Observation of t_T is a first condition for the execution of a meaningful PTPA.

The shortening of the transit time with increasing temperature that is seen for electrons and holes in Fig.3.3 and with increasing field as seen for holes in Fig.3.5.a confirms the validity of the transit-time interpretation of the change of slope. The electron and hole drift mobilities calculated from the transit times agree with the room-temperature values of $4 \times 10^{-7} m^2 V^{-1} s^{-1}$, respectively $10^{-5} m^2 V^{-1} s^{-1}$ that are found in the literature [9].

Applying the PTPA procedure outlined above to the data of Fig.3.3 reveals, parts of the DOS distribution in the gap, as is shown in Fig.3.4. On the valence band side of the gap, the DOS structure shows a clear maximum at $E - E_v = 0.40$ to 0.45 eV. On the side of the conduction band, a maximum in the DOS is resolved at $E_c - E = 0.53$ eV. These values compare well with the energy positions resolved earlier for the defect levels by Song et al. [75] and with the values derived in the previous section, as well as with the expected location in the gap of the thermally accessible levels of the KAF model for a-Se [11].

It will be noticed in the DOS profiles in Fig.3.4.b that the position of the maximum is influenced by the strength of the applied electric field. This field dependence is a manifestation of the Poole-Frenkel effect whereby, in sufficiently insulating materials, the applied electric field lowers the potential barrier for escape of a trapped charge, or ionisation of a particular lattice configuration. The barrier energy changes according to the equation:

$$\Delta E = -\left(\frac{e^3 F}{\pi \epsilon}\right)^{\frac{1}{2}} = -\beta F^{\frac{1}{2}},\tag{3.3}$$

where e is the electronic charge, F the applied field, ϵ the dielectric constant of the material, and β is the Poole-Frenkel constant. In order to check the validity of this assumption measurements of transient TOF photocurrent were curried out on a 10 μm thick sample at different fields, the results being shown in Fig.3.5.a. Applying the PTPA to this set of results, the DOS structure above the valence band is resolved at different fields. Taking the onset of the defect band (as marked by the arrows) in Fig.3.5.b as energy reference, Fig.3.5.c shows that the $F^{1/2}$ law is obeyed. For the parameter β , the value $2.98 \times 10^5 \ {\rm eV}/({\rm V/m})^{1/2}$ is found, which is in good agreement



Figure 3.4: Distribution of gap states deduced from post-transit TOF signals from the samples also used in Fig.3.3 for an attempt-to-escape frequency of $\nu = 10^{12} \ s^{-1}$ and $g(0) = 5 \times 10^{21}$ (a) valence band side, $Q_0 = 7 \times 10^{-11}C$, (b) conduction band side, $Q_0 = 5 \times 10^{-10}C$.

with the theoretical value of $2.84 \times 10^5 \text{ eV}/(\text{V/m})^{1/2}$ [9][76]. The onset of the defect band was used instead the maximum of the feature itself because the former is more precise as it can be easily seen. Fig.3.5.d, showing the dark current in function of $F^{1/2}$ for a 28 μm thick a-Se film, further illustrates that transport in a-Se is subject to the Poole-Frenkel effect for the field range used in these experiments. Here, the deduced value of the Pool-Frenkel constant β is $2.6 \times 10^5 \text{ eV}/(\text{V/m})^{1/2}$.

3.2.2 Discussion

The features that appear at 0.42 eV above the valence band edge for holes, and at 0.53 eV below the conduction band edge for electrons (Fig.3.4), can be interpreted as the emission from the occupied states of the negative-U model, i.e. the C_3^0 and C_1^0 that correspond to the occupied defects C_3^+ and $C_1^$ respectively. These two energetic positions do agree well with the predictions of the negative-U model [11],[25], and the values deduced from SSPC for the T⁺ and T⁻ levels in the earlier section. The above values for the energy positions of the defects are calculated with the assumption that the attemptto-escape frequency equals $10^{12} s^{-1}$; a variation of this value by one order of magnitude, which is a possible variation for this parameter, will change the energetic position of the features in the DOS, according $kTln(\nu t)$, by some 0.05 eV at room temperature. This uncertainty introduced by the assumed value of ν will have to be kept in mind when looking at the energy positions of defects.

Further support for the validity of the negative-U model for a-Se is offered by the observed Poole-Frenkel effect on the TOF emission currents. Indeed, the fact that the field-dependent lowering of the Coulombic barrier is observed with carrier emission indicates that the defect centers are charged in equilibrium, i.e. when unoccupied, as postulated in the negative-U model.

Model calculations

Recently Koughia et al. [42] measured TOF photocurrent transients for electrons as a function of the applied field, and analyzed them in terms of a multiple-trapping model in which a trial-and-error-based inverse Laplace technique was used to derive the DOS distribution below the conduction band edge. The DOS distribution is determined by comparison of the shapes of the measured and calculated photocurrent, the DOS being step-wise adjusted until there is a good agreement between measured and calculated currents. The results were then further checked by means of a Monte Carlo simulation



Figure 3.5: (a) Time-of-flight transient photocurrent for holes from 10 μm thick sample at different fields . (b) Distribution of gap states deduced from transients in (a) for an attempt-to-escape frequency $\nu = 10^{12} s^{-1}$, where the arrows show the onset of the defect level. (c) Shift of the corresponding energy of the onset in (b) as a function of $F^{1/2}$. (d) Dependence on field of the dark current through a 28 μm thick sample.

of the transients. The authors concluded that the DOS distribution consists of four elements:

- An exponential tail with a characteristic energy of 20 meV, that will be discussed in more detail later.
- A fairly strong peak, some 0.30 eV inside the gap, that also, will be discussed later.
- A weaker feature at 0.45 to 0.50 eV below the conduction band mobility edge. This peak does agree, in the energetic position, with the 0.53 eV feature resolved in this work by means of SSPC and PTPA.
- A less well defined concentration of deep states beyond 0.65 eV.

Although the position of the 0.45 - 0.50 eV level is in acceptable agreement with the result deduced above from PTPA, it differs from the latter in significant ways. Specifically: the PTPA results produce a more prominent and wider defect peak. To examine this discrepancy more closely, an independent comparison of measured and calculated TOF signals was carried out. An experimental data set covering sufficient variation in temperature and field was measured on an 18 μm thick a-Se sample. The TOF data were collected over the wide time domain that is required for the standard post-transit analysis, providing an extended current range to be fitted. Fig.3.6 shows some of these TOF signals. Calculations based on the analytical description of the TOF transients as formulated by Rudenko and Arkhipov were made by Emilianova et al. [77] to generate theoretical TOF transient that can be compared with the experimental ones.

The calculations used the DOS distribution proposed by Koughia et al. [42] and given as:

$$g(E) = \frac{N_e}{\Delta E} \exp(-\frac{E - E_c}{\Delta E}) + \sum_{k=1}^{3} \frac{N_k}{(2\pi\sigma_k)^{\frac{1}{2}}} \exp(-\frac{(E - E_k)^2}{2\sigma_k^2}), \quad (3.4)$$

where E_c is the electron mobility edge, ΔE the width of the conduction band tail, E_k and σ_k are the maxima and widths of the respective Gaussian peaks, N_e and N_k are the densities of localized states in the band tail and in the Gaussian peaks, respectively. Calculation based on the Koughia's DOS are matched to the new data set in Fig.3.6.a where it can be seen that, while the pre-transit photocurrent can be fitted rather well with that DOS, calculated post-transit curves especially at the higher temperatures and longer times show significant deviations from the experimental traces.



Figure 3.6: Experimental electron TOF curves (full lines) together with theoretically calculated photocurrent traces (symbols) for two different DOS with the following parameters: (a) $N_e = 4 \times 10^{19} \text{ cm}^{-3}$, $N_1 = 6 \times 10^{15} \text{ cm}^{-3}$, $N_2 = 5.6 \times 10^{12} \text{ cm}^{-3}$, $N_2 = 10^{12} \text{ cm}^{-3}$, $E_1 - E_c = 0.3 \text{ eV}$, $\sigma_1 = 35 \text{ meV}$, $E_2 - E_c = 0.48 \text{ eV}$, $\sigma_2 = 32 \text{ meV}$, $E_3 - E_c = 0.65 \text{ eV}$, $\mu_c = 8 \times 10^{-2} \text{ cm}^2/(\text{Vs})$, $c_0 = 10^{-8} \text{ cm}^3 \text{s}^{-1}$, $\nu = 10^{12} \text{ s}^{-1}$. (b) $N_e = 4 \times 10^{19} \text{ cm}^{-3}$, $N_1 = 8 \times 10^{14} \text{ cm}^{-3}$, $N_2 = 1.6 \times 10^{13} \text{ cm}^{-3}$, $N_3 = 0$, E = 20 meV, $E_1 - E_c = 0.3 \text{ eV}$, $\sigma_1 = 44 \text{ meV}$, $E_2 - E_c = 0.46 \text{ eV}$, $\sigma_2 = 80 \text{ meV}$, $\mu_c = 1.65 \times 10^{-2} \text{ cm}^2/\text{Vs}$, $t_0 = 5 \times 10^{-13} \text{ s}$, $\nu = 10^{13} \text{ s}^{-1}$.

In these calculations the positions and widths of the DOS features were kept as used in [42], but the heights of peaks and the value of free carrier mobility μ_0 were allowed to vary as those quantities can depend on sample preparation. The figure caption lists the parameter values that were used.

If changes in the positions and the widths of the Gaussian peaks are allowed, the agreement between the calculated and experimental transients is much better as it can be seen in Fig.3.6.b. It is remarkable that for this agreement, the width of the second peak was enlarged to 80 meV rather than the 32 meV used by Koughia et al, and that the third peak was completely omitted. There are still small deviations between the calculated and experimental transients, for instance in the transit time region; they can be explained by the lack, in the mathematical model, of a factor representing the field-assisted diffusion that might play a role in the transients at room temperature. Fig.3.7 shows the DOS used for fitting of the current transients together with the DOS of Koughia et al.. It should be reiterated that the densities of the Gaussian defect peaks are sensitive to sample preparation and accidental doping and are therefore subject to variation from sample to sample. This notion implies that the densities of Gaussian peaks are of less importance than the widths and average energies of the peaks. While positions and widths of the first peak are comparable in the two simulations, only the position of the second peak is in agreement with the one in [42]; its width turns out to be significantly broader.

It has to be noted that the time domain of the measurements reported by Koughia et al. was restricted to just one or two decades around the transit time, and that all measurements were carried out at room temperature. Based on such measurements, it is very difficult, if not impossible, to give a reliable estimate for the width and exact position of a deep peak because, within this time interval, the post-transit photocurrent is still dominated by carrier release from shallower states, and the pre-transit current cannot provide information about either the average energy of deep states or their distribution.

In contrast with the results in [42], the data in this study do not indicate the need for an additional defect density below 0.6 eV (which was entered in the calculation, as the third peak). The obvious reason for this difference in interpretation lies in the estimated width of the second peak. The total density of states in the broad second peak of this DOS model (some 10^{12} cm^{-3}) does in fact match the combined density of the second peak and the additional deep states in [42]. Within a restricted time domain around the transit time, only the total density of deep states and not their distribution can be estimated. To illustrate this point, it was shown that one of the experimental TOF transients of [42] can be precisely generated on the basis of a DOS without the additional deep states, but with the 80 meV wide second Gaussian [77].

A more recent study by Koughia and Kasap [78], using the same technique described above, claims that TOF hole transients indicate a monotonic and featureless distribution of states up to 0.5 eV above the valence band edge. It was further stated that adding some deep state density (about 10^{13} cm^{-3}) beyond 0.5 eV leads to better results. These results are of course in total disagreement with the feature at 0.42 eV above E_V that was resolved in this work by PTPA and SSPC and that will be confirmed by the TPC technique in the next section.

For this hole TOF study, the authors measured room-temperature TOF photocurrents at different fields, and used data taken from [79] [80] for different temperatures. Unfortunately the common characteristic in all these



Figure 3.7: DOS used to fit experimental TOF curves of Fig.3.6.b (full line) in comparison with DOS obtained in Koughia et al. (dotted line).

data is that they do not cover a large time domain, each of them only using TOF traces around the transit time. This forms the key point to explain the difference of the results. Indeed it is easier to fit transients covering small time ranges with an approximate DOS, than this would be the case for transients covering wide time ranges such as the standard transients used in the PTPA technique. Thus, the controversy can be traced to the limited time range used in the Koughia and Kasap experiments.

3.3 Transient photocurrent decay

As mentioned in the previous chapter, several simulation studies showed how a discrete feature on top of an exponential DOS would produce a depression in the power-law decay of the transient photocurrent, with its position in the time domain indicating the energetic location of the discrete trap according to the thermalization relation [64]. In the TPC technique both electrons and holes are participating in the current, but the more mobile carriers will dominate it. Therefore, TPC can be used to examine the valence band tail.

3.3.1 Experimental results

On a hot-pressed a-Se sample, two parallel gold contacts separated by a gap of ~ 0.5 mm were evaporated. On this bulk gap-cell sample standard transient photocurrents were measured at different temperatures, using the blue laser flash (440 nm). A DC Voltage of 300 V was applied for these measurements. Fig.3.8 shows the transients. At the lower temperatures, the current



Figure 3.8: Transient photocurrents from a hot-pressed bulk a-Se gap cell after pulsed laser excitation. The arrows show the approximate time positions of the kink. Transients at 24° C and 0° C are offset for clarity by the factors shown. The inset shows the time position of the depression in function of inverse temperature (symbols) and there linear fitting.

transients start out along a power law $I(t) \propto t^{-\gamma}$. On the assumption of an exponential tail, which is not precisely the case for a-Se, as already shown in the previous section, γ can be written as $1 - \alpha$ with $\alpha = kT/E_0$ allowing an estimate for the width of the exponential distribution, namely $E_0 \approx 29$ meV. This estimate will be discussed in a later chapter. Also of interest in these transients is the temperature-dependent depression seen at the higher temperatures. This depression is the signature [64] of a discrete feature in the DOS, located 0.43 eV above the valence band, in full agreement with the results of the previous sections. This defect energy position is calculated assuming a value for the attempt-to-escape frequency of 10^{12} s⁻¹. However, this assumption may not be warranted. The inset in Fig.3.8 represents the times corresponding to the kink of the transients, as shown by the arrows, in function of inverse temperature. Using the thermalization formula, a linear fitting of the points in the inset gives, according to $t = \nu^{-1} \exp(E/kT)$, an attempt to escape frequency $\nu = 2.9 \times 10^{12} \ s^{-1}$ and defect energy position E = 0.45 eV are found. The inset of the Fig.3.8 shows that fitting.

3.3.2 Discussion

As can be seen in Fig.3.8, the depression in the power-law-like transient photocurrent is thermally activated, such that at lower temperatures the kink appears at longer times. Therefore, the use of the thermalization formula is justified. It is unfortunate that only three points are available to determine the value of ν . This is caused by the loss of a recognizable depression at those temperatures, which is probably due to recombination and dispersion at low temperatures. This high ν value 2.9×10^{12} s⁻¹, reflects a large trapping cross section of the defect according to the detailed balance equation $\nu = N_0 v_{th} \sigma$, where N_0 is the density of states at the band edge, v_{th} a thermal velocity of the charge carrier and σ is the trapping cross section. This high trapping cross section is compatible with charged defects. The value 0.42 eV deduced from the PTPA in the previous section was calculated using $\nu = 10^{12} s^{-1}$. The newly measured value of ν puts the energy position of that defect at about $0.45 \ eV$. Therefore, the two techniques, PTPA and TPC, indicate the same defect level above the valence band edge. It should be pointed out here that the TPC measurements were done on a bulk sample which has not necessarily the same characteristics as thin evaporated films.

3.4 Concluding discussion

Fig.3.9 is an energy diagram showing the defect levels that were deduced by the different experimental techniques described in the previous pages. Although there is a small difference in the energy position of the level $T^$ deduced by SSPC on one hand and PTPA and TPC on the other hand, this is probabely due to the sensitization effect discussed in a later chapter. A generally good agreement is found between the positions obtained for the thermally accessible levels of the defects, T^+ and T^- , from SSPC, TOF and TPC measurements. This scheme for a-Se mirrors similar ones that are familiar from studies of the density of states of a- As_2Se_3 .

One common feature of all experimental data sets is the asymmetric position of the defect levels with respect to the band edges; in each instance they are shifted towards the valence band. such asymmetric shift of the negative-U energy levels towards the valence band has been reported for a- As_2Se_3 [28] [102], a- As_2Te_3 [102], a- $AsSe_2$, a- $As_{47}Se_{53}$ [81], and a- $GeSe_2$ [82]. The assumption that the two-fold coordinated chalcogen sites induce a common preferred defect configuration in all of these compounds would explain such group behavior. While a specific model for the defect configurations is available for a-Se for the moment, it is not obvious how to extend it to other



Figure 3.9: Sketch of the energy level diagram deduced for thermal transitions T^+ and T^- at the negative-U co-ordination defects, on the basis of SSPC, TOF and TPC techniques.

chalcogenide compounds.

The high attempt-to-escape frequency calculated from the data in Fig.3.8 means that the capture cross section of the defect is high, which is in total agreement with the notion that the trap is charged when empty, as is characteristic for the charged defects in negative-U model. The high capture cross section is also in agreement with the observed potential barrier lowering under applied field, i.e. the Poole-Frenkel effect, at these defects.

Since the thermally accessible levels have been resolved using several known techniques, the logical next step for this study would be the detection of optical transitions related to the negative-U model, as indicated in Fig.1.11 of the first chapter. That will be the subject of the next chapter.

Chapter 4

Optical transitions in negative-U model

Apart from the thermal transitions discussed in the previous chapter, a number of purely optical transitions to and from the negative-U centers can also be observed. In the energy level diagram that is reproduced below as Fig.4.1, the transitions 1 and 1' represent the absorption of an optical photon whereby an electron is promoted from the top of the valence band to the positively charged defect D^+ or from the negatively charged D^- to the bottom of the conduction band. The charge state of the defects is of course modified in this process. As already explained in Chapter 2, the strong electron-phonon coupling found in the chalcogenide glasses then leads to a polaronic lattice deformation around the defects sites. Consequently, while the original absorption takes place at the equilibrium configuration q_0 of the defect sites, all subsequent optical transitions will involve the deformed configuration q_n . Such is the case for the transition 2 and 3 of Fig.4.1. Transition 2 represents photoluminescence whereby the excited electron radiatively recombines with a hole of the valence band, while transition 3 is referred to as photoinduced absorption since it involves excitation to the conduction band of an electron whose presence at the defect site resulted itself from an earlier photon absorption.

It is clear that experimental observation of some of these optical transitions in a-Se will provide further evidence for the presence of the negative-U defects in this material. This chapter, therefore, presents and discusses the results of three different experiments: the spectral distribution of steady-state photoconductivity, the constant photocurrent method(CPM) and photothermal deflection spectroscopy (PDS).



Figure 4.1: Energy level diagram for charged defects D^+ and D^- with the different transitions are represented. The right-hand part of the figure is the energy-configuration diagram for the D^+ defect.

4.1 Experimental conditions

4.1.1 Samples

For the CPM and spectral response technique gap cells have been used with either simple parallel electrodes or interdigitated contacts. The gap defined by the interdigitated electrodes was 31 μ m. In some samples the gold electrodes were deposited on the Corning glass substrate followed by deposition of the a-Se film, and the others the a-Se film is first deposited on the substrate, followed by the deposition of the gold contacts on the surface of the a-Se film. In the former case illumination has been done through the substrate as well as directly on a-Se film. For the PDS technique a-Se films are evaporated on Corning glass substrate. No electrodes are required, and in this case the illumination should come directly upon the a-Se film.

4.1.2 Experimental set-ups

CPM and spectral response measurements can make use of the same set-up. As light source, a 250 W tungsten-halogen lamp plus monochromator with 10 nm band pass are used. The desired wavelength is selected mechanically



Figure 4.2: Schematic representation of the photothermal deflection spectroscopy (transverse configuration).

with an error of less than 2 nm. A p-i-n photodiode and lock-in amplifier are used to measure the light intensity. The current is measured using either a Keithley pico-ampèremeter or a Keithley current amplifier and a milivoltmeter. A DC power supply is used to bias the sample during measurements. The sample is placed on a metal support in a vacuum chamber, where its temperature can be controlled using a combination of liquid-nitrogen cooling and regulated electrical heating. As a result of the slow stabilization of the photocurrent, the light intensity required to keep the photocurrent at a certain constant level needs to be adjusted manually.

PDS is an optical technique where, as mentioned earlier, an electrodeless sample is used. This technique is based on the measurement of the thermal energy released following light absorption. The sample is submerged in a transparent deflection medium (CCl_4) whose index of refraction is temperature dependent. As the sample is irradiated by monochromatic light, the medium will be heated. As shown schematically in Fig.4.2, this causes the deflection of the laser beam parallel to the sample surface. The deflection is proportional to the absorption coefficient of the material. Measurements using this technique were carried out at the Institut for Materials Research (IMO) in Diepenbeek.

As absolute values are not needed in this study, no calibration of the CPM and PDS data is required.



Figure 4.3: Spectral photocurrent on an a-Se thin film sandwich sample at three different voltages.

4.2 Experimental results

An important number of samples have been analyzed by the techniques described above. While the samples had different pre-histories of illumination and aging, the spectroscopic results proved to be reproducible within experimental errors. Therefore, what will be presented here are typical results. Fig.4.3 represents the spectral distribution of the photocurrent in a sandwich sample under three different voltages at room temperature. This photocurrent logically reflects the increasing absorption in the increasing tail-state density as the excitation energy approaches the optical absorption edge of 1.95 eV, but it also shows a shoulder in the 1.45 to 1.5 eV region that can be linked to additional absorption between the bands and the defect centers. Specifically, that energy could correspond to transitions between the valence band and the D^+ center, or between the D^- center and the conduction band.

Fig.4.4 represents the spectral photocurrent response from an a-Se film provided with interdigitated electrodes, when illuminated either through the substrate or directly on the a-Se film. The interdigitated contacts, in fact, give the possibility of measuring higher currents in a coplanar cell than can be achieved with standard gap cell samples, thus allowing measurement at low fields that are too difficult in the case of a standard gap cell sample. In these results the subgap absorption is no longer seen as just a shoulder



Figure 4.4: Photocurrent in function of photon-energy at different applied voltages. Full symbols corresponds to illumination through the substrate while the empty ones correspond to illumination from the surface of a-Se film.

on the main curve , but as a wide feature covering the same energy domain as the shoulder in Fig.4.3. This feature is less pronounced, i.e. a shallower minimum appears at the absorption edge, when illuminating through the substrate than when illuminating the a-Se film directly. It is also clear from Fig.4.4 that the minimum becomes more pronounced when measurements are done under lower fields.

Fig.4.5 shows a typical CPM spectrum, measured at room temperature, from an evaporated a-Se layer on a Corning glass substrate provided with gold contacts, having a narrow gap (~ 200 μ m). A local maximum in the absorption stretching from 1.4 eV to 1.8 eV, matches the photocurrent maximum of Fig.4.4 in the same energy range. This absorption must correspond to the optical transitions from the valence band edge to the $D^+(C_3^+)$ level and from the $D^-(C_1^-)$ level to the conduction band edge of the negative-U energy diagram, as proposed above on the basis of spectral photocurrent data. The subgap absorption decreases fast at energies larger than 1.7 eV, and finishes by a minimum in the signal at 1.95 eV, which corresponds to the optical band gap.

Subgap absorption, upwards of 1.4 eV, is also seen in the PDS signal from a 5 μ m thick sample as shown in Fig.4.6.a. A local maximum at 1.5 eV and a shoulder above 1.7 eV can be recognized, but no minimum of the type seen in Fig.4.4 and Fig.4.5 is observed. Since the PDS data were acquired through lock-in amplification, the phase of signal can also be monitored. Fig.4.6.b



Figure 4.5: CPM signal from a coplanar 16 μ m thick a-Se sample, contacts being evaporated gold.



Figure 4.6: (a) PDS signal on a 5 μm thick a-Se film. (b) Phase of the PDS signal.

4.3. Discussion



Figure 4.7: CPM spectra (\times, \circ, \bullet) for a-Se, in comparison with a transmission-based absorption spectrum (full line) and the photogeneration quantum efficiency (dotted line). The CPM data are obtained using planarelectrode samples with gap distances of 10 µm (×), 100 µm (\circ), and 1 mm (\bullet). (from Tanaka et al. [83]).

shows that the phase is stable at the high-energy range, but from ~1.75 eV on down oscillations indicate the appearance of other absorption processes. The PDS signal is directly proportional to the a-Se optical absorption coefficient and can therefore be used to determine the optical Tauc gap of 1.95 eV, and the slope of the exponential Urbach tail ($E_0 = 62$ meV).

It is important to point out that in the PDS technique one deals directly with the optical absorption while in the CPM and spectral photocurrent techniques photoconductivity is involved. Therefore, in the former every absorbed photon contributes to the measured signal, while in the latter the photogenerated electron-hole pairs have to separate before the carriers can contribute to the photocurrent and hence be included in the measured signal.

4.3 Discussion

The three techniques do agree that there is marked subgap absorption in a-Se at about 1.5 eV. This absorption can find an interpretation in the optical transition 1 in Fig.4.1, i.e from the valence band to the D^+ level at configuration q_0 . The transition 1' from A^- to the conduction band requires higher energy, since the A^- level has to lie below the T^- level, which makes the distance to the band larger than 1.50 eV. Therefore, the absorption at ~1.75 eV may be interpreted as due to the 1' transition. This higher-energy subgap absorption may also find an explication in the non-related shallow defects, that will be discussed in the next chapter. Indeed, shallow states have been identified at 0.2 eV above E_V and 0.3 eV below E_c . Nevertheless, the observation of optical transitions that can fill the role of the 1 and 1' transitions of the negative-U system do provide experimental support for this model.

The absorption minimum at the band gap energy (1.95 eV) is remark-It is deeper with lower fields, or when illuminating from the a-Se able. film surface, i.e not directly through the contacts. This suggests that the electron-hole pairs generated at this energy do often geminately recombine rather than participate in the photocurrent. Since high fields help to dissociate the electron-hole pairs, the minimum in the measured signal is deeper at lower fields. Illuminating the sample from the a-Se film surface causes most of the electron-hole pairs to be generated away from the region immediately between the electrodes where the electric field is highest. In other words: this way of illuminating corresponds to the low-field case. The fact that such geminate recombination does not happen for the electron-hole pairs generated through the subgap absorption provides further evidence that this absorption is caused by optical transitions related to the negative-U model. Indeed, the polaronic lattice deformation and energetic relaxation that accompanies electron excitation to or from a negative-U center will break the link between the generated electron and hole and thus prevent geminate recombination. An analogous situation exists with respect to above-gap absorption: There, it is the thermalization to lower-energy states that will disconnect the electrons and holes.

CPM results that show some similarity to the ones in Fig.4.5 have been reported before by Tanaka et al. [83]. They are shown by the data points in Fig.4.7. All relate to bulk a-Se samples and show a lower photoresponse near the optical gap energy than would be expected on the basis of the optical absorption coefficient (full line). No detailed analysis is given in [83], except for a reference to geminate recombination and a comparison with reported quantum efficiency values [84] that are shown by the dotted line of Fig.4.7.

Fig.4.8 shows the energy level diagram that has emerged so far with the thermal transitions and the estimates for the A^+ and A^- absorptions involving D^+ and D^- . The optical transition level O^+ that is also shown at 0.8 eV above E_V corresponds to the photoluminescence as measured before [85]. As explained earlier, this transition results from the radiative de-excitation of the occupied D^+ center and occurs at a changed site configuration as illustrated

4.3. Discussion



Figure 4.8: Sketch of the energy level diagram deduced for the negative-U coordination defects on the basis of the present study. Thermal levels T^+ and $T^$ were discussed in chapter three. A^+ and A^- are the optical Levels. O^+ level corresponds to the photoluminescence.

by transition 2 in Fig.4.1. The large energy shift between photoluminescence and absorption fits the requirements of the negative-U model.

The small energy distance between the A^+ and T^+ and the A^- and $T^$ levels, as deduced from the experiments described in this work, suggests that the D^+ and D^- defects have a rather flat energy surface in configuration space; in other words, that the energy increase due to the presence of an electron in the anti-bonding orbital [11] is roughly compensated by the polaronic lattice deformation energy. The larger energy distance between the O^+ level and the others indicates that the potential energy surface of the valence band has a stronger configurational dependence.

It is accepted that the quantum efficiency η is photon-energy [84] and field dependent [86][87]. Therefore the measured CPM and spectral photocurrent depend on η , while the PDS signal does not. A precise α measurement on a thick a-Se sample using the PDS technique could help to determine the spectrum of η by combining it with the results of a CPM measurement. The precise α measure could also give more precise information about the subgap absorption that is related to defect levels in the gap. However, applying the above procedure on the basis of the η curve from [84], cannot warrant proper values for α , since it was pointed out in [84] that these results are very sensitive to preparation conditions.

4.4 Conclusion

Sub-bandgap optical absorption that is observed in photoconductivity and PDS spectra can be linked to optical transitions involving the negative-U centers. As shown in Fig.4.8, the optical transitions from A^- to the conduction band and from the valence band to A^+ involve larger energies than the thermal ones, in agreement with the model. On the other hand, the small energetic distance between the A and T levels suggests that the D^+ and D^- defects have only weakly curved energy profiles in configuration space.

Chapter 5

Defects not related to the negative-U system

The fact that a-Se is a negative-U system does not exclude the possibility for other defects to exist. Experimental results that will be presented in this chapter do give evidence for the existence of deep levels around the Fermi level, and shallow defects in the neighborhood of the band-edges . Wong et al. [41] studied the effect of changes in dihedral angle in a fragment from an helical chain of a-Se and found that it gives two shallow defect levels near the band edges. These defects are of course non-related to the charged ones involved in the negative-U model. Already at an early stage of the investigation of a-Se, studies using the xerographic discharge indicated the presence of deep trapping levels; see e.g. Abkowitz and Markovics [88] or Kasap et al.[89]. It was not possible, however, on the basis of these experiments to quantify the designations "deep" or "shallow".

5.1 Experimental considerations

To explore the possibility of seeing those additional defect levels (shallow and deep) with the same experimental techniques used in this thesis, one should take in account the following considerations:

• Since steady-state dark and photoconductivity is the result of a stationary balance between recombination and generation of charge carriers, this technique can be sensitive to the deep levels at low temperatures where a quasi-Fermi level can be shifted to the neighborhood of the defect level. Indeed, as described in Chapter 2, the energetic distance between the equilibrium Fermi-level and any of the two quasi-Fermi levels increases with increasing light intensity and decreasing temperature. Thus under a constant light intensity the position of the quasi-Fermi level will be controlled only by temperature, and then the steady-state photoconductivity should be sensitive to any defect band that one of the quasi-Fermi levels crosses in the temperature range studied. Since the holes are the more mobile charge carriers in a-Se, this technique will be sensitive only to the electron traps that play a role as recombination centers for holes. That also the steady-state *dark* conductivity can be sensitive to a deep level when this level is crossed by a thermally induced shift of the equilibrium Femi-level may be observed in Qamhieh et al. [90].

- In the time-of-flight experiment where it is possible to drift either electrons or holes separately, the decrease of the transient current in successive flashes may be a tool to probe the deep recombination centers for both electrons and holes.
- The post-transit currents that were measured to determine the positions of the T⁺ and T⁻ levels cannot in the same way be used to locate the shallow states. It would require very short transit times, as could be achieved with very thin sandwich cells. However, when one makes the sample thinner its capacitance becomes high and the ensuing large RC time constant will distort the transient beyond the time domain of interest. The alternative in this case is to use the pre-transit electron current in the TOF measurements to probe possible shallow states below the conduction band edge, and the TPC to probe those above the valence band edge. In both cases the accessible energies are related to the minimum time domain that the TOF setup can measure, in practice some 10^{-7} s.

5.2 Experimental results

5.2.1 Deep levels

As described in Chapter 3 the steady-state dark and photoconductivity measurements were performed on a-Se films using different excitation wavelengths [91]. All confirmed the typical behavior near and above room temperature, with a thermally activated dark current above 300 K and a transition from the monomolecular to the bimolecular recombination regime in the photocurrent. On the other hand, below room temperature, where the observation of an anomalous maximum in the dark conductivity was reported earlier [90],



Figure 5.1: Temperature dependence of the steady-state photocurrent for an a-Se film under 470 nm illumination for three intensities: $I_0 = 2 \times 10^{13}$ photons cm⁻²s⁻¹ (\circ), $5 \times 10^{-2}I_0$ (\triangle), and $3.8 \times 10^{-3}I_0$ (\bigtriangledown). 50 V was applied across a 7 µm thick co-planar cell. The full symbols indicate the level of the dark current; (b) Dependence of the photocurrent on the light intensity at indicated temperatures; the slopes correspond to the exponents of the $I_{ph} \propto (Intensity)^{\gamma}$ relationship.

an analogous maximum is now observed in the photocurrent. The open symbols in Fig.5.1.a show the temperature dependence of the photocurrent in an a-Se film in a log I_{ph} versus $10^3/T$ diagram for three different light intensities: I_0 , $5 \times 10^{-2}I_0$, and $3.8 \times 10^{-3} I_0$, where $I_0 = 2 \times 10^{13}$ photons cm⁻² s⁻¹ represents the full light intensity. At temperatures below 278 K ($10^3/T > 3.6$) the increase in the dark current (full symbols) is mirrored in the behavior of the photocurrents. The maximum in the photocurrent intensity occurs at somewhat higher temperatures than the one that maximizes the dark current, and the offset between those maxima increases with increasing illumination intensity.

Fig.5.1.b shows Lux-Ampère characteristics for the photocurrents induced by 2.64 eV (470 nm) illumination at three temperatures. The chosen temperatures, room temperature (297 K, $10^3/T = 3.4$), 259 K ($10^3/T = 3.9$), and 210 K ($10^3/T = 4.8$), are characteristic for the regions above, near, and below the low-temperature photocurrent maximum. At all temperatures the photocurrent, I_{ph} , grows with light intensity, and therefore photocarrier generation rate G, according to $I_{ph} \propto G^{\gamma}$. Fitting these data for 297, 259, and 210 K, the values of γ are 0.69 \pm 0.02, 1.08 \pm 0.06, and 0.88 \pm 0.04 respectively. In other words, the photocurrent light-intensity dependence changes from sub-linear to super-linear and back to sub-linear as the photocurrent passes through its low-temperature maximum.

The above results were obtained with the 2.64 eV illumination that resulted in the largest photocurrents. However, since the a-Se absorption depth is shallow for such photons, a follow-up set of measurements was carried out with the more uniformly absorbed 1.96 eV light of a He-Ne laser to ascertain that the observed behavior is not just due to surface states. The shift in dominant recombination regime from bimolecular to monomolecular and back to bimolecular was again observed with decreasing temperature. As will be argued in a next section, the above observations point to photocurrent sensitization through an electron trap close to the Fermi level.

5.2.2 Shallow levels

Below conduction band edge

The pre-transit electron photocurrent is a suitable tool to probe for the presence of shallow states on the conduction band side. Fig.5.2.a shows electron TOF photocurrents in a 16 μ m thick a-Se sandwich cell, measured at different temperatures between -40 °C and room temperature, and with 50 V applied to the sample. The abrupt change of slope of the current in the 10^{-5} to 10^{-3} s region indicates the TOF transit time, with increasing tran-



Figure 5.2: (a) Electron TOF transients from a 16 μ m a-Se sandwich cell at indicated temperatures and with 50 V applied. The arrows indicate the time t^{*}. (b) The temperature dependence of t^{*}.

sit times corresponding to decreasing temperatures as expected. A much less pronounced change of slope can be perceived at all temperatures in the pre-transit part of the current. Arrows have been added to the figure to point out this feature. As described in Chapter 2, the appearance of such cusp in the photocurrent transient points to the presence of a discrete protruding feature in an otherwise monotonously varying density of localized states (DOS). A sufficiently well-defined defect and the enhanced trapping into and subsequent release from it will cause such effect. From the temperature dependence of the elapsed time between the laser pulse at t = 0and the occurrence of the kink at time t^* , the energy position of the discrete feature with respect to the transport path can be deduced according to the relationship $E^* = kT ln(\nu t^*)$, where k is Boltzmann constant, T the temperature, and ν the attempt-to-escape frequency. Fig.5.2.b shows that the experimentally determined t^* is in fact thermally activated. Therefore, according to the above expression, the activation energy locates the energy position of the defect level at $E^* = (0.28 \pm 0.02)$ eV below the conduction band mobility edge. A value for the attempt-to-escape frequency of 4×10^{10} s^{-1} can also be deduced for the center from the intersection of the curve with the time axis at 1/T = 0 as can be seen in the following equation:

$$ln(t) = E/kT - ln(\nu).$$
(5.1)

Measurements show that the position in time of the cusp is field independent, which makes this defect center different from the charged ones involved in the negative-U model as described in Chapter 3.

Above valence band edge

Since holes are the more mobile carriers in a-Se, the signature of a shallow trap at the valence band side would occur in the time frame where, for the standard sandwich cells, the true pretransit TOF signal is obscured by the RC time response of the measurement system. Therefore, TPC measurements on samples with interdigitated contacts offer an alternative to deal with possible shallow states above the valence band edge. Fig.5.3.a shows transient currents in such ~15 μ m thick a-Se film deposited on Corning glass and fitted out with interdigitated gold contacts. The illumination, using blue laser flashes, was done through the substrate, i.e. directly at the contacts. The transient currents were measured at different temperatures and for 200 V applied on the sample. Similarly to the case of the pre-transit current in electron TOF measurements, a cusp can be seen in the microsecond region in these transients, except for the ones at room temperature and the one at 0 °C. The time position of this cusp vs the inverse temperature is shown in



Figure 5.3: (a) Transient photocurrent from an a-Se gap-cell sample provided with interdigitated gold electrodes, at different temperatures. The applied voltage on the sample is 200 V. The arrows shows the kinks discussed in the text. (b) The temperature dependence of the time corresponding to the first kink. (c) The temperature dependence of the second kink.



Figure 5.4: Zoom in of the time frame 5×10^{-5} s to 10^{-2} s of the TPC curves shown in Fig.5.3.a. The intersection between the dotted lines at any TPC trace designates the time position of the second kink.

5.3. Discussion

Fig.5.3.b. This of course suggests, following Eq.5.1, the presence of a defect level in the DOS of a-Se at 0.19 eV above E_V with an attempt-to-escape frequency $\nu \simeq 9 \times 10^9 \text{ s}^{-1}$. Apart from this cusp in the microsecond region, a second cusp can be seen later in the TPC curves. The time position of this cusp is shown in either Fig.5.3.a or for more clarity in Fig.5.4. This cusp corresponds to a defect at 0.39 eV above E_V with an attempt -to-escape frequency of $3 \times 10^{11} \text{ s}^{-1}$ as deduced from Fig.5.3.c using the Eq.5.1. This later cusp does agree with the thermal defect T^- resolved by SSPC , PTPA and by TPC in bulk samples.

Analogous measurements using either red or green light were done on the same sample. Qualitatively, the results are the same but the current level is lower and does not allow to follow the evolution of the transient currents at different temperatures with sufficient clarity. Measurements were also done with illumination directly on the a-Se film surface. There again the results are qualitatively the same but the current level is lower than with the transients of Fig.5.3, making that alignment not suitable for measurement at low temperatures.

5.3 Discussion

5.3.1 Deep levels

Based on measurements at higher temperatures as shown in Chapter 3, and on the known behavior of photoconductivity in other chalcogenide glasses, bimolecular recombination and a monotonically decreasing photocurrent upon temperature were expected in the temperature region with $10^3/T > 3.4$. The current maximum that was observed instead indicates the action of a sensitization process. Sensitization in a-Se occurs when the electron quasi-Fermi level is shifted across an electron trap with a small capture cross section for holes by changes of either the measurement temperature or the illumination intensity [92]. It thus becomes more difficult for holes to recombine and an increase in the photocurrent is observed. The changes in recombination behavior that then ensue, are amply demonstrated by the results in Fig.5.1. Indeed, where the observation of a power exponent $\gamma = 0.5$ indicates a bimolecular recombination process, and $\gamma = 1.0$ points to monomolecular recombination, values above 1.0 indicate photosensitization.

In Fig.5.1, the γ value of 0.69 measured at 297 K does not continue to drop towards the expected 0.5 as the temperature is lowered, but reaches the super-linear value of 1.08 instead at 259 K before decreasing below 1.0 again as the temperature decreases further. This pattern of initially increasing and



Figure 5.5: Temperature dependence of the power exponent γ of the Lux-Amp ère characteristic measured on two pure a-Se ($\triangle \bullet$) and one stabilized a-Se (\circ) samples.

subsequently decreasing values of γ is also seen, be it without actually exceeding the 1.0 value, in Fig.5.5, which summarizes results from different a-Se samples. That the sensitization can be observed in a-Se at low temperatures and low illumination intensities indicates that the discrete trap level involved must be located close to the equilibrium Fermi level. This level of course is unrelated to the negative-U defects, because the two thermal transitions involved in this model have been already located in the Chapter 3 at 0.4 and 0.5 eV from the valence band, respectively the conduction band edge.

The presence in a-Se of deep traps that, at room temperature, do not release trapped carriers for many seconds or even minutes can also be deduced from TOF experiments. Successive measurements of the TOF signal for either holes or electrons, under DC bias conditions [93], do show that the waveforms decrease in amplitude with the number of repetitions. The phenomenon is more drastic for electrons than for holes. It suggests that at every laser flash part of the generated charge carriers are deeply trapped, such that at the next laser flash part of the drifting charges can recombine with the trapped ones of opposite sign. This explanation means that there is a deep level at either side of the equilibrium Fermi-level, i.e one at the

5.3. Discussion

conduction band side that also causes the sensitization effect, and the second one at the valence band side. Since electrons are the less mobile carriers in a-Se, the probability for them to recombine with trapped holes is larger, which can explain the fact that the observed phenomenon is more drastic for electrons than holes.

While the above observations suggest the presence of deep trapping levels in a-Se, they do not give either a precise measure for their energetic positions or their physical origin. However, there is ample support in the literature for the existence of such deep levels. Most of the evidence has been based on xerographic potential measurements [89] [94] [95] [88], but variations on the standard TOF technique have also contributed [96] [97]. Abkowitz [8] deduced the energetic positions of these deep defects from the residual potential xerographic discharge. In a framework of a gap of 2.2 eV (large for a-Se), the first level is situated at 0.87 eV above the valence band edge while the second level lies 0.013 eV higher at the other side of the Fermi-level. These two levels were derived on the basis of an interpretation that links the xerographic discharge potential V at any time to a DOS that is proportional to $dV/dt \times t$ for $E = kT ln(\nu t)$. The defect at the energy E = 0.87eV appears as a kink in the voltage decay at time greater than 83 s for an attempt-to-escape frequency of 1.4×10^{13} s⁻¹. It is unclear how much weight should be given to these measurements far in the decay curve, which does not promise much sensitivity, and given that the utilized attempt-to-escape frequency is very high and does in practice suggest a charged defect.

In fact, the author traced these two deep levels to the T^+ and T^- levels involved in the negative-U model. However, such assignment would not fit well with the measured defect photoluminescence at about 0.8 eV in view of the accepted polaronic effects in a-Se. And it would contradict the achieved positioning, in this work, of the T^+ and T^- levels at 0.5 eV below E_C and 0.4 eV above E_V on the basis of multiple experimental data, as shown in Chapter 3. In fact, the later kink in the transient photocurrents in Fig.5.3.a is a further manifestation of the T^- level as shown in Fig.5.3.c. In summary: there is evidence for the existence of two deep levels, at either side of the equilibrium Fermi level, but more work is needed to clarify their physical origin and their precise position in the bandgap.

5.3.2 Shallow levels

The shallow electron trap, some 0.28eV below the conduction band, that causes the cusp in the pre-transit TOF current matches the 0.3 eV level of the DOS distribution that Koughia et al. [42] deduced from their study of the TOF transients as already described in Chapter 3. on the other hand, the

shallow hole trap lying at 0.2 eV above the valence band edge that is seen as the first kink in the transient photocurrents in Fig.5.3.a, has not been experimentally reported before. These two shallow levels represent thermal transitions energies, but they do not match one of the thermally accessible levels of the negative-U model in a-Se described in Chapter 3.

It is remarkable that these two defects have a low characteristic attemptto-escape frequency $\sim 10^{10} \text{ s}^{-1}$ in comparison with the one for the charged defects that is $\sim 10^{12} \text{ s}^{-1}$, which means, according to the detailed balance principle, that they have low capture cross sections. Consequently, the shallow defects will not be charged.

It is also remarkable that these two shallow levels more or less agree with the energetic positions that Abkowitz [8] deduced from the drift mobility data in function of temperature, measured by Kasap and Juhasz [9] for both electrons and holes. As already pointed out elsewhere [75] as well as here in Chapter 3, that assignment followed from a misinterpretation of the mobility data. Indeed, the zero-field activation energy of the drift mobility (for electrons and holes) vs the inverse temperature was interpreted as the energy position of a trap level that controls the conduction. Marshall [69] has shown that such interpretation of a mobility set is unwarranted.

As mentioned in Chapter 1, Lucovsky [7] introduced a model for the microstructure of a-Se, where a-Se is constituted of long chains which lack the regular helicity of chains in crystalline Se_{γ} where the sign of the dihedral angle is kept constant either positive or negative. The a-Se chains contain a small fraction of atoms that mimic the 8-atom ring structure. Thus the sign of the dihedral angle can becomes random. Wong et al. [41] proposed, on the basis of tight-binding calculations, that a distortion in the dihedral angles can introduce pairs of shallow localized states into the gap. These states are introduced into the gap when the lone-pair orbitals on adjacent Se are almost in parallel alignment as in Fig.5.6.b, which is to be contrasted with the normal bonding where these states are nearly at right angles as shown in Fig5.6.a. The shallow states are located in a range of 0.1 to 0.3 eV from the band edges. Therefore, the shallow states observed through the transient photocurrents can have the distortion in dihedral angle as origin.

The pre-transit electron TOF data, as well as the TPC curves shown in Fig.5.3.a have been analyzed independently (and without reference to kink designations) by Marshall on the basis of a fourier transform method [98]. He used the Fourier transform methods, worked by Main [99], and found in addition to the couple of levels at E_C -0.5 eV and E_V +0.4 eV that are related to the negative-U model, two shallow levels, the first one at 0.33 eV below E_C and the second one at 0.3 eV above E_V . Representative curves of these results are shown in Fig.5.7. The energetic positions of the defects were


Figure 5.6: (a) Normal bonding arrangement for nearest-neighbor Se atoms. B indicates the bonding directions, and LP the orientation of the lone-pair orbitals. For the normal bonding the dihedral angle is either 90 or 270 degrees. (b) Bonding arrangement with a dihedral angle distortion of 0 or 180 degrees. This places the lone-pair orbitals on nearest-neighbor Se atoms into a parallel allignment in the normal bonding arrangement. [41]



Figure 5.7: Calculated DOS from (a) TPC data from an a-Se sample at 193 K, a voltage of 200 V was applied. (b) TOF data from an a-Se sample at 263 K. The electrons are drifted under an applied voltage of 50 V.

deduced using $E = kT ln(\nu t)$ and an attempt-to-escape frequency ν of 10^{12} s⁻¹ over the full energy range. Since $\nu \simeq 10^{10}$ s⁻¹ is more appropriate for the shallow states, this high ν value explains the somewhat larger energy values in the Fourier analysis. Therefore, those results are in good agreement with the ones deduced here.

As already described in Chapter 3, the electron TOF transients shown in Fig.5.2.a were also used in Emelianova et al. [77] as a reference for theoretical calculations of the TOF transients on the basis of the analytical description of TOF by Rudenko and Arkhipov [100]. It was found that the DOS that optimally reproduces the experimental transients does contain a shallow narrow defect band that is situated some 0.3 eV below E_C .

5.4 Conclusion

Although the defects that form the negative-U system have received most attention in the past, a-Se does contain other defects that are not related to the model. Evidence for the existence of such defects has been given in this chapter. A shallow electron trap, located at 0.28 eV below E_C , and a shallow hole trap, lying at 0.19 eV above E_V , make their presence known through their signature in the transient photocurrent. It is more difficult, on the other hand to gain precise information on the deep traps near the Fermi-level for both holes and electrons. The depth of these traps makes it difficult to locate their energetic positions with the techniques used in this study. A schematic representation of the different defect states in the a-Se gap, as determined in the present work, is shown in Fig.5.8.



Figure 5.8: Sketch of the defect levels related and non-related to the negative-U model in a-Se. Exact positions of A^-e and deep levels are still uncertain.

102

Chapter 6

Tail-state distributions in a-Se

The tailing and localization of electronic states caused by the topological disorder in amorphous semiconductors were introduced in the first chapter. The tail-state distribution is an important part of DOS in the gap of the semiconductors. In fact, the defect levels resolved in previous chapters are superposed on these tail-state distributions at the two sides of the gap. Although the physical origin of tail-states and coordination or configuration defects are different, they play a similar role in determining the electronic properties of the material. The tail-state distribution can be probed by means of TOF and TPC measurements.

6.1 Experimental results

6.1.1 Transient photocurrent method

Transient photocurrents, together with the multiple-trapping transport model, have traditionally been used to investigate the tail-state distribution of amorphous semiconductors. In the best-known cases such as $a-As_2Se_3$ [101] or hydrogenated amorphous silicon (a-Si:H) [102], that distribution proved to be roughly exponential in energy and gives rise to a simple power-law behavior of the transient current.

The results of the previous chapters have shown that it is not accurate to assume that there is an exponential tail-state distribution in a-Se, neither at the valence band edge nor at the conduction band edge. Consequently, it is expected that the photocurrent decay should not follow the power-law indicated in Chapters 2 and 3. Nevertheless, the overall shape of these photocurrent decays at different temperatures can be used to estimate the steepness of the average tail-state distribution at the valence band side (holes being



Figure 6.1: Time evolution of transient photocurrent in a-Se gap cells after pulsed excitation at 440 nm. Part of the a-As₂Se₃ transient from [101] is shown for comparison.

the more mobile and hence TPC dominating carriers in a-Se).

Fig.6.1 shows the transient current decay, after 440 nm pulsed optical excitation, from an a-Se sample in comparison with the well-known roomtemperature $a - As_2Se_3$ decay from [101]. At first sight, a power-law current decay $I_{ph} \propto t^{-(1-\alpha)}$ of the type seen for a-As₂Se₃ seems to be observed for the a-Se as well. However, the slope of the 233 K curve should be steeper than the one of the 295 K curve for an exponential distribution of states. Indeed, the parameter α should then have the form $\alpha = kT/E_0$, i.e. increasing with rising temperature, with E_0 defining the width of the exponential DOS. Using the slope measured at the lowest temperature of 233 K and $\alpha = T/T_0$, a value $T_0 \approx 320 \text{ K} (E_0 = 28 \text{ meV})$ follows. Although, this value does agree with the one estimated using the same technique at low temperatures, for a bulk sample that has been described in Chapter 3 (Fig. 3.8), this is not the case for the TPC curves described in Chapter 5, (Fig.5.3.a). On the latter curves, the average slope of the transient currents gives an α value close to 0 at all temperatures (a value that suggests an infinite tail width), which is also the case for the transient current at room temperature in Fig.6.1. This confirms that the total tail-state distribution is not exponential. Even if there were an exponential distribution of tail states in the background, it clearly does not control the transport, which is rather controlled by the defect band levels at

0.2 eV and 0.4 eV above E_V superposed on this background.

6.1.2 Drift mobility method

The standard MT analysis, which has successfully been used in the earlier studies of $a-As_2Se_3$ [59][101] and a-Si:H [103], also predicts that the width E_0 of the exponential tail can be deduced from the field dependence of the carrier drift mobility, as measured in a TOF experiment, according to the relationship

$$\mu_d \propto (L/F)^{1-1/\alpha} \tag{6.1}$$

where $\alpha = kT/E_0$ is the parameter already introduced above, L is the sample length and F the applied field.

In TOF experiments, the drift mobility μ_d is calculated from the measured transit time t_T of the carriers generated by the light pulse according to $\mu_d = L/t_T F$. In this study and in the case of a-Se it is known, as mentioned above, that the tail-state distribution is not strictly exponential, but the technique can be used to obtain a first-order estimate for the slope of the tail. To confront this method of determining the width of the distribution, E_0 , with the one based on TPC, we have measured the temperature and field dependence of the hole drift mobility in a 27 μ m thick a-Se cell provided by Prof. Safa Kasap.

The results are shown in the traditional $log(\mu_d)$ vs. $10^3/T$ diagram in Fig.6.2.a. Based on those results, the $log(\mu_d)$ vs. log(L/F) diagram of Fig.6.2.b is constructed that allows the determination of $\alpha(T)$ from the slopes $(1 - 1/\alpha)$. The temperature dependence of this parameter is shown by the full symbols in Fig.6.2.c. Although as expected, the values do not agree too well with the MT prediction for an exponential DOS, which is apparent from the fact that a straight line through the values of α crosses the T axis at some 80 K rather than the 0 K expected by the formula $\alpha = kT/E_0$, a 'best approximating' exponential (a straight line passing through the origin) with $E_0 \approx 22$ meV indicated by the dashed line can be obtained. Fig.6.2 also includes a second data set (open symbols) that was generated in similar fashion from the drift mobility data published by Kasap and Juhasz [9]. Here the agreement with the exponential DOS is better, giving 24 meV as E_0 value.

In principle, a similar determination of the slope of the conduction band tail states can be envisioned since holes and electrons can be studied separately in the TOF experiment. However, as already found in [9] and as confirmed by the measurements shown in Fig.6.3, the electron drift mobility in a-Se is independent of the applied electric field and Eq.6.1 cannot be used. In fact, the field independence signifies that equilibrium carrier transport has



Figure 6.2: (a) Hole drift mobility data set from a 27 μ m thick sandwich cell with Al bottom contact and Au top contacts; (b) drift mobility values taken from the fitted lines of part (a), plotted as a function of L/F; (c) full squares: temperature dependence of the parameter α as calculated from the lines in part (b); open symbols: analogous results based on the data from [9].

6.2. Discussion



Figure 6.3: Electron drift mobility in a-Se as a function of inverse temperature and applied voltage. The dashed line corresponds to a 0.30 eV activation energy.

been established before the transit time t_T of the electrons. Observation of such equilibrium transport rules out an exponential distribution of tail states on the conduction band side of the gap [104]. A Gaussian, or similar steeply decreasing DOS is needed to account for the experimental results.

6.2 Discussion

For the valence band tail states, the TOF drift mobility analysis indicates a much steeper distribution than the exponential one observed for a-As₂Se₃: a width of less than 25 meV for a-Se compared to the a-As₂Se₃ 47 meV. However, It should be pointed out that Eq.6.1 for the drift mobility and the $t^{-(1-\alpha)}$ power law for the TPC results not only presume an exponential DOS, but are only valid for $\alpha < 1$. Consequently a slope below 25 meV means that even room temperature may be too high to obtain a meaningful result. This may be the case for the 295 K on Fig.6.1, and of the curves on Fig.5.3. Results that are similar to the drift mobility data set of Fig.6.2, and the analogous one by Kasap and Juhasz, were also obtained by Marshall and Owen [76]. There the analysis leads to a 50% higher value, with E_0 of the order of 35 meV, but it should be noted that hot-pressed bulk a-Se samples were used rather than evaporated layers. These results are in good agreement with ones deduced from TPC traces on a bulk sample at low temperatures Fig.3.8 in Chapter 3.

calculations

The problems pointed out above do, of course, make the deduction of the slope of the tail states distribution questionable. Nevertheless, this deduced value of $\sim 25 \text{ meV}$ is confirmed by calculations, done by Prof. Joe Marshall, on the basis of a Fourier transform of the TPC data. In fact, the results shown in Fig.5.7 can be fitted with two Gaussian defects and an underlying exponential tail with a 25 meV slope. (Fig.6.4 shows a similar decomposition for the case of Fig.5.7.b). This is also in agreement with published calculations. Indeed, Naito [105] has compared a broad range of transient hole transport data in a-Se with computer simulations based upon a trap-controlled band transport mechanism (multiple-trapping) for continuous distributions of localized tail states. The steepness of the deduced distribution of tail states was calculated and found to be some 23 meV (Fig.6.5.a). A similar slope is deduced from the calculation made by Koughia and Kasap [78] as shown in Fig.6.5.b. These results of course reinforce the validity of the approach used in this chapter to estimate the width of the tail-state distribution.

Comparable information on the a-Se conduction band tail states cannot be procured easily through photocurrent measurements: Classical phototransients will only reflect the properties of the dominant carrier, which is the hole for the chalcogenides, and the TOF transients for electrons exhibit equilibrium characteristics, which necessitates a detailed fitting of the current transients with a complex set of analytical equations to extract an estimate for the DOS [77][42]. For the conduction band side of the gap where the field independence of the mobility precluded the application of Eq.6.1 to estimate the distribution of tail states, Koughia et al. [42] used the TOF current transients themselves as input to a numerical model for the DOS, as described in Chapter 3. The best DOS deduced in this simulation has an exponential tail-state distribution background of 20 meV in addition to the features discussed in Chapter 3.

A similar slope was found in the Emilianova et al. [77] calculations. As mentioned in Chapter 3, whereas Koughia et al. only used the same parts of the TOF transients that are used to determine the transit times, and hence the field-independent drift mobilities, Emilianova used a data set covering a large time domain. It is acceptable, therefore, to consider this 20 meV exponential tail as one element of the DOS near the conduction band, with the defect states described in the previous chapters being superimposed on it.

6.3. Conclusion



Figure 6.4: The DOS below the conduction band edge deduced by the Fourier transform of TOF transient photocurrents from an a-Se sandwich sample (black line), together with the exponential and Gaussian compounds (open circles) that do fit it [98].

6.3 Conclusion

The measurements and simulations do suggest that the width of the valence and conduction band tails are comparable. The fact that both band tails are relatively narrow clearly reduces the probability that the observation of the defect states is hindered by a background density due to those tails, as has been suggested for the case of $a-As_2Se_3$ [12].

The DOS in the gap of a-Se looks to be qualitatively symmetric, in the sense that it has comparable features on both sides of the gap and comparable slopes for the tails. This similarity, gives rise to the simple question why the electron mobility is field-independent while the hole mobility is field-dependent. In line with the examination of such phenomenon for the case of a-Si:H [102] [103] this difference suggests that at the transit time, transport of electrons is dominated by the trapping and release at the Gaussian distributed shallow tail states, which allows a quasi-equilibrium of charge carriers between the transport path and those states, while this is not the case for holes where the shallow defect band is located close to the edge.

As described in Chapter 1, the top of valence band in selenium is constituted essentially of lone pairs orbitals while the bottom of the conduction



Figure 6.5: (a) The calculated valence band states distribution by Naito et al. [105]. (b) DOS used by Koughia et al. to reproduce transient photocurrents of holes, the inset table gives the value of mobility edge thermal shift and concentration of deep states.

band is constituted of anti-bonding states σ^* . This undoubtedly allows tail states at the conduction band side to have different electronic properties from those at the valence band side. Experimentally it will be worthwhile to analyze hole and electron mobility in function of the applied field and temperature for samples with different thicknesses in such a way that measured transit times can sample a wide equivalent energy range of the tail states distributions.

Chapter 7

Photoinduced changes in a-Se

Up to this point, only intrinsic defects in a-Se have been dealt with, without the effect of external influences being considered. One of the known effects is the change of chalcogenides properties under illumination. Photoinduced changes in a variety of chalcogenide properties have of course been studied widely in the past [106], but very rarely have these studies included a-Se amongst the study objects. The best-known of these effects is the photodarkening of the material, i.e. the narrowing of the optical gap of the chalcogenides under the influence of illumination. The darkened sample can be bleached again by illumination with sub-gap light, or by annealing at a temperature close to the glass transition temperature. In a-Se, room temperature is sufficient to anneal this photodarkening, since its glass transition temperature is just above room temperature. In other words, photodarkening is only stable in a-Se well below room temperature [40].

Of special interest for the defect structure of a-Se are the light-induced electron spin resonance (LESR) experiments that showed that a considerable defect density could be photoinduced in chalcogenide glasses at low temperatures, but that the defects annealed out completely at room temperature. While a-Se is only mentioned in passing in the original study of Biegelsen and Street [107], a detailed investigation of the LESR in a-Se has since been carried out by Kolobov et al. [108]. It was reported that no measurable ESR signal could be obtained at 20 K in the dark. Only by illuminating the a-Se sample with across-gap light could a signal be detected and measured. The intensity of this signal was seen to increase with illumination duration, fast at first and more slowly after some minutes, but no saturation of the photo-induced ESR signal persists at low temperatures after the light is turned off, but annealing at 150 K makes the signal disappear. It appears that the ESR signal is due to a combination of activated native defects and newly photoinduced ones, neither of which are stable near room temperature.

Photoinduced changes in the DOS defect structure have been measured before in chalcogenide compounds such as $a-As_2Se_3$ by, for instance, transient photoconductivity [28] or modulated photoconductivity [109]. Those changes consist of an increase of the defect density that is stable at room temperature and can be annealed out at higher temperatures.

During this work, light-induced changes in the position and intensity of the DOS feature that is resolved from the post-transit TOF analysis were observed at room temperature. These observations will be presented and discussed in this chapter.

7.1 Experimental results

Samples of a-Se prepared for TOF measurements were illuminated over times from hours to several weeks either under natural light in room ambient conditions or with a halogen lamp in the TOF sample holder. In the latter case the illumination was done through a water filter as well as directly on the sample. Also the repeated use of the same sample for TOF measurements led to the observation of photoinduced changes. Thus the results will be presented using this division.

7.1.1 Excessively used TOF samples

Fig.7.1.a shows hole TOF transient photocurrents from a 5 μ m thick a-Se layer with Al circular top contacts of 3.5 mm diameter. Curves 1 and 2 of Fig.7.1.a were measured with two different applied fields when the sample was fresh. Curve 3 was obtained after many measurements using the same top contact of the sample, and curve 4 shows the result of a subsequent measurement through a neighboring top contact that had been co-illuminated with its neighbor but without an electric field being applied. All measurements were made at room temperature. The TOF transit time, corresponding to the change of slope at 3×10^{-7} s, is clearly not being influenced by the repeated measurements. Application of a lower field, as for curve 2, does result in the anticipated lengthening of the transit time.

For post-transit currents on the other hand, it is the excessively repeated illumination of the sample that makes a difference while the change of applied field has no influence. While a highly similar convex curvature is seen around $t = 10^{-5}$ s in the post-transit current of traces 1 and 2, no such curvature is observed on curves 3 and 4 that were taken after repeated illumination of the sample. A clearer image of the changes in the post-transit current,



Figure 7.1: (a) TOF hole transients from 5 μ m thick a-Se sandwich cell with Al electrodes under changing conditions (1) 15 V 23 °C, (2) 12.5 V 23 °C, (3) 15V 23 °C after several measurements, (4) 15 V 23 °C on different dot on the same sample; curves 1, 2 and 3 were offset for clarity by factors of 5, 3 and 2. (b) The DOS calculated from the previous transients with the parameters $\mu = 10^{12} s^{-1}$, $\mu_0 = 1 cm^2/Vs$ and $g(0) = 10^{21} cm^{-3} eV^{-1}$ (bottom); curves 1, 2 and 3 were offset for clarity by factors of 5, 4 and 1.5.

which is due to carrier emission from deep traps, can be obtained by extracting the underlying DOS using $g(E) = (2g(0)/Q_0t_0\mu)I(t)t$ where Q_0 is the total charge participating in the transient photocurrent, t_0 is the free-carrier transit time, and g(0) is the DOS at mobility edge. Fig.7.1.b shows the DOS distributions that correspond to the 4 curves shown in Fig.7.1.a. The DOS maximum seen on curves 1 and 2 around 0.42 eV is in full agreement with previously discussed results in Chapter 3. However, in curves 3 and 4 this DOS structure has moved deeper in the gap. Since the shift is more pronounced with curve 4, i.e. when measured at the companion spot that was co-illuminated but not field-stressed, it is assumed that a photo-induced change in the DOS of a-Se is being seen. That change is stable at room temperature.

7.1.2 Samples illuminated with natural light

A twin sample to the one that led to the results described in the previous paragraphs was kept under ambient room lighting and temperature conditions for two weeks before being used for TOF measurements. The two samples were co-deposited and turned into TOF samples at the same time. Hole TOF transients obtained with this second sample are shown for 2 measurement temperatures in Fig.7.2.a. The general behavior of the transient photocurrent is again the one typically seen with a-Se samples, but with the emission from the deep states occurring at later times than what is normally seen with freshly prepared samples (as described above and in Chapter 3 in detail). Fig.7.2.b again shows the DOS structure above the valence band edge that is resolved from the current traces. A clear maximum around the energy of 0.55 eV is seen, very reminiscent of the shift in the DOS seen with the "companion sample" after many TOF measurements (curve 4 of Fig.7.1).

There is one further aspect in the change in the DOS that deserves some attention. The density of states in the shifted localized level is noticeably more pronounced against its background than is the case for the peak density in the freshly prepared samples. The DOS rise by more than a factor of five in Fig.7.2.b may be compared to the increase by just a factor of two for curves 1 and 2 of Fig.7.1.b.

7.1.3 Halogen lamp illumination

An a-Se sandwich sample was prepared for TOF measurements. Hole TOF transients were measured on this sample while it was fresh, and the results were just like those described above for fresh samples. Next, the sample was illuminated using a halogen lamp. The illumination was directly onto the



Figure 7.2: (a) TOF current transients from an a-Se sandwich cell exposed to natural light and room temperature ambient conditions, and measured at 23 °C and 35 °C. The curves are offset slightly for clarity. (b) The DOS resolved from the post-transit emission currents; the parameters listed with Fig. 7.1 were used for the DOS conversion.

sample, i.e. no filter was used between the sample and the lamp. TOF hole transients measurements were being taken every day (the illumination was continuous for more than two weeks). In this condition no photoinduced changes were detected; the TOF hole transient does duplicate itself every day. Illumination by the halogen does increase the sample temperature by some 10 $^{\circ}$ C, i.e the sample temperature is raised to about 35 $^{\circ}$ C.

The situation is not the same when illumination with the halogen lamp happens through a water filter. In this case after 24 h of illumination the DOS feature above the valence band edge shifts to 0.55 eV from the position of 0.42 eV of either the fresh or directly illuminated sample. It was observed that when illuminating through the water filter the sample temperature does increase by only 3 to 4 °C.

7.1.4 Annealing effect

Photoinduced structural changes in chalcogenides do - as a rule - anneal out close to or at the glass transition temperature. Therefore, the light-exposed sample that was discussed in section 7.1.2 was annealed at 43 °C for 24 hours. Subsequently measured hole TOF photocurrents are displayed, together with the resolved DOS curves in Fig.7.3. Comparison of the DOS after annealing with its counterpart before annealing (Fig.7.2) reveals that, apart from a small shift by some 0.05 eV towards the valence band edge, annealing did not return the DOS to the initial conditions found in a freshly prepared a-Se sample. Fig.7.3 further shows that the applied electric field influences the position of the defect peak. A field-induced shift, due to the Poole-Frenkel effect, was observed in earlier measurements on fresh samples as described in Chapter 3, but the magnitude of the effect is larger here.

The experimental results that are described above have been confirmed with other sample series, prepared and measured under comparable conditions. Data were also collected from samples that were kept in the dark after preparation for times equal to the ambient exposure times of a companion sample. Such 'dark' samples could not be distinguished from fresh samples, indicating that aging is not the cause of our observations.

7.2 Discussion

The most remarkable aspect of the photoinduced changes that were observed in the a-Se defect structure is that they are stable at room temperature, and are barely influenced by annealing at the glass transition temperature. The observation of photoinduced changes in a-Se that are stable at room



Figure 7.3: (a) TOF current transients from the a-Se sandwich cell used for the data of Fig.7.2, after annealing at the glass transition temperature for 24 hours. (b) The DOS resolved from the post-transit emission currents in part (a).

temperature is not evident. Up to now, observed photoinduced changes have proven unstable at room temperature. The well-known LESR signals of Biegelsen and Street [107] or Kolobov et al. [106] anneal out completely at 150 K, just as did the photodarkening observed by Nagels at low temperatures [40]. That the effect is photo-induced follows from the observations that prolonged exposure to the light, even in the absence of any field stressing of the sample as was the case for curve 4 in Fig.7.1 or the sample used for Fig.7.2, does lead to the observed shifting of the defect peak away from the valence band edge. Along with the changes in the energy position of the peak, its intensity with respect to the background is also changing. However, it is difficult to ascertain whether this relative change is due to an increase of the defect density, to a recession of the background, or to a combination of both, given that some of the constants that are needed for the DOS calculation have to be estimated and may conceivably be subject themselves to change under prolonged illumination. More analysis is clearly needed to resolve these questions. It may be added at this point that the observation of photoinduced changes in the defect structure that is revealed by electron rather than hole transients is more difficult, just as the observation of the DOS structure on the conduction band side of the gap itself is more difficult. An apparent minor shift of the defects towards the conduction band is seen in some samples, but on this point as well, a more extended study is needed to clarify the results.

Possible alternative reasons for the observed effects may be examined. Since the samples are sandwich cells, it is justified to exclude humidity or oxidation as possible causes. But as the contacts have to be semi-transparent for the TOF measurements, light soaking and aging remain as possible causes. Aging can be excluded on the basis of the experience accumulated in working with various a-Se samples that were intermittently used for measurements, and stored in the dark otherwise over many months, without any significant changes in the results being observed. Crystallization of the a-Se layer can also be excluded as cause on the basis of attempts to anneal out the photoinduced changes: Annealing at the glass transition temperature would have increased the amplitude of the peak if crystallization were in play, rather than just shift it back a bit towards its original position as seen in Fig.7.3. Nevertheless, some reports of crystallization have appeared in the literature. Palyok et al. [110] reported that crystallization occurs in an a-Se layer when illuminating (for some holographic recording purposes) at room temperatures. They reported also that this effect is stronger above room temperature. Interestingly, Reznik et al. [111] reported that grains of micro-crystals, less than 0.5 mm in diameter, appear in an a-Se layer when the film is kept in daylight at room temperature, and that this effect does not happen when the film temperature is about 35 °C. This of course matches the experimental

7.3. Conclusion

observation in this work that no photoinduced changes are recorded when the sample is directly illuminated thus elevating the sample temperature to 35 °C. That could be explained by the fact that this temperature immediately anneals out the effect of light, which does not give the changes a chance to accumulate, and thus no photoinduced changes are recorded. The macro-agglomerations seen in [111] do not explain the effect measured in this work, but the correspondence in the temperature effect leads to the deduction that much smaller microcrystals than the ones reported in [111] might be the cause of the energy shift of the defect level in the gap reported above.

The parameters used to calculate the DOS might themselves play a role in the observed shift if they should be subject to light-induced variations. Indeed, the energy scale is determined by the relationship $E = kT ln(\nu t)$, where $\nu = 10^{12} \text{ s}^{-1}$ has been used for all calculations. A photo-induced change of this parameter by two orders of magnitude would cause a room-temperature shift of some 0.1 eV in the position of the defect peak, but the likelihood of such change seems remote. As none of the above suggestions offer a good explanation for the observed changes in the a-Se DOS upon illumination, and as the feature that is most prominently changed has been tied to one of the charged coordination defects of the negative-U model, the most logical assumption seems to be that a photoinduced change in the native negative-U defects is being seen, possibly even involving the generation of some additional centers. The set of such defects that is frozen in upon condensation of the amorphous film conceivably contains a number of them that can be further relaxed under optical excitation, thus shifting their average energy deeper into the gap as well as increasing the peak's prominence over the background by reducing the width of the distribution of defects.

7.3 Conclusion

A photoinduced shift of the T^+ level has been observed in a-Se films. It shifts nearly 0.15 eV deeper in the gap. This happens when the sample is kept in natural light in room ambient conditions, or by illuminating through a water filter using a halogen lamp. When illuminating by a halogen lamp without water filter the sample temperature rises up to 35 °C and no photo-induced changes are recorded. This was interpreted as due to the fact that at this temperature the changes anneal out immediately and thus no build-up of the effect is possible. More work is needed to elucidate the origin of this change.

Summary and conclusions

This thesis deals with the electronic properties of amorphous selenium. Despite its long history as the first photoconductive semiconductor, used for decades in the copying machines and other applications like switching devices, some of its properties are still either unknown or in doubt. For instance: A very specific model for the negative-U centers is available for a-Se, but without experimental positioning of the defect levels in the bandgap. Additionally, it is not yet generally accepted that a-Se is a negative-U system.

The density of states model commonly used for a-Se is the Abkowitz model, which consists of two shallow defect levels at about 0.3 eV away from the valence and conduction band edges, and two deep defect levels at both sides of the Fermi level that is roughly in the middle of the bandgap. These two pairs of defect levels are superposed on a steep tail-state distribution on both sides of the bandgap. However, several elements of this DOS model have to be questioned. The activation energies of the hole and electron drift mobility were erroneously used to position the shallow defects, and the deep levels were taken to indicate thermal transition energies in the negative-U model, even though that model itself predicts higher energies for these transitions. Consequently, a new and detailed study of the a-Se DOS is justified.

To explore the DOS in a-Se, this thesis mainly used a number of steadystate and transient photoconductivity methods. It could be concluded that, effectively, a-Se is a negative-U system, and the energy level diagram for the negative-U defects in a-Se could be constructed.

On the basis of the TOF technique and the PTPA analysis, the T⁻ level was positioned at ~0.4 eV above E_V while the same level is positioned at ~0.36 eV above E_V according to the SSPC technique. This difference is interpreted to be due to a sensitization effect caused by a deep electron trap near the Fermi level that disturbs the SSPC at low temperatures. On the other hand the T⁺ level, positioned at 0.53 eV below E_C on the basis of the PTPA, is in good agreement with the result deduced from SSPC.

The optical levels A^+ and A^- were explored through the subgap optical absorption using the CPM and PDS techniques. The A^+ was located at ~1.5 eV above E_V while the A^- level was located at ~1.75 eV below E_C . This puts the A^+ and A^- levels just beyond the corresponding T^+ and $T^$ levels and suggests that the D^+ and D^- defects have only weakly curved energy profile in configuration space. The energetic positions of the thermal and optical levels described above agree well with the general concept of negative-U defects and with the known radiative recombination of electrons characterized by the photoluminescence at 0.8 eV. This image of course is in complete disagreement with the Abkowitz model.

Nevertheless, shallow and deep levels were retrived in a-Se, in addition to the negative-U centers. On the basis of the TOF technique and specifically the pretransit electron current, a defect level at 0.3 eV below the E_c was deduced. On the other hand, on the basis of TPC technique a defect level at 0.2 eV above E_v was resolved. These two shallow levels are characterized by a low attempt-to-escape frequency in comparison with the one for the D⁺ and D⁻ charged defect centers. This led to the conclusion that the shallow defect centers are neutral ones. These centers were attributed to a specific molecular configuration where two neighboring lone-pair orbitals are parallel rather than perpendicular as is the case for the optimal Se configuration.

A deep electron trap in the neighborhood of the Fermi level was deduced through the observation of SSPC sensitization at low temperatures. In addition, the loss of amplitude with repeatedly measured TOF electron and hole TOF currents led to the conclusion that, in addition to the deep electron trap, a similar one exists for holes. The fact that these deep electron and hole traps are located in the neighborhood of the Fermi level makes it difficult to locate their exact energetic positions.

The band tails of a-Se were also examined. From the analysis of the hole mobility in function of temperature and field and from TPC measurements a 25 meV exponential tail-state distribution for the DOS background at the valence band side was deduced. This value was confirmed by calculations. Similar calculations showed that also at the conduction band side the tailstate distribution has an exponential background that is about 20 meV wide. Bringing all the above DOS information together in the bandgap diagram of the concluding figure, a documented alternative for the heuristic Abkowitz proposal is now available. However it should be stressed again that this DOS is in fact only an "effective DOS", since it is based on widely used assumption that capture cross-sections are energy independent across the bandgap of amorphous semiconductors.

Nowadays the technologically interesting Se is stabilized by addition of traces of As and Cl. Although in this work, the focus was on the electronic properties of pure a-Se, some SSPC and TOF measurements on stabilized a-Se samples failed to detect significant differences. Nevertheless, studying the effect of additives on the a-Se properties as well as the influence of preparation parameters should be a worthwhile continuation of the work presented in this thesis.



Figure : Density of states in the a-Se bandgap as deduced in this work (full line), and as proposed by Abkowitz (dotted line). The position of the position of the deep states can only be fixed approximately.:

Summary and conclusions

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132

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