

Highly disordered amorphous selenium studied by ultraviolet photoemission spectroscopy

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Highly disordered amorphous (HDA) selenium films were prepared by vapor deposition onto a cold substrate held at 77 K under ultrahigh vacuum. He_I photoemission spectra of these films were found to be considerably different from the previously observed spectrum of the amorphous film prepared at room temperature (RT film). Characteristic features in the spectra of the HDA films compared with those in the spectrum of the RT film are as follows: (1) the width of the 4p nonbonding band is remarkably narrower; (2) the intensity of the upper 4p bonding band is decreased, and the intensity ratio of the upper and lower 4p bonding bands is reversed; (3) the upper 4p bonding band is located at higher initial energy; and (4) a part of the 4s band is well resolved. The HDA films underwent thermal annealing effects and at room temperature gave a photoemission spectrum similar to that observed in earlier work. In order to interpret the experimental results, CNDO molecular-orbital calculations were made on a newly proposed model for amorphous selenium, in which distorted infinite chains consist of small spiral units including a few selenium atoms. On this model, dependence of the density of states on the following factors was studied: (1) the number of atoms in a unit cluster, (2) the dihedral angle for the bonds on the junction of the units, and (3) the bond angle. The results of the calculations well explained the spectrum of HDA selenium and its thermally induced changes. The importance of the above three factors for the structure of amorphous selenium was stressed.

I. INTRODUCTION

The structure and electronic properties of amorphous selenium have been the object of great interest. It is well known that there are two types of crystalline selenium: the monoclinic form which consists of eight-membered puckered rings of atoms and the trigonal form which consists of straight spiral chains. On the other hand, the structure of amorphous selenium has been controversial for a long time.¹⁻³

Various models were proposed on the basis of x-ray-diffraction analyses; these models involve random chains,^{4,5} zig-zag chains,^{6,7} Se₈ (Ref. 8) or Se₆ (Ref. 9) rings, or a mixture of chains and rings.¹⁰⁻¹⁴ Studies of viscosity,¹⁵⁻¹⁷ copolymerization,^{18,19} and neutron diffraction^{20,21} gave evidence that amorphous selenium contains chainlike structure, but ringlike structure cannot necessarily be ruled out by these experiments. Infrared²² and Raman²³ spectra were studied and the results seemed to favor ringlike structure. However, these spectroscopic results may also be understood on a chain model.²⁴ Thus, the structure of amorphous selenium has not yet been well established on these investigations.

Photoemission spectroscopy is a powerful means to give us a better insight into the structure of amorphous solids in connection with their electronic structure. Photoemission spectra of crystalline trigonal selenium^{25,26} were measured, and the electronic structure was studied on the basis of various theoretical calculations.²⁷⁻³⁵ Nielsen³⁶ presented ultraviolet photoemission

spectra of amorphous selenium for the first time. Three well-resolved bands were found in the 0 to -6-eV initial-energy region. These bands were assigned as follows: The first band is due to ionization of 4p nonbonding electrons, and the second and third ones are ascribed to the upper and lower bonding states, respectively. A remarkable difference between the spectra of the amorphous and trigonal forms is in the intensities of the second and third bands; the intensity ratio of these two bands is reversed between the amorphous and trigonal forms. Theoretical calculations have been made on various models for the density of states of the amorphous form in connection with their structure.²⁸⁻³⁵ Calculations based on a distorted trigonal form without long-range order of the lattice^{30,31} gave a poor agreement with the above observation. A role of interchain interaction was discussed by Joannopoulos *et al.*³³⁻³⁵; a part of the density of states for the second band can be related to interchain bonding which may be increased in amorphous form. Distortion of dihedral angles in a spiral chain may also be a possible cause of the spectral difference; Shevchik's calculation^{28,29} including this effect gave a good agreement with experiment. Successful calculations were also made by Robertson³⁷ and Bullett³² on the basis of a chain model in which dihedral angles can take positive or negative values of $\pm 101^\circ$ alternately or at random.

Alternative models including ring structure have been proposed for amorphous selenium on the basis of photoemission studies³⁸ and theoretic-

cal calculations.³³ Recent studies of x-ray photoemission spectra of amorphous selenium^{25,26} showed that the 4s band has a little dip in the density of states. Joannopoulos *et al.*³³ suggested that this dip might be due to ringlike structure; they discussed possible structures of ringlike units in amorphous selenium on the basis of their calculation, with Se₈ rings being most likely to be involved. Salaneck *et al.*,³⁸ however, suggested that Se₈ rings are one of the favorable constituents because the 4s band in monoclinic selenium has a fairly deep dip.

Although photoemission spectroscopy has given us considerable information about local structures and electronic structures in amorphous selenium, none of the previous models has given a strong confirmation. It should be stressed here that this confusion can not be removed without further experimental studies.

A new experiment may be made if one can modify or control structural properties of amorphous samples. It is well known that properties of amorphous solids depend on preparation methods; in the case of vapor-deposited films, their properties may change sensitively with the temperature of the substrates. It is also well known that amorphous solids often undergo thermal annealing effects. It is, therefore, of great interest to perform those experiments involving change in temperature.

II. EXPERIMENTAL

Measurements of the photoemission spectra were carried out using an ultra-high-vacuum photoemission spectrometer constructed at our laboratory.³⁹ It has a preparation and analyzer chambers which can be separated by a gate valve. The base pressure in the chambers is lower than 3×10^{-10} Torr. The excitation sources are the He I (21.22 eV), Ne I (16.85 and 16.67 eV), and Ar I (11.83 and 11.62 eV) resonance lines. For the Ne or Ar doublet, the mean value was used to analyze the spectra. The energy of photoelectrons are analyzed by a 180° hemispherical analyzer (5-cm mean radius), the resolution of which is about 0.15 eV full width at half-maximum (FWHM).

Selenium films were prepared in the preparation chamber by vapor deposition onto a stainless-steel substrate held at 77 K (LT film) or at 296 K (RT film) in a vacuum of less than 3×10^{-9} Torr. The temperature of the evaporation source was kept at about 500 K. The deposition rate was controlled to be at about 1 Å/sec. The thickness of the films was monitored by a quartz oscillator monitor and was estimated to be about 300 Å.

Photoemission spectra of the RT film was measured at 296 K. Temperature dependence of the photoemission spectra of the LT film was studied from 77 to 328 K. The increasing rate of the substrate temperature was kept to be at about 1 K/min.

III. EXPERIMENTAL RESULTS

Figure 1 shows the photoemission spectra of the amorphous selenium films. The He I spectrum of the RT film agrees with that of earlier work.^{25,26} The He I spectrum of the LT film is, however, markedly different from that of the RT film: (1) the spectral bandwidth of the first band at about -1.6 eV is clearly narrower in the LT film, (2) the second band at about -4 eV of the LT film has shifted toward higher initial energy, (3) intensity of the second band becomes considerably decreased in the LT film and the intensity ratio of the second and third (at about -5 eV) bands is reversed, and (4) the fourth band at about -12 eV is clearly resolved in the spectrum of the LT film. These features of the LT film were also observed for the first three bands in the Ar I and Ne I spectra.

Figure 2 shows the temperature dependence of the photoemission spectra of the LT film. The spectral bands gradually changed with the increase in temperature; (1) the first band became broader

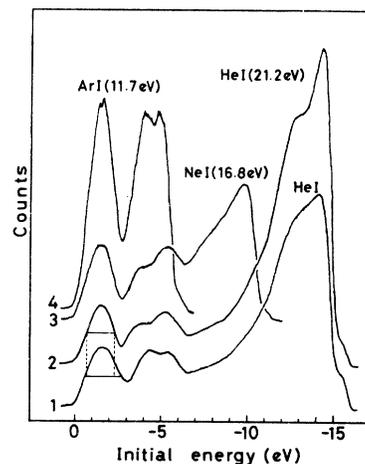


FIG. 1. Photoemission spectra of amorphous selenium films deposited on a substrate held at 296 K (spectrum 1; RT film) and 77 K (spectra 2-4; LT film). During the UPS measurements the substrate was kept at the same temperature as on deposition. Excitation sources are the He I, Ne I, and Ar I resonance lines. For the Ne or Ar doublet, the mean value is used for analyzing the spectra. The initial energy on the abscissa is taken from the top of the valence states of the spectrum at 296 K (spectrum 1). For the first bands of the spectra 1 and 2, the bandwidths are specified.

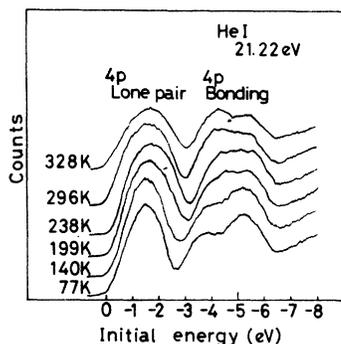


FIG. 2. Thermally induced changes of the He I spectra of the highly disordered amorphous selenium film (LT film). For the abscissa, see Fig. 1.

and shifted toward the lower initial energy, (2) the second band increased in intensity and shifted remarkably toward the lower energy, and (3) no noticeable change could be observed in the third band. The present spectrum in the LT film at 328 K agrees approximately with that of the RT film. This spectral change associated with the increase in temperature was found to be irreversible.

One can make a further comment on the present results. The photoemission spectrum of the unannealed LT film is different from that of either trigonal or monoclinic crystal. Although the total profile of the spectrum of the unannealed LT film looks similar to that of the trigonal, the width of the first band and the position of the second band in the spectrum of the LT film are clearly different from those of the trigonal, and further the triplet substructure in the first band observed for the trigonal selenium^{25,26} is not found in the LT-film spectrum.

IV. CALCULATIONS

According to a previous study,⁴⁰ clusters of selenium atoms including Se_5 or Se_8 are dominant gaseous products on low-temperature (less than 600 K) evaporation. This condition was fulfilled in the present study. These clusters of a few selenium atoms adhere onto the substrate in the deposition process and motions of these clusters are suppressed on the cold substrate. Therefore, these clusters (rings or chains) are expected to be unit constituents of the deposited films. One should, however, note here that calculations based on ring models including Se_5 or Se_8 rings do not yield consistent results with the present experiment; a ring model led to the larger density of states for the second band with respect to the third one,^{33,38} whereas in the spectrum of the

unannealed LT film the density of states of the second band is smaller than that of the third one (Fig. 1).

Accordingly, a chain model was employed for interpretation of the present experimental results. Figure 3 illustrates the present model. Clusters of a few selenium atoms are unit constituents of this model, and long chains consist of these unit clusters which are connected to one another, with the dihedral angles (ϕ) being altered from those in the trigonal crystal. The bond angles within each unit are almost the same as those in chains of the trigonal crystal. The dihedral angles (θ) are also almost unaltered from the trigonal value. A thermal annealing effect may cause the distorted dihedral angles and bond angles to relax into their most stable values. Further, the average number of atoms in a unit cluster (N) is expected to increase through the annealing process.

CNDO molecular-orbital calculations were carried out on the above model. The parameter values were taken from those employed by Salaneck *et al.*³⁸ in their calculation on monoclinic selenium. A periodic boundary condition was introduced for the junctions between the unit clusters. Intercluster interactions were taken into account in the Fock matrix for a unit cluster; resonance integrals for a pair of the end atoms in a unit cluster are replaced by those integrals for adjacent atoms on the junction of the connected units. Two-center-electron repulsion integrals were neglected for intercluster atomic pairs. The bond length was taken to be 2.36 Å. Dependence of the density of states on the following factors was studied: (1) the number of atoms in a unit cluster (N), (2) the dihedral angle for the bonds on the junction of the units (ϕ), and (3) the bond angle (θ).

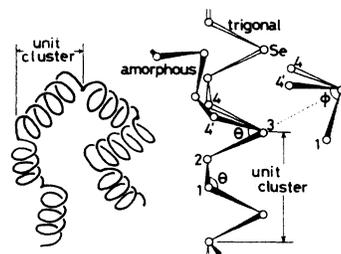


FIG. 3. A new structural model for amorphous selenium proposed on the basis of the present experiments. Each cluster contains a few selenium atoms which are arranged nearly the same way as in a chain of trigonal selenium. The clusters are connected to one another with the dihedral angle (ϕ) at the junction being altered from those in the trigonal crystal. The dihedral angles within each cluster are almost unaltered from the trigonal value. Bond angles (θ) are slightly distorted.

In the calculation, one of the three parameters was varied with the other two being fixed at the following values: $N=9$, $\phi=101^\circ$, and $\theta=103.7^\circ$. These values for ϕ and θ are those of the trigonal crystal and they are considered to be the most stable ones. Figures 4–6 show the calculation results. Envelopes of the density of states were illustrated on an assumption of the Gaussian of a width of 0.55 eV for each calculated level. In Fig. 4, the levels were specified by bars.

V. DISCUSSION

The first band at about -1.5 eV in Fig. 1 is attributed to the $4p$ nonbonding states. As can be seen in Fig. 2, the first band becomes broader with an increase in temperature. This thermally induced change of the band width can be explained as follows. The thermal annealing process leads to an increase in the average size of a unit cluster, which is accompanied by the increase in the number of interacting lone pair electrons within the cluster. The width of the first band attributed to the interaction among lone pair electrons is, therefore, expected to increase upon annealing. This interpretation is supported by the results of calculations (Fig. 4); the first band becomes broader as the number of atoms in a unit cluster increases. The slight shift of the first band upon thermal annealing (Fig. 2) can also be understood from the results in Fig. 4.

The second and third bands are assigned to the $4p$ bonding states. From Fig. 2, one can find that the second band exhibits remarkable changes in both intensity and position on annealing, while the third band has a relatively stationary feature. These observations may be interpreted by a thermally induced relaxation of distorted dihedral

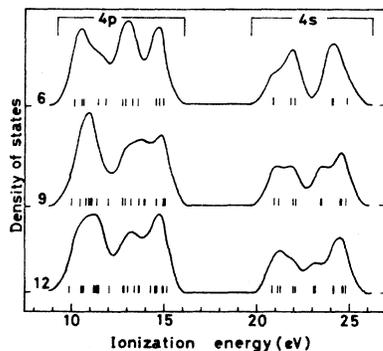


FIG. 4. The $4p$ - and $4s$ -derived portions of the density of states. Each curve is labeled by the numbers of selenium atoms (N) in a cluster. The dihedral angle $\phi=101^\circ$ and the bond angle $\theta=103.7^\circ$. Calculated levels are indicated by bars.

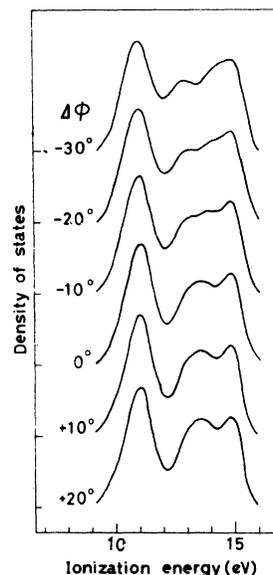


FIG. 5. The calculated density of the $4p$ states. The dihedral angle at the junction between two clusters is altered from the trigonal value $\phi=101^\circ$, $\Delta\phi=-30^\circ$ to $+20^\circ$. The number of selenium atoms (N) in a cluster is 9, and the bond angle $\theta=103.7^\circ$.

angles and bond angles of selenium chains. Calculation results in Fig. 5 show that the observed changes of the second band (Fig. 2) can be explained by the relaxation of a large negative distortion of the dihedral angles; the second band grows and at the same time shifts as the dihedral angle (ϕ) is altered from negative distorted

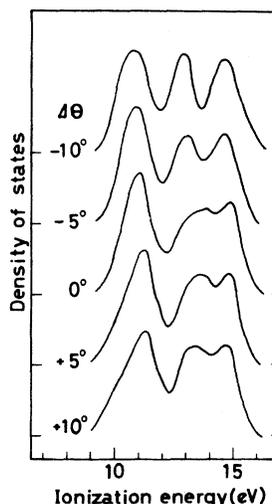


FIG. 6. The calculated density of the $4p$ states. The bond angle is altered from the trigonal value $\theta=103.7^\circ$, $\Delta\theta=-10^\circ$ to $+10^\circ$. The number of selenium atoms (N) in a cluster is 9, and the dihedral angle $\phi=101^\circ$.

values to the stable one. A negative distortion of the bond angle (θ) (Fig. 6) may also explain the observed shift of the second band; the separation between the upper and lower bonding bands is found to depend on the bond-angle distortion, as pointed out by Joannopoulos *et al.*³³ As can be seen in Fig. 6, the distortion of the bond angle (θ), however, also yields the shift of the third band. In view of no observable shift of the third band in the present experiment (Fig. 2), the bond-angle distortion is estimated to be less than 5° , which agrees with a recent simulation on amorphous selenium.⁴¹ The calculation results (Figs. 4–6) show that the third band is rather insensitive to the structural parameters N , ϕ , and θ compared with the second band. This tendency explains the observed stationary feature of the third band upon annealing.

The fourth band at about -12 eV in the He I spectrum (Fig. 1) is due to the upper 4s valence states which correspond to the lower-energy peaks (20–22.5 eV) of the calculated 4s band (Fig. 4). As can be seen from Fig. 1, the fourth band is better resolved in the unannealed LT film than in the RT film. This observation can also be explained by the size of the unit clusters in amorphous selenium films; Fig. 4 shows a deeper dip

for the case of smaller clusters which are expected to be main constituents in the unannealed LT films.

VI. CONCLUSIONS

Ultrahigh-vacuum photoemission measurements have been made for highly disordered amorphous selenium films prepared on a cold substrate. We found that the films show quite different spectra from those observed for amorphous films of earlier work^{25,26,36} and that the spectra cannot be understood on the earlier ring^{33,38} or chain models.^{28,29,32,37} In order to explain the spectra and their thermally induced irreversible changes, we presented a new structural model for amorphous selenium. The model consists of relatively regular small spiral chains which are connected to one another. CNDO molecular-orbital calculations based on the model yielded results in good agreement with the present experiments. The present study shows that size of selenium clusters and dihedral angles has significant effects on the electronic structure of amorphous selenium. This means that "an intermediate-range order" plays an important role in amorphous selenium.

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