



STRUCTURAL AND OPTICAL PROPERTIES OF AMORPHOUS SELENIUM PREPARED BY PLASMA-ENHANCED CVD .

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The preparation of layers of amorphous Se by plasma-enhanced CVD using the hydride H_2Se as precursor gas is described. Information concerning the structure of the films was obtained from Raman spectroscopy. The spectra of amorphous Se indicated that the dominant molecular structure is the eight-membered ring and/or a chain with Se_8 molecular fragments. This material exhibited reversible photodarkening when illuminated at 77 K. In order to explain this phenomenon, we propose a mechanism which takes into account the role of the lone-pair electron orbitals of Se in their contribution to structural ordering. Illumination can cause a distortion in the normal bonding direction between nearest-neighbour Se atoms and induce in this way intrinsic defect states located at the band edges. In the photo-darkened state, optical transition will occur between these defect states.

Keywords : A. disordered systems A. thin films
D. optical properties E. light absorption

1. INTRODUCTION

IN RECENT YEARS, there has been a great deal of interest in changes of structural and optical properties of amorphous chalcogenides when the materials are exposed to light having a photon energy comparable to the bandgap. The photo-induced changes are mostly unique to the amorphous state and have rarely been observed in crystalline semiconductors. They can be either irreversible or reversible, in the sense that the changes are permanent after illumination, or that they can be removed by annealing. A phenomenon which received much attention is the shift of the optical absorption edge to lower energies ("red" shift) or higher energies ("blue" shift). These phenomena are known as photodarkening and photobleaching. The photostructural changes have primarily been studied in amorphous chalcogenides containing substantial amounts of sulphur, selenium and tellurium, e.g. As_2S_3 , As_2Se_3 , GeS_2 and $GeSe_2$. Photodarkening, i.e. the shift of the optical absorption edge to lower energies upon light illumination, is commonly observed in chalcogenide alloys. Little is known about this phenomenon in amorphous Se. Observation of photodarkening has previously been reported¹⁻³ when Se films were illuminated at low temperature (77 K). It is interesting to examine photodarkening in this elemental chalcogenide material, since it is built up only with homo-

bonds, while in the chalcogenide alloys hetero-bonds are always preferred. Most studies have dealt with thin films (of the order of 1 μm thick) prepared by evaporation. In our study we have prepared films of amorphous selenium by plasma enhanced chemical vapour deposition (PECVD). This technique, although widely applied for the production of amorphous silicon, e.g. in solar cells, has rarely been used for the deposition of amorphous chalcogenides. We believe that PECVD is a promising technique for growing thin layers of these materials, in particular with respect to their possible technological applications. Some of our previous work devoted to the deposition of amorphous As_xS_{1-x} , Ge_xS_{1-x} and Ge_xSe_{1-x} was recently published^{4,6}.

2. MATERIAL PREPARATION

We have deposited thin films of amorphous Se (1 μm thick) in a plasma discharge stainless steel reactor. A low pressure plasma (of the order of 0.1 mbar) was created by an rf discharge (13.56 Mhz) between two parallel plate electrodes, 8 cm in diameter. The gas flow was controlled by an electronic mass flow controller. The gas pressure was measured and automatically regulated through a butterfly valve by a Baratron pressure gauge. Crystalline silicon and glass substrates were fixed on both electrodes. Depositions were made without additional heating of the substrate by a furnace, but due to heating by the plasma the temperature may rise to about 50°C. The precursor gas was pure H_2Se .

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The deposition conditions were :

flow rate	6 sccm
pressure	0.1 mbar
rf power	30 Watt
deposition time	10 min.

Film growth only occurred on the grounded electrode.

X-ray diffraction showed that the film was completely amorphous.

3. STRUCTURAL CHARACTERISATION

We studied the structure of the amorphous film by Raman spectroscopy. Measurements were made with the help of a Bruker 66 V spectrometer in a reflection mode using the 1.06 μm YAG : Nd³⁺ laser source. The Raman spectrum of an as-deposited Se film is shown in Fig. 1a. It shows a strong peak at 250 cm^{-1} and two small bands at 80 and 112 cm^{-1} . Moreover, a small shoulder appears at 235 cm^{-1} on the 250 cm^{-1} band.

In the past the structure of amorphous Se has been studied by several workers using different techniques. The amorphous state has been known to consist of two types of atomic arrangement which are mixed together; one is the Se₈-ring and another form is the helical chain. The fraction of each one depends essentially on the method of preparation. In bulk glasses prepared by quenching of the melt, the fraction of the Se₈-ring decreases with increasing temperature of the melt.

The Raman peaks of amorphous Se have been identified by Lucovsky et al.⁷. They observed a much closer resemblance of the Raman spectrum of melt quenched selenium to that of Se₈ in monoclinic Se than to that of trigonal Se. According to their assignment the dominant peak at 250 cm^{-1} originates from vibrations in the Se₈-rings. Those at 80 and 112 cm^{-1} were also assigned to vibrations in the Se₈-ring. In trigonal selenium the predominant Raman band lies at 235 cm^{-1} . A reexamination of the Raman spectrum of melt quenched Se by Lucovsky⁸ showed that the peaks at 250, 112 and 80 cm^{-1} can also be associated with Se₈ molecular fragments that are incorporated into a chain structure. He proposed a model in which the dominant molecular structure is described by both helical chain-like and ring-like

arrangements of the Se atoms (a "meandering" chain). The Raman spectrum of the plasma deposited Se film is similar to that of a bulk glass quenched from 250 °C. This indicates that the structure contains predominantly Se₈ rings and Se₈ molecular fragments. The shoulder that appears on the 250 cm^{-1} band can be associated with a small fraction of "pure" helical chains. Upon heating at 150°C for 1 hour the film was crystallized. The Raman spectrum (see Fig. 1b) showed a sharp peak at 235 cm^{-1} and a small shoulder at 250 cm^{-1} . Upon crystallization the complex ring-like structure undergoes transformation to the orderly array of chains of trigonal Se.

4. OPTICAL ABSORPTION

Considerable work has been published on the optical absorption in amorphous semiconductors but its interpretation is not straightforward. In these materials the optical absorption spectrum is usually divided into two parts dealing with optical transitions at energies above and below the mobility gap, separating the extended from the localized states. Interband transitions between extended states in the valence and conduction band occur in the strong absorption region of the absorption edge. In this region the absorption coefficient α lies between 10³ and 10⁵ cm^{-1} (transmission range below 15 %).

Most of the experimental data on amorphous semiconductors in the strong absorption region were found to be in agreement with the so-called Tauc law, that is

$$\alpha h\nu = C (h\nu - E_T)^2 \quad (1)$$

where $h\nu$ is the photon energy.

The constant E_T can be used to define an optical gap. C is a constant indicating how steeply the absorption rises with energy. A notable exception to the quadratic frequency dependence of α was found to be amorphous Se which followed a linear law⁹. The Se layer used in this experiment was a hot-pressed sample obtained from a bulk glass.

We recorded the optical transmission spectrum of an amorphous Se film prepared by PECVD at room temperature. Two features became immediately apparent: 1. the spectrum shows strong interference fringes and 2. the transmission drops markedly around 650 nm. The transmission range below 15 % was used to determine the optical absorption coefficient α by inverting the equation

$$T = \frac{(1-R)^2 \exp(-\alpha d)}{1-R^2 \exp(-\alpha d)}$$

where T is the transmission, R the reflectance and d the sample thickness.

We measured the reflectance R as a function of wavelength and found a value of 0.27.

The experimental data of α were plotted versus photon energy in two ways : according to a linear law and according to Tauc law. A square root plot gave a better fit in the 2.1 - 2.4 eV range. The extrapolated gap occurs at E_T equal to 1.936 eV. Upon annealing to 100°C, we did not observe any change in this spectrum.

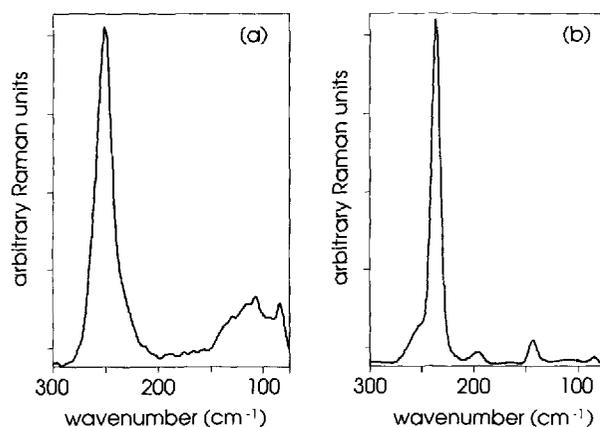


Fig. 1. Raman spectra of (a) as-deposited Se film; (b) annealed at 150°C for 1 hr.

5. PHOTODARKENING IN AMORPHOUS SELENIUM

We illuminated our Se films with white light from a halogen lamp (light intensity 100 mW cm^{-2}) and recorded the transmission spectra before exposure and after illumination at 77 K for a period of 5 and 120 minutes, respectively. At room temperature no shift in the optical absorption edge was observed. The films illuminated at 77 K revealed a definite decrease in the optical bandgap-energy. This induced shift in the optical absorption edge could be completely removed when the samples were annealed at room temperature. The process was completely reversible. Figure 2 shows the results of the photo-induced changes of the optical absorption. The data are plotted as $(\alpha h\nu)^{1/2}$ versus $h\nu$. The value of the optical gap given by the extrapolation of the straight lines varies between 2.092 eV for the virgin films and 1.987 eV for the same film after 120 minutes of illumination. The saturated value of the shift ΔE_T is about 0.1 eV. In order to explain the photodarkening in amorphous Se, we shall first discuss the structural configuration of the Se atoms and the specific features of the band structure of the material. The two-fold coordination for the Se atoms leaves two outer shell electrons in a non-bonding state. The top of the valence band originates from these lone-pair non-bonding orbitals. The p-antibonding orbitals form the conduction band. The interaction between lone-pair electrons on different Se atoms will contribute to the structural ordering, in particular in the range of intermediate distances. In the disordered state many atomic configurations with slight differences in energy can exist so that the energy of a photon is large enough to cause a transition to a different configuration.

Our interpretation of the photodarkening in amorphous Se is based on a study by Wong and coworkers¹⁰ dealing with the formation of intrinsic defect states originating from dihedral angle distortions. The

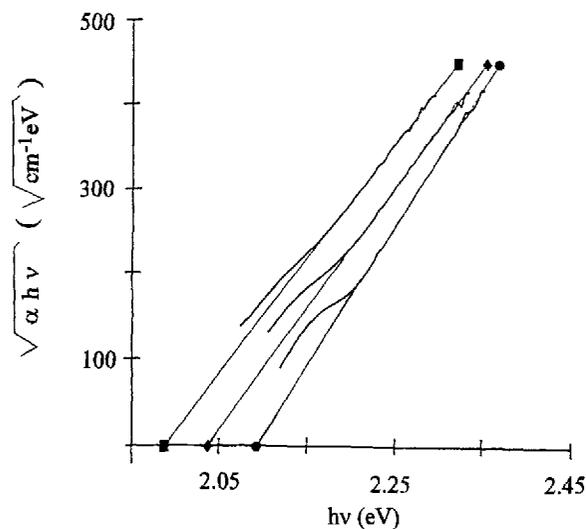


Fig. 2. Optical absorption edge at 77 K of amorphous Se in the virgin and photodarkened state: ● as-deposited film; ◆ after 5 min. illumination; ■ after 120 min. illumination.

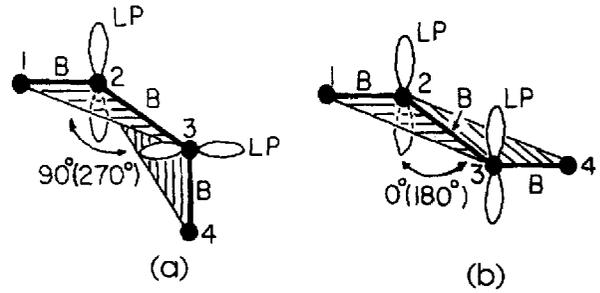


Fig. 3. Bonding arrangement in Se bonding : (a) normal bonding : orthogonal alignment of lone-pair orbitals of Se atoms; dihedral angle 90° or 270° . (b) bonding arrangement with dihedral angle distortion of 0° or 180° : parallel alignment of lone-pair orbitals of Se atoms (after C.K. Wong et al.¹⁰).

main features of their work indicate that in the normal bonding arrangement the bonding directions B of two nearest-neighbour Se atoms form an angle of either 90° or 270° (see Fig. 3a). This places the lone-pair p orbitals at right angles and minimizes Coulomb repulsion.

Wong and coworkers have found using a tight binding calculation that the distortion in 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 atoms approach parallel alignment (see Fig. 3b). In Fig. 4a the density of states for the valence band and the conduction band are shown for Se atoms with all dihedral angles at 90° or 270° degrees, which is the normal bonding configuration. Figure 4b gives the density of states that results from a dihedral angle bonding defect which forces the lone-pairs into a parallel alignment. This arrangement splits two states off of each of the bands. The state just above the top of the valence band is a hole trap. The state just below the bottom of the conduction band is an electron trap.

Using these ideas, we can explain the decrease in the optical gap upon illumination in the following way. We assume that before illumination the bonding between the Se atoms is in its normal arrangement. Then the optical

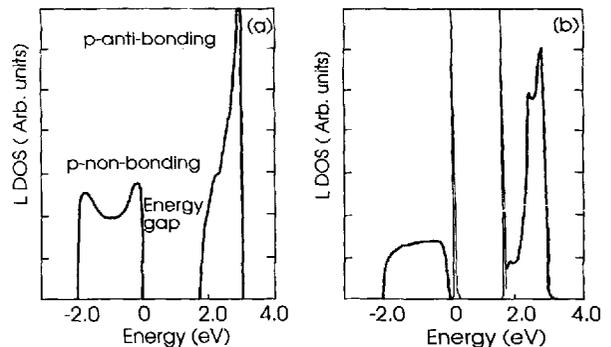


Fig. 4. Local electronic density of states (LDOS) (a) for Se atoms in the normal bonding configuration : (b) for Se atoms of a 0° or 180° dihedral angle bonding distortion (after C.K. Wong et al.¹⁰).

transitions occur between the top of the valence band and the bottom of the conduction band as shown in Fig. 4a. Illumination can cause a distortion in the normal dihedral angle and induce in this way intrinsic defect states (see Fig. 4b). The optical transitions will then occur between these defect states over a smaller energy gap than before illumination. The observed shift of the absorption edge equal to about 0.1 eV is in good agreement with Wong's calculation that the separation of the defect state from the band edge is of the order of 0.1 eV. Upon annealing the normal bonding arrangement can be restored.

As can be seen from Fig. 2, illumination shifted not only the absorption edge but also caused a decrease in the slope of the Tauc curve. As indicated by Mott and Davis¹¹ the slope, i.e. the constant C in eq.(1), is inversely proportional with the width of the localized states region at the band edges. This means that an increase in disorder reduces the slope of the edge. It seems reasonable to assume that the distortion of the dihedral angle can vary

systematically upon illumination, yielding a spread in the localized states.

A thorough understanding of the photodarkening in amorphous Se will depend on more elaborate experiments, in particular a study of the reaction kinetics upon annealing. The observation of photodarkening in this elemental material is an important feature, because it demonstrates that the occurrence of wrong homopolar bonds in heteropolar coordinated chalcogenide alloys is not a necessary condition. In our investigation no irreversible photodarkening, sometimes described by the disappearance of wrong bonds in chalcogenide alloys, was observed. Further work for elucidating the photodarkening in amorphous Se is in progress now.

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