

FUNDAMENTAL OPTICAL ABSORPTION ON FRACTALS: A CASE EXAMPLE FOR AMORPHOUS CHALCOGENIDES

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The fundamental optical absorption in amorphous chalcogenides is described by the extended Tauc plot, $(\alpha h\nu)^n \propto (h\nu - E_0)$, where E_0 is the so called optical gap. The value of n , experimentally found, lies between 1 and 0.4 for typical amorphous chalcogenides, while $n = 1/2$ for 3-dimensional (3D) case is well known for disordered semiconductors and insulators. It is shown that the presence of disorder can greatly influence the nature of the electronic density of states (DOS) even for the extended states. The concept of DOS on fractal structures is introduced to interpret the deviation from $n = 1/2$.

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1. Introduction

Although a great number of studies have been undertaken to understand the characteristics of electronic and optical properties of amorphous semiconductors, there is still no well-established physical model for disordered systems. The analysis of optical absorption spectra is one of the most useful tools for understanding the electronic structure of amorphous semiconductors. As found in a Fermi free electron gas, it is expected that the density-of-states (DOS) for both conduction and valence extended states is proportional to the square root of the energy in 3D materials [1]. This leads to the well known Tauc plot for the optical absorption coefficient α as a function of photon energy $h\nu$ giving $(\alpha h\nu)^{1/2} \propto (h\nu - E_0)$, where E_0 is the optical gap which is a measure of the bandgap in amorphous solids [2]. However, this quadratic energy dependence of the absorption coefficient on photon energy is not always observed; e.g. a linear energy dependence for amorphous Se (a-Se) and a cubic energy dependence for multicomponent chalcogenide glasses have been observed [1]. The deviation from the simple Tauc relation may be regarded to arise from the deviation of DOS from a simple power law. The DOS in disordered materials, in general, should be described by taking into account the *fractals* that are known to dominate many physical properties in amorphous semiconductors [3].

In the present paper, we revisit the classical problem for interpreting optical properties of amorphous semiconductors on the basis of the form of DOS applicable to amorphous chalcogenides. We find that the fundamental optical absorption in amorphous chalcogenides can be written as $(\alpha h\nu)^n \propto (h\nu - E_0)$, where the value of n deviates from $1/2$, and the deviation is attributed to the DOS in fractals.

2. Experimental

Thin films ($0.5 \div 1 \mu\text{m}$) of Ge-based amorphous chalcogenides (a-GeS₂ and a-GeSe₂), As-based (a-As₂S₃ and a-As₂Se₃), and just a-Se were prepared onto Corning 7059 glasses by thermal evaporation in vacuum $\sim 2 \times 10^{-6}$ Torr at room temperature. Two types of depositions, oblique and normal, were performed. The oblique films were deposited with an angle of 80° between the normal to the substrate and the direction of the incidence of the evaporated atoms as giant changes in optical band gap were observed at this incidence [4]. The optical transmittance was measured in the interband absorption region and then the optical absorption coefficient was deduced in the usual way. These measurements were performed before and after thermal annealing for 2 hr in vacuum below the glass transition temperature T_g . The annealing temperatures are shown in the tables 1 and 2.

3. Experimental results

First, we show the experimental results for As-based chalcogenides. The examples before and after annealing are shown for obliquely deposited a-As₂S₃ in Fig. 1 (a) and (b), respectively, which are given in the plot of $(\alpha h\nu)^n$ vs. $h\nu$.

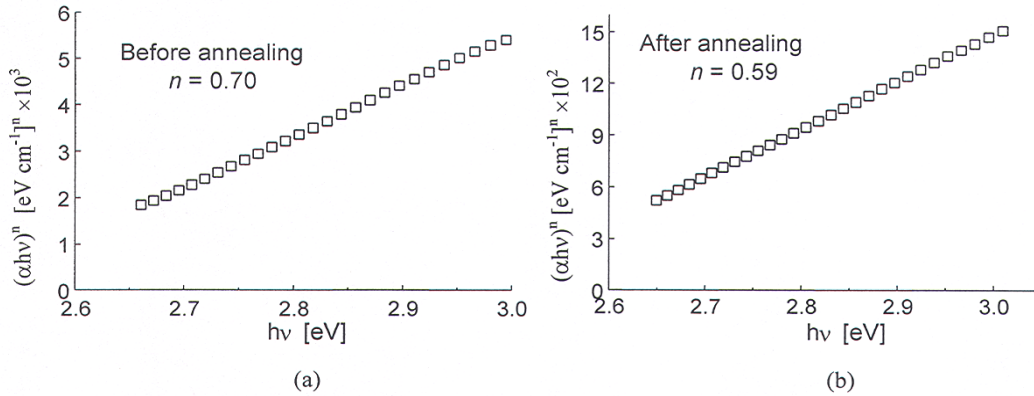


Fig. 1. Optical absorption spectra plotted for $(\alpha h\nu)^n$ vs. $h\nu$ in obliquely deposited a-As₂S₃. (a) $n = 0.70$ before annealing and (b) $n = 0.59$ after annealing at 170°C for 2 hr.

Another example for obliquely deposited a-GeS₂, before and after annealing, is shown in Fig. 2 (a) and (b), respectively. These are also plotted in the form $(\alpha h\nu)^n$ vs. $h\nu$. The fitting to the experimental data produces $n = 0.38$ before annealing and $n = 0.44$ after annealing at 200°C .

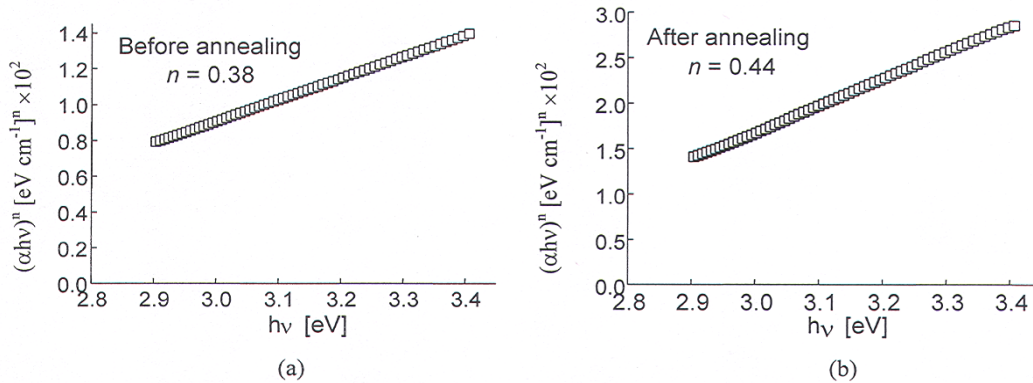


Fig. 2. Optical absorption spectra plotted for $(\alpha h\nu)^n$ vs. $h\nu$ in obliquely deposited a-GeS₂. (a) $n = 0.38$ before annealing and (b) $n = 0.44$ after annealing at 200°C for 2 hr.

Fig. 3 shows the $(\alpha h\nu)^n$ vs. $h\nu$ with $n = 1$ for a-Se before annealing and this behavior is unchanged by annealing at 30 °C for 2 hr. The n values for other materials are tabulated in Table 1, together with the optical bandgap E_0 for the obliquely deposited systems.

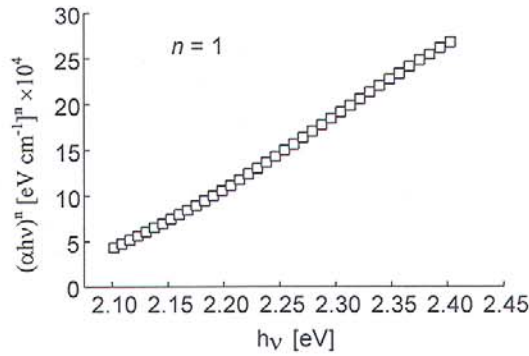


Fig. 3. Optical absorption spectrum plotted for $(\alpha h\nu)^n$ vs. $h\nu$ in obliquely deposited a - Se. $n = 1$, which remains unchanged before and after annealing.

Table 1. Values of n and optical bandgap E_0 before and after annealing, and annealing temperature T_a for obliquely deposited systems.

Sample	Annealing temperature T_a [°C]	Before annealing n	After annealing n	Before annealing E_0 [eV]	After annealing E_0 [eV]
As ₂ S ₃	170	0.70	0.59	2.50	2.46
As ₂ Se ₃	160	0.73	0.58	1.90	1.80
GeS ₂	200	0.38	0.44	2.24	2.43
GeSe ₂	200	0.56	0.62	2.12	2.19
Se	30	1.00	1.00	2.05	2.06

The results for the flat (normally deposited) samples are also listed in Table 2. It is interesting to note from Tables 1 and 2 that E_0 for As-based chalcogenides decreases after annealing (thermal darkening), while E_0 for Ge-based chalcogenides increases after thermal annealing (thermal bleaching).

Table 2. Values of n and optical bandgap E_0 before and after annealing, and annealing temperature T_a for normally (flat) deposited systems.

Sample	Annealing temperature T_a [°C]	Before annealing n	After annealing n	Before annealing E_0 [eV]	After annealing E_0 [eV]
As ₂ S ₃	170	0.44	0.49	2.34	2.39
As ₂ Se ₃	160	0.61	0.56	1.89	1.80
GeS ₂	200	0.41	0.43	2.16	2.28
GeSe ₂	200	0.61	0.65	2.11	2.22
Se	30	1.00	1.00	2.04	2.05

4. Derivation of absorption coefficient

Here, a brief derivation of the absorption coefficient is given to facilitate the interpretation of the experimental results given above. For interband electronic transition the optical absorption coefficient under some conventional assumptions can be given as

$$\alpha(\nu) = B \int \frac{N_v(E)N_c(E + h\nu)dE}{h\nu}, \quad (1)$$

where B is a constant and the integration is over energy involving all pairs of states in the valence states (valence band; V.B.) and the conduction states (conduction band; C.B.). If the density of states for the C.B. and V.B. are assumed to be $N_c(E) = \text{const} (E-E_A)^s$ and $N_v(E) = \text{const} (E_B-E)^p$, respectively, then Eq. (1) produces

$$\alpha(\nu)h\nu = B' (h\nu - E_0)^{p+s+1}. \quad (2)$$

This gives

$$[\alpha(\nu)h\nu]^n = B'^n (h\nu - E_0)^n, \quad (3)$$

where $1/n = p+s+1$. If the form of both $N_c(E)$ and $N_v(E)$ is parabolic, i.e. $p = s = 1/2$ for 3 D, then the photon energy dependence of the absorption coefficient obtained from Eq. (3) becomes

$$[\alpha(\nu)h\nu]^{\frac{1}{2}} = B'^{\frac{1}{2}} (h\nu - E_0). \quad (4)$$

5. Discussion

Here we discuss the experimental data by comparing with the theoretical results. As shown above all experimental data cannot be fitted to Eq.(4). First, we will discuss the simple case of a-Se, where $n = 1$ is observed. Applying Eq. (3), we get $(p + s) = 0$ for $n = 1$. This is only possible if the product of DOS is independent of the energy. The origin for this was argued long time ago but was unclear [1]. A chain-like structure is basically expected in a-Se. The top of the V.B. is known to be formed by p-lone pair (LP) orbitals (lone pair interaction) of Se atoms. The interaction between lone pair electrons should have 3D in nature and therefore the parabolic DOS near the V.B. edge can be expected, i.e. $p = 1/2$. The bottom of the C.B., on the other hand, is formed by anti-bonding states of Se. If the interaction between chains is ignored, the DOS near the C.B. may have 1D nature, i.e. $s = -1/2$. We thus obtain $n = 1/(p+s+1) = 1$, producing linear dependence of energy, i.e. $(\alpha h\nu) \propto (h\nu - E_0)$.

Next, we discuss As- and Ge-based binary systems. Although there is no systematic deviation from $n = 1/2$ in these systems, when it occurs, is larger for the oblique systems in comparison with that observed for normal systems. Therefore, it seems likely that the DOS for the normal (flat) films, before and after thermal annealing, are closer to 3D in nature. Let us discuss the properties of the obliquely deposited films. As_2Se_3 , for example, shows $n = 0.73$ and 0.58 before and after annealing, respectively. GeS_2 , on the other hand, shows $n = 0.38$ and 0.44 before and after annealing. The value of n is approaching 0.5 after annealing, while GeSe_2 does not show such a manner. The normally deposited films of GeSe_2 also show a similar tendency (see Table 2).

Structurally, As- and Ge- based systems are suggested to have layered structures [5, 6]. The top of V.B. are formed by the LP bands and the parabolic DOS near V.B. can be expected also in these systems, since LP-LP interactions occur in 3D space as already mentioned. Unlike a-Se, the bottom of C.B. basically should arise from a 2D structure in nature, if the layer-layer interactions can be ignored for anti-bonding states (C.B.). This means that the corresponding DOS is independent of energy ($s = 0$). The value of n , in this case, should be given by $2/3$, since $p = 1/2$ and $s = 0$ are predicted from the argument of space dimensions, and it is close to some of the observed values for

as-deposited oblique films of As-based chalcogenides (see Table 1). Note, however, that the layer-layer interactions cannot be ignored for the DOS of V.B. [7].

This argument, however, cannot be applied to all binary systems (see Table 1 and 2), because the value of n lies between 0.73 and 0.38. The deviation from $n = 1$, $2/3$ or $n = 1/2$ may be attributed to the fractal nature in the DOS; i.e. p or s cannot be given as just $1/2$ (3D), 0 (2D), and $-1/2$ (1D). In obliquely deposited As_2Se_3 and GeS_2 , for example, $n = 0.73$ and 0.38 (before annealing) produce $p + s = 0.37$ and 1.63 , respectively. For interpreting these results, we may need to consider the DOS for fractal structures. The DOS for the extended states on d -space dimension in usual Euclid space is given as

$$N(E)dE \propto \rho^{d-1} d\rho, \quad (5)$$

where ρ is defined as $(2m^*E)^{1/2}/\hbar$, instead of the wave vector k , since k is not a good quantum number in disordered materials and m^* is the effective mass [8]. On fractal space, on the other hand, a fractal dimension D is introduced, instead of d [9]. The DOS for the extended states on fractal space D can be given by [10]

$$N(E)dE \propto \rho^{D-1} d\rho \propto E^{\frac{D-2}{2}} dE. \quad (6)$$

Note that D is introduced as $M(r) \propto r^D$, where M is the “mass” in a space, and hence D can take any fractional value (even larger than 3). A similar argument of fractional dimensionality on interband optical transition has also been presented in anisotropic crystals applicable to low dimensional structures [10].

As we discussed already the energy dependence of DOS for the C.B. is expected to be different from that for the V.B. in amorphous chalcogenides, but usually the space dimensionality for V.B. is larger than that for C.B. Therefore, we introduce D_v and D_c for the dimensionality of V.B. and C.B., respectively. Then $p + s + 1$ in Eq.(2) is replaced by

$$p + s + 1 = \frac{D_v + D_c - 2}{2}, \quad (7)$$

for fractional dimension systems. From the value of n ($=2/(D_v+D_c-2)$), $D_v + D_c$ can be deduced. In As_2Se_3 and GeS_2 , for example, $D_v + D_c$ are 4.74 and 7.26, respectively. The basic structural unit for As-based and Ge-based chalcogenides is different [5,6] and it may affect the fractal dimensionality. After thermal annealing, the value of n tends to 0.5 for both the oblique and flat samples ($D_v + D_c \approx 6$), indicating that each D_v and D_c approach 3-dimension. This is due to the fact that thermal annealing produces more ordered and dense structural network. For a cubic energy dependence, $n = 1/3$, observed for multicomponents (e.g. Ge-As-Te-Si), $D_v+D_c = 8$ is obtained. This higher fractal dimension may be related to “branching” or “cross-linking” between Te chains by introducing As, Ge, and Si atoms [3]. The “branching” may be equivalent to “Bethe lattice” (or Cayley tree), resulting in an increase in space dimension [3].

Finally, we should take a brief look at the validity of Eq.(1) in which the transition matrix element is implicitly assumed to be independent of energy; i.e. B is independent of energy. Dersh et al. [11], on the other hand, suggested that the transition matrix element is energy-dependent and has a peaked nature near the bandgap energy. This discrepancy is unclear at present. More details will be discussed in a future publication.

5. Conclusions

The fundamental optical absorption, empirically presented by the relation $(\alpha h\nu)^n \propto (h\nu - E_0)$, where $0.3 < n < 1$, in amorphous chalcogenides was interpreted by introducing the density-of-states (DOS) on fractals. The energy-dependent form of DOS for conduction and valence states is suggested to be not the same. The presence of disorder can greatly influence the nature of DOS even for the extended states. The concept of DOS on the fractal structures is successfully applied to interpret the fundamental optical absorption spectra.

Acknowledgements

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