Hybridization of 3d states of photodoped Cu in amorphous GeSe₂ by resonant photoemission spectroscopy

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Photoemission spectra of Cu-photodoped a-GeSe$_2$ have been measured at several excitation energies near Cu $3p$ core-excitation threshold in detail. In the spectra, the Cu $3d$ satellite is clearly observed, and from its position it is concluded that the valency of Cu is monovalent. The satellite intensity shows a Fano-type resonance near the Cu $3p$ threshold. The resonance indicates that the Cu $3d$ state mixes with the Se $4p$ state to some degree. These results support a recent structural model in which photodoped Cu makes one covalent and three dative bonds to four surrounding Se atoms in a-GeSe$_2$.

I. INTRODUCTION

Photodoping effect is notable as one of many photoinduced effects in amorphous chalcogenides, because of its application to a high-resolution photoresist in the microfabrication technology of semiconductors.[1] For example, ultraviolet-light irradiation on an evaporated amorphous GeSe$_2$ film (a-GeSe$_2$) coated with a thin layer of Ag metal causes rapid diffusion of Ag into the amorphous film. The diffusion occurs only in the irradiated portion, which, as a result, becomes resistive against chemical etching process. Understanding of the microscopic mechanism of the photodoping is very important not only for developments of photoresist techniques but more widely for solid-state physics, because the photodoping is a unique phenomenon related to both network structures and electronic states in amorphous solids. Previously, we have studied the amorphous structures in a-GeSe$_2$ by Raman and photocrystallization experiments,[2,3] and the electronic states by wide-range reflection and photoemission measurements.[4,5] In the present study, we investigate electronic states around photodopants by means of resonant photoemission experiments.

Recently, local structures around dopant Cu and Ag atoms in amorphous Ge-S, Ge-Se, As-S, and As-Se systems have been investigated by extended x-ray-absorption fine structure (EXAFS) (Refs. 6 and 7) and x-ray scattering.[8-10] The established points are summarized as follows.

(1) Local structure of the photodoped amorphous film is similar to that of the melt-quenched doped glass.

(2) Dopant atoms are surrounded by chalcogen atoms. There are no pronounced correlations of dopant-dopant or dopant-Ge or -As.

(3) Coordination number of dopant is most likely 4.

As for the electronic state of the dopant, the charge state of dopant has been examined by x-ray photoemission (XPS) for photodoped chalcogenide films.[11-13] These authors have compared the chemical shifts of constituent atoms with those in reference materials, for example, Ag₂Se and Cu₂Se, and concluded that the charge state of the dopant is monovalent.

In this paper, photoemission spectra of Cu-photodoped a-GeSe$_2$ film (a-GeSe$_2$:Cu) are measured by use of synchrotron radiation for the clarification of electronic states in the dopant. We observe Cu $3d$ resonant photoemission near the Cu $3p$ core-excitation threshold, to discuss details of bonding between the dopant and the host. Since the resonance behavior is sensitive to the configuration of the $3d$ state, it is confirmed that the dopant is in a monovalent state, and that the Cu $3d$ state is partially mixed with Se $4p$ states.

II. EXPERIMENTAL DETAILS

Synchrotron radiation from SOR-RING, the 0.4-GeV electron-storage ring at the Institute for Solid State Physics of the University of Tokyo, was used through a modified Rowland monochromator as an excitation light from 55 to 90 eV. Photoelectrons were analyzed by a double-stage cylindrical-mirror analyzer in angle-integrated energy-distribution-curve (EDC) mode. Spectral resolution was typically about 0.3 eV. Samples were prepared by an evaporation method in two steps: at first, enough Cu is deposited on a stainless substrate in a preparation chamber, and immediately, a-GeSe$_2$ is evaporated onto the Cu film in the same vacuum. Film thickness of a-GeSe$_2$ was monitored by a standard quartz monitor to be about 100 nm or less. Photodoping of Cu into a-GeSe$_2$ is fully succeeded by the illumination from the evaporation heater. After the evaporation, the sample is immediately transferred into an analyzer chamber in a vacuum less than 2×10^{-10} Torr.

III. RESULTS AND DISCUSSION

A. Photoemission spectra of the Cu 3d state

Valence-band photoemission spectra of a-GeSe$_2$:Cu are shown on the left-hand side of Fig. 1, and for a compar-
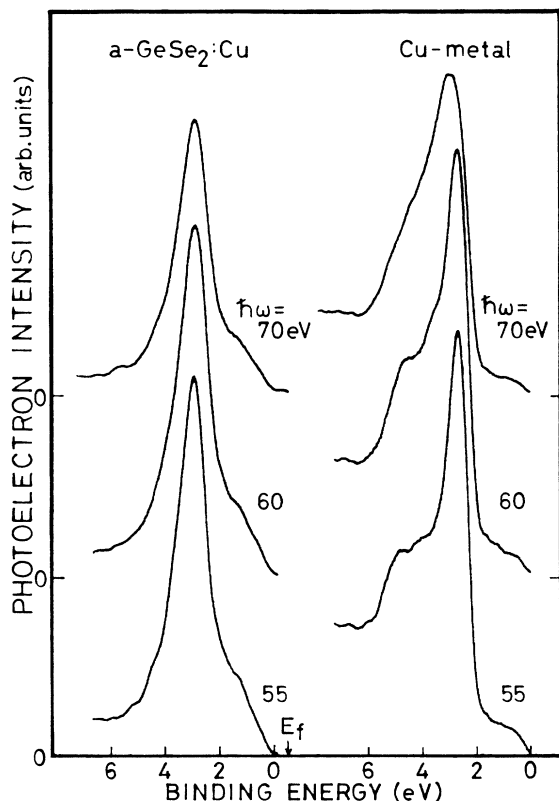

FIG. 1. Comparison between Cu 3d band photoemission spectra before and after the photodoping into a-GeSe$_2$. Energy values in the figure describe the excitation photon energies. Binding energy is measured from the valence-band maximum. The narrow 3d bandwidth of dopant Cu as compared with that of Cu metal suggests that the 3d band is somewhat localized.

ison, spectra of Cu metal film are shown with the same resolution on the right-hand side of the figure. In all the spectra, an intense peak at about 3 eV is remarkable, which is attributed to Cu 3d electrons. As for the line shape of the Cu 3d spectra, however, there are some differences between the spectra of the photodoped and the metallic Cu. In the spectra of the Cu metal on the right-hand side of Fig. 1, the 3d band spreads from 2 to 5 eV, and fine structures appear and change noticeably depending on the excitation energy. For example, the structure at 5 eV is clearly observed in the metallic spectra at 55-eV excitation, but it becomes obscure at 70-eV excitation. On the other hand, in the photodoped spectra on the left-hand side of Fig. 1, the 3d bandwidth is less than half of that of the metal, and no fine structure is resolved even at 55-eV excitation, though one will notice that the line shape is somewhat asymmetric. Excitation-energy dependence of the photodoped Cu 3d band is negligible.

The band structure of Cu metal has been well studied.[14,15] The maximum of the 3d band is located at the X_5 point and the 3d bandwidth of about 3 eV corresponds to X_5-X_3 splitting. The excitation-energy dependence of the metallic spectra in Fig. 1 may be reflecting the joint den-

sity of states in the photoemission process from dispersive 3d bands to higher conduction states. On the other hand, the 3d band in the photodoped spectra has narrow bandwidth, and is almost independent of the excitation photon energy as mentioned above. These observations indicate a localized character of the 3d electrons. It has been concluded by EXAFS experiments that there is no correlation of Cu—Cu bonds in the photodoped state.[6,7] The overlap between the 3d wave functions of the photodoped Cu atoms will be smaller than that in Cu metal, and therefore the 3d band does not have large dispersion such as in the metal. Nevertheless, the 3d state of the photodoped Cu is not the same with the pure atomic state; small hybridization will rise from the bonding to the surrounding Se atoms as discussed later.

B. Photoemission spectra of the valence band

Figure 2 shows the photoemission spectra of a-GeSe$_2$:Cu at several excitation energies from 70 to 90 eV. The assignment of the several peaks in Fig. 2 should first be discussed. The intense peak at the binding energy of about 3 eV is due to the Cu 3d electrons as discussed before, while another intense peak at about 30 eV is due to Ge 3d electrons. From the comparison of these peak intensities, the photodoped amount of Cu is estimated to be
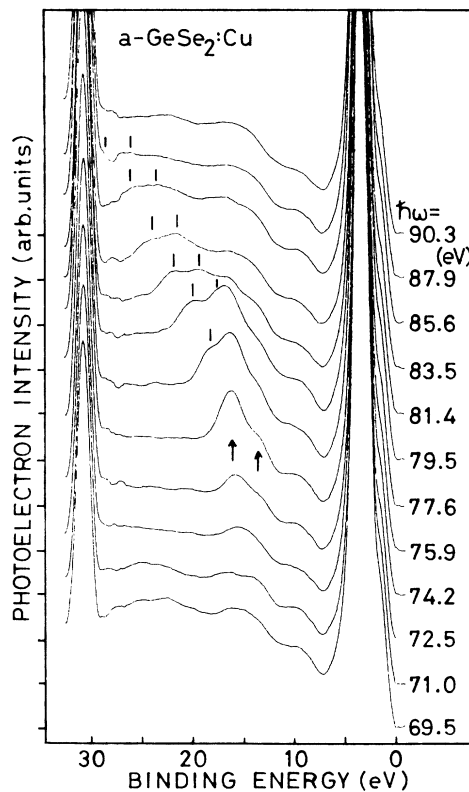

FIG. 2. Resonant photoemission spectra of Cu-photodoped a-GeSe$_2$ near the Cu 3p core-excitation threshold. Energy values in the figure describe the excitation energies. Arrows indicate the Cu 3d satellite peaks at 13.5 and 16.0 eV binding energy. Vertical bars show the positions of Cu $M_{2,3}M_{4,5}M_{4,5}$ sCK lines.

nearly the same order to the concentration of Ge.

Between the two intense peaks, several structures are notable. To assign them, one should compare them with the a-GeSe$_2$ valence-band spectra reported in previous papers.[5,16] In the spectra of a-GeSe$_2$ in Fig. 1 of Ref. 5, there are broad peaks at about 8 and 13 eV, which are due mainly to $4s$ states of Ge and Se, respectively. Three structures due to bonding and lone-pair $4p$ electrons are located shallower than 7 eV. Those structures are expected also in the spectra of a-GeSe$_2$:Cu. In the spectra in Fig. 2, however, shallow p bands are not resolved owing to the overlapping of the intense Cu $3d$ band, except for a small shoulder at the valence-band maximum. As for the s bands, a broad peak at about 9 eV in Fig. 2 is considered to be due to Ge $4s$ band of host a-GeSe$_2$. Excitation-energy dependence of the 9-eV peak is negligible in the region in Fig. 2. The peak at 15 eV in the spectra of 90.3-eV excitation in Fig. 2 will be attributed mainly to the Se $4s$ peak. The spectral shape around this peak, however, changes dramatically near 77-eV excitation, though the Se $4s$ peak is expected to be almost independent of the excitation energy in this region similarly to the Ge $4s$ peak at 9 eV. As clearly seen in the spectra at 75.9 eV excitation, two peaks indicated by arrows at 13.5 and 16.0 eV appear, exceeding the 15 eV peak. These new peaks will be the Cu $3d$ band satellites, which is observed similarly in copper metal and copper compounds.[17,18] We will discuss details of the satellite later.

Weak doublet peak indicated by vertical bars appears in the spectra by the excitation above 77 eV in Fig. 2, and shift linearly with the excitation energy. The linear shift means that photoelectrons have a constant kinetic energy, which is close to the energy difference between Cu $3p$ and $3d$ levels approximately. The doublet is attributed to Cu $M_{2,3}M_{4,5}M_{4,5}$ super-Coster-Kronig (sCK) lines. In the sCK process, a $3p$ core-hole created by the excitation above 77 eV collapses into two $3d$ holes and a kinetic electron. Besides, similar Auger decay of Se $3d$ core-holes is expected. A broad hump at about 25 eV in the spectra by the 69.5 and the 71.0 eV excitations in Fig. 2 will be due to the Se $M_{4,5}VV$ Auger electrons whose resonance has been reported at the Se $3d$ excitation threshold in a-GeSe$_2$.[16]

C. Resonance of the satellite

The peaks at 13.5 and 16.0 eV in Fig. 2 are resonantly enhanced by the excitation around 77 eV. The binding energies of Cu $3p$ levels are 75.07 ($j = \frac{3}{2}$) and 77.23 eV ($j = \frac{1}{2}$) in the metallic state.[19] The $3p$ threshold of the photodoped Cu is expected to be located near 77 eV, and therefore the Cu $3p$ excitation will be responsible for the large enhancement. We will discuss the satellite position first and the enhancement later in detail.

A similar satellite has been observed in the spectra of copper metal and some copper compounds.[17,18] The position of the satellite in the spectra depends mainly on the valency of Cu. In CuO (divalent), for example, satellite peaks appear at the binding energies of 10.5 and 12.9 eV, while in Cu$_2$O (monovalent) they appear at 15.3 eV.[17] In the metal (monovalent), they are located at 11.9 and 14.6
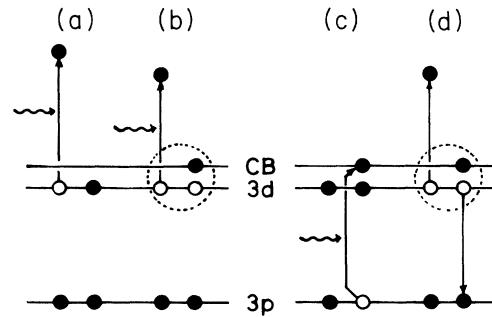

FIG. 3. Schematic diagrams of the transitions related to the satellite. Photoemission processes from the Cu $3d$ state are shown in (a) and (b). In process (b), a trion state indicated by a dotted circle is created through Cu $3d$–Se $4p$ mixing. (c) shows the Cu $3p$ core-excitation process which is followed by a sCK transition (d). Identical final states (b) and (d) are considered to be the origin of the satellite.

eV.[7] The satellite positions of the spectra of Cu dopant photodoped into a-GeSe$_2$ are close to those of monovalent Cu. It will be concluded that the valency of Cu dopant is monovalent. To explain the reason why the satellite position is sensitive to the valency of Cu, we must understand the mechanism of the satellite, which is closely related to the enhancement as discussed below.

A recent theory developed by Igarashi[20] and Nakano[21] for the understanding of the similar resonant photoemission in copper halides is useful in the present case. The outline of the resonant process will be described according to the theory as follows: The configuration of the monovalent state of Cu is represented as $(3d)^{10}$. However, if the $3d$ state of Cu is hybridized with $3p$ states of surrounding Se atoms to some degree, a small amount of $(3d)^9$ (CB) configuration mixes with the $(3d)^{10}$, where $(3d)^9$ refers to one hole in the $3d$ band and (CB) refers to one electron virtually in the conduction band (mainly Se $4p$ antibonding state). When photoemission occurs from such ground states, as the final-state configuration, it is possible to create $(3d)^9 + (PE)$ from $(3d)^{10}$ and $(3d)^8(CB) + (PE)$ from $(3d)^9(CB)$ as schematically shown in Figs. 3(a) and 3(b), respectively, where (PE) is a photoelectron. In process (b), the $(3d)^8(CB)$ state remaining after the photoemission is a three-particle binding state of two holes in the same Cu site and one electron in the conduction state (a "trion" state). Since the photoelectron kinetic energy is reduced by the amount of repulsive energy between the two holes, the trion state is observed as a satellite that is located at higher binding energy (lower kinetic energy) from the $3d$ band in photoemission spectra. Strictly, also the energy of the bound (CB) electron as well as the dielectric screening energy of the host a-GeSe$_2$ should be taken into account, but the most important interaction is the correlation of the two holes.

In another point of view, transition (b) in Fig. 3 is a two-electron-excitation process through Cu $3d$–Se $4p$ mixing, in which the incident photon excites one $3d$ electron to the photoelectron state (PE) and another $3d$ electron to the conduction band (CB) at the same time. The

process $(3d)^{10} \rightarrow (3d)^8(CB)+(PE)$ will be weak and will not depend on the excitation energy so much. At the Cu $3p$ threshold where the resonance occurs, the excitation of the $3p$ state makes the trion state through the following path. First, as shown in Fig. 3(c), the Cu $3p$ electron is excited at the threshold: $(3p)^6(3d)^{10} \rightarrow (3p)^5(3d)^{10}(CB)$, which means one hole in th Cu $3p$ band and one electron in the conduction band, that is, core-exciton state, in the final state. Such a final state, however, decays immediately by the sCK interaction, as is shown in Fig. 2(d), and as a result it becomes $(3p)^6(3d)^8(CB)+(PE)$, a trion state and a photoelectron. Since processes (c) and (d) are so fast that they are regarded as one quantum-mechanical process, the sequence of the $3p$ excitation (c) and decay (d) processes will interfere with the continuum transition (b). Such interference will induce a Fano-type resonance.

Figure 4 shows the satellite intensity versus the excitation energy. Circles show the 16.0-eV satellite intensity, and triangles the 13.5-eV satellite intensity. In Fig. 4, it is shown that there is a small dip at about 72 eV, and the dip is followed by a drastic enhancement that starts from 75 eV. The maximum is located near 79 eV. This behavior is considered to be a Fano-type resonance. From the comparison of the excitation spectra in Fig. 4 with the theoretical line shapes in Fig. 3 of Ref. 21, the hybridization parameter h_0 is to be about 1 eV, which is near that in copper halides.[21]

According to the theory, the 16.0-eV satellite is assigned to ^1G multiplet of two $3d$ holes, and the 13.5-eV

satellite to ^3F multiplet.[20] In the spectra in Fig. 2, it is shown that the ^3F is somewhat broad. The reason will be explained by the fact that degenerate ^3F levels split more widely than ^1G, owing to the anisotropy of the hybridization with the surrounding atoms.[20]

In the above explanation, the following two points are important: the monovalent valency of Cu and the mixing of the Cu $3d$ state with the Se $4p$ state. If the valency of Cu is divalent, the $3d$ state is not filled in the ground state: that is, $(3p)^6(3d)^9$ is the initial state of the transition. Accordingly, the satellite state will be $(3p)^6(3d)^8$, a two-hole bound state. The Cu $3p$ excitation and decay processes will be described as $(3p)^6(3d)^9 \rightarrow (3p)^5(3d)^{10} \rightarrow (3p)^6(3d)^8+(PE)$ similar to the trion creation in Figs. 3(c) and 3(d), except for the absence of the (CB) electron. The absence of the (CB) creation energy will increase the photoelectron energy in the two-hole bound-state process in comparison with the trion process, and therefore the satellite of divalent Cu will appear in shallower binding energy than that of monovalent Cu in the photoemission spectra. Thus the reason why the satellite position is sensitive to the valency will be explained.

As for the mixing of the Cu $3d$ state with the Se $4p$ state, the necessity of such mixing for the explanation of the Fano resonance will support a recent model of the local bonding structure in a-GeSe$_2$:Ag. In the model, the bonding of the photodopant Ag to the host a-GeSe$_2$ consists of one Ag—Se covalent bond and three Ag—Se dative bonds.[8,22] Also in the present case, dopant Cu is expected to make similar bonds to the four surrounding Se atoms. Such bonding character will imply the Cu $3d$–Se $4p$ mixing as well as some covalency of Cu.

IV. SUMMARY

In summary, we measured photoemission spectra of a-GeSe$_2$:Cu at several excitation energies, and the Cu $3d$ satellite is clearly observed in the spectra near the Cu $3p$ core-excitation threshold. The following results are obtained. (1) The narrow $3d$ bandwidth of dopant Cu indicates that the $3d$ band will be somewhat localized, since Cu atoms are separated from each other in a-GeSe$_2$. (2) From the satellite position, it is concluded that the valency of Cu is monovalent. (3) The Fano-type behavior of the resonance indicates that the Cu $3d$ state mixes to the Se $4p$ state to some degree. These results support the structural model in which photodoped Cu makes one covalent and three dative bonds to the surrounding four Se atoms in a-GeSe$_2$.
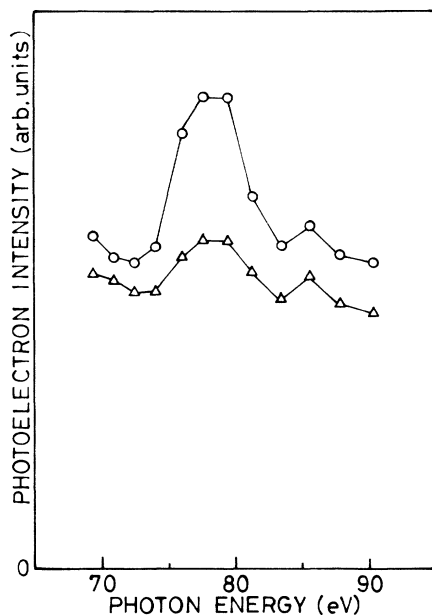

FIG. 4. Photoelectron intensities as a function of the excitation energies. Circles shows the intensity at the binding energy of 16.0 eV and triangles at 13.5 eV, whose positions are pointed by the arrows in Fig. 2. There is a small dip at about 72-eV excitation, which is followed by a drastic enhancement that starts from 75 eV, and the maximum is at nearly 79 eV. The enhancement will be due to the interference between the two final states (b) and (d) in Fig. 3.

ACKNOWLEDGMENTS

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