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STRUCTURE AND ENERGY LEVEL SCHEME OF AMORPHOUS As-Se SYSTEM

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UPS, Raman and photoconductivity of amorphous As_xSe_{1-x} system ($0\leq x\leq 0.5$) are investigated. The density of states of upper valence band and Raman spectra are well described by the superposition of those of Se, As_2Se_3, As_4Se_4 and As_2Se_4. The matters suggest that the hetero-bondings are predominant in this system. Dependence of photoconductivity on the chopping frequency of the illumination is observed, and the dependence is interpreted in terms of the mono- and bi-molecular recombination processes.

I. Introduction

Although UPS, Raman and photoconductivity of amorphous As_2Se_3 have been extensively studied, the study of the chemical ordering of the As-Se system has not been reported so much. The change in the density of valence states due to the change in the composition has not yet been made clear. In the present paper, densities of upper valence band states (U-DOVS) of As_xSe_{1-x} are determined by the ultraviolet photoelectronic emission spectroscopy, and the determined U-DOVS are explained in terms of the chemical ordering in the network.

Chemical ordering on As-Se system and the molecular species of the structural units for each composition are identified also by Raman measurements. Photoconductivity was measured to obtain the information on the density of localized states in the gap.

II. Experimental

Amorphous ingots were prepared by the melt quench of the mixture of As and Se. UPS measurements were carried out on evaporated amorphous films of As_xSe_{1-x} in the range of $0\leq x\leq 0.5$ in the vacuum of 5×10^{-9} Torr. He I resonance line at 21.2eV was used as a light source. Films were deposited on the aluminum substrate at a rate of ca. 10 A/sec and the thicknesses were ca.1000A. The binding energy from Fermi level in U-DOVS was determined by adjusting UPS datum to agree with that obtained with XPS. The C(1s) line at 284.3 eV in XPS was used as a energy standard.

Raman spectra were obtained in a standard back scattering geometry at 77 K with Ar laser lines of 5145A and 4880A. Photon counting system was employed.

The photoconductivity was measured with the incident light source of 670 W halogen lamp chopped with 400 Hz, 16.7 Hz and 1/60 Hz etc. A lock-in amplifier and a digital microvoltmeter were used for the conductivity measurement. The electrodes separated by 0.8 mm were made with evaporated gold on the surface, and the illuminated light was vertical to the applied electric field.

III. Results and Discussions

U-DOVSs of various samples are shown in Fig.(1). The intensities of U-DOVSs are normalized according to the average number of 4p-electrons per an atom in each sample. Three peaks are seen in the spectra for As rich films, however, the middle peak disappears in the spectra for Se rich films.

Bishop and Shevchick have shown that U-DOVS of As_2Se_3 can be constructed from that of As and Se [1]. It is, however, impossible to synthesize U-DOVS of $As_{50}Se_{50}$ by simple superposition of the properly weighted U-DOVSs of the constituent elements.

It is also impossible to synthesize the observed U-DOVS spectra by simply superposing the properly weighted spectra of Se, and $As_{50}Se_{50}$. On the other hand, the observed U-DOVS spectra for the samples which have the composition in the range of $0 \leq x \leq 0.4$, and $0.4 \leq x \leq 0.5$ are synthesized by superposing the properly weighted U-DOVS spectra of Se and $As_{40}Se_{60}$, and $As_{40}Se_{60}$ and $As_{50}Se_{50}$, respectively as seen in Fig.(2).

These facts show that the hetero-bonding is predominant compared with homo-bonding in all composition range, and they support the correctness of the chemically ordered network model (CONM) suggested by Lucovsky et at. on As_xSe_{1-x} [2].

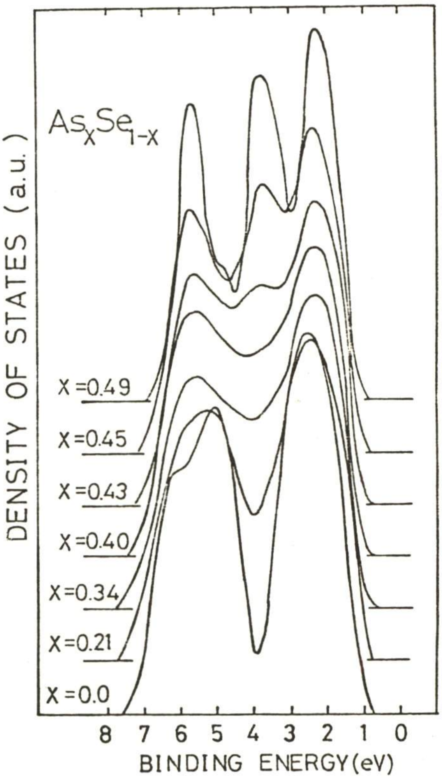

Fig.1 The U-DOVSs of As_xSe_{1-x} obtained by UPS

From a simple consideration we can say that Se has one 4p bonding energy level, and both As_2Se_3 and As_4Se_4 have three 4p bonding energy levels. For As_2Se_3, all three levels are originated from As-Se bond. For As_4Se_4, one of the levels is originated from As-As bond and the other two are originated from As-Se bond, and the intensity of the former is a half of the latter. When the energy level of lone pair electrons is taken into consideration, Se, As_2Se_3 and As_4Se_4 have two, four, and four energy levels, in the U-DOVS respectively. With the assumption of the Gaussian shape broadening for each level, positions of energy levels in Se, As_2Se_3, and As_4Se_4 were determined. By comparing the results for Se with the analysis by Shevchick, energy levels of Se at binding energy $E_b=2.4$ and 5.5 eV are originated from Se 4p lone pair orbital and Se-Se 4p σ-bonding orbitals, respectively.

For As_2Se_3, the energy level at $E_b=2.0$ eV is originated from Se 4p lone pair orbital and the energy levels at $E_b=3.3$, 4.8, and 6.0 eV are originated from As-Se 4p σ-bonding orbitals.

For As_4Se_4, the energy level at $E_b=1.8$ eV is originated from Se 4p lone pair orbital, and the energy levels at $E_b=3.5$ and 5.4 eV are originated from As-Se 4p σ-bonding orbitals. The energy level at $E_b=2.7$ eV is originated from As-As 4p σ-bonding orbital.

Our results show that the top of the valence band for As_xSe_{1-x} in the range of $0 \leq x \leq 0.5$ is constructed from the Se lone pair orbital energy level. This argument agrees with the model of Kastner [3] and the theoretical results of Shimizu and Ishii [4].

The binding energy of Se lone pair orbital electron is shifted from 2.4 eV in Se to 2.0 eV in As_2Se_3 and to 1.8 eV in As_4Se_4. Since Se atom has larger electronegativity than As atom, the energy level of Se lone pair electron shifts to higher energy side with the addition of As atoms.

In Fig.(3), the intensities of Raman scattering by the component of As_2Se_3 in proportion to x and by the other components are shown by dashed-dotted and dashed lines, respectively. The intensity $I_x(\omega)$ of Raman scattering in Se rich region is expressed by

$$I_x(\omega)=\frac{5x}{2}I_1(\omega)+(1-\frac{5x}{2})I_2(\omega),\text{for } \frac{4}{15}\le x\le\frac{5}{2}, \quad (1)$$

$$I_x(\omega)=\frac{5x}{2}I_1(\omega)+\frac{5x}{4}I_2(\omega)+(1-\frac{15}{4}x)I_3(\omega), \quad (2)$$

for $0\le x\le\frac{4}{15}$;

where I_1, I_2 and I_3 are the intensity of Raman scattering of As_2Se_3, As_2Se_4 and Se, respectively. The dependence of the Raman intensity of the peak at 270cm^{-1} on the concentration $x(x\ge0.3)$, is well described by the I_2 term in eq. (1).

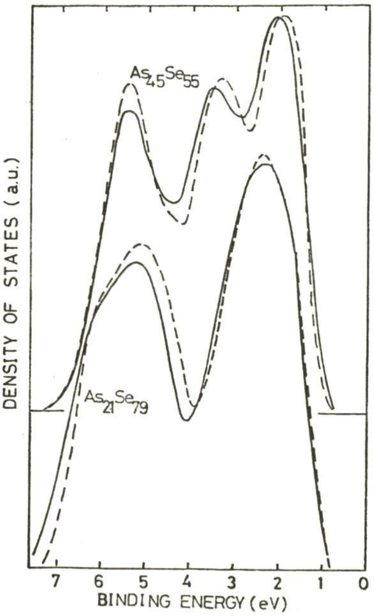

Fig.2 The experimental (solid line) and synthesized (broken line) U-DOVSs for $As_{21}Se_{79}$ and $As_{45}Se_{55}$

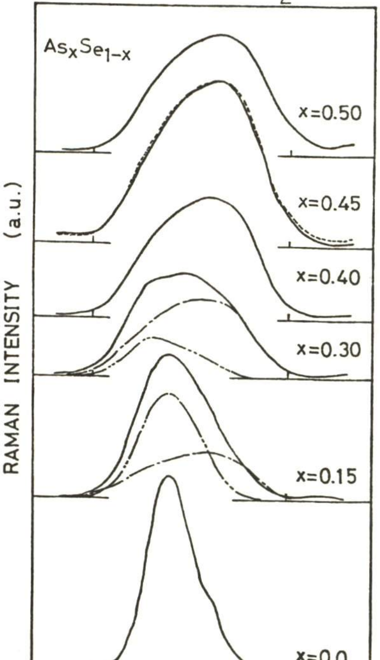

Fig.3 Raman spectra of As_xSe_{1-x}

The Raman scattering measurements of the stretching modes of Se-Se and $AsSe_3$ pyramidal unit suggest that the ratio of the force constants of As-Se and Se-Se is $k_{As-Se}/k_{Se-Se}=1.4$. From this ratio and the mass ratio $m_{As}/m_{Se}=0.95$, the value of the vibration frequency 270 cm^{-1} is assigned to the Se-Se stretching vibration mode of As-Se-Se-As chain, and this structure unit is surely As_2Se_4 molecule. The lower tail shown by dashed line in Fig.(3) of the As concentration $x\ge0.3$ may be due to the stretching mode of Se-Se bond, but since the frequency of this mode is similar to that of the stretching mode of $AsSe_3$ pyramidal unit, the identification of the Se-Se stretching mode is difficult. The dependence of the Raman intensity of the peak at 260 cm^{-1} on the As concentration $x(x\le0.15)$, is well described by the I_3 term in eq.(2). The shoulder in the higher energy for x=0.10 and 0.15 is due to the I_2 term in eq.(2) since the spectrum of pure Se does not have this shoulder.

The spectrum for x=0.45 is well reproduced by the arithmetic average of the spectra for x=0.4 and x=0.5. This suggests the existence of an As_4Se_4-type construction unit.

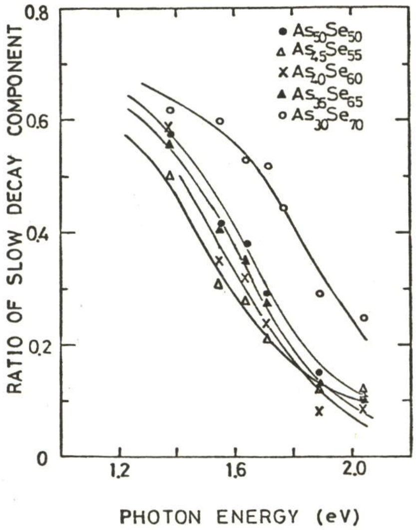

Fig.4 The ratio of the slow decay component in the photoconductivity spectrum to the total photocurrent

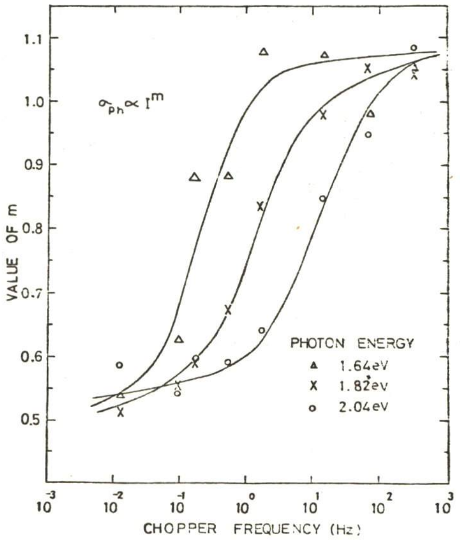

Fig.5 The plot of the value m versus chopping frequencies of the incident light

The photocurrent is composed of a fast decay component (life time in the order of 10^{-3}sec) and very slow decay component (life time in the order of 10 sec). The transient photon energy from fast to slow component region for $As_{0.30}Se_{0.70}$ is about 1.8eV and that of $As_{0.45}Se_{0.55}$ is about 1.5eV, and the energy difference between these two is similar to the shift of photocurrent peak energy with composition change at the chopping frequency of 1/60 Hz.

The dependence of the photoconductivity σ_{ph} on the illuminated light intensity I on the a-As_2Se_3 for various chopping frequencies in the range 400-1/60 Hz is expressed by the formula $\sigma_{ph}=I^m$, and the value of m for each chopping frequency are shown in Fig.(5).

For the exciting photon energy greater than the mobility edge delocalized electrons and holes are generated in the extended states. The probability of the mono-molecular trapping and the recombination with the thermally generated carriers may be proportional to the photo-generated carrier numbers, and the life time of these carriers may be short.

When the irradiated photon energy is smaller than the mobility edge the additional thermal excitation is necessary for the generation of delocalized carriers. The carriers may bi-molecularly recombine at the recombination centers near the Fermi level in the gap.

References

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