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A soft-x-ray core absorption study on the electronic states in Ag- and Cu-photodissolved amorphous GeSe$_2$ using synchrotron radiation

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Abstract. Conduction-band electronic states of amorphous (a-)GeSe$_2$ photodissolved by Ag and Cu metals have been examined by means of soft-x-ray core absorption spectroscopy. Both the Ge and the Se 2p$_{3/2}$ spectra of the photodoped samples are similar to the corresponding spectra of undoped a-GeSe$_2$ in contrast with the Se 3d core absorption spectra, which suggests that the prominent change in the conduction band density of states by Ag or Cu photodoping is caused through the Se 4p contributions. The Cu 2p$_{3/2}$ core absorption spectrum has a clear peak which would originate from the Cu–Se covalent bonds. These results do not contradict the structural model described by Fischer-Colbrie *et al*.

1. Introduction

Photodissolution or photodoping is one of the most interesting phenomena of photochemical reaction for amorphous materials. This phenomenon was discovered by Kostyshin *et al* [1] and, since then, much attention has been devoted to the atomic structure and electronic properties of photodissolved amorphous materials [2].

Local structures around dopant Ag atoms in amorphous (a-)GeSe$_2$ have been investigated by x-ray scattering [3], anomalous x-ray scattering [4] and extended x-ray absorption fine-structure (EXAFS) [4, 5] measurements. The established points are as follows.

(i) Dopant atoms are surrounded by chalcogen atoms. There are no pronounced dopant–dopant or dopant–Ge correlations.

(ii) The coordination number of the dopant is most probably four.

The electronic states of the dopant have been examined by x-ray photoemission spectroscopy for photodoped a-Ge–Se mixtures by Zembutsu [6]. He has compared the chemical shifts of the Ge, Se and Ag 3d levels in the photodoped amorphous materials with those of the reference crystals, such as Ag$_2$Se, and reported that the dopant is positively charged. Ultraviolet photoemission spectroscopy measurements were also performed for Ag- and Cu-photodoped a-GeSe$_2$ using synchrotron radiation by Inoue *et al* [7, 8], and it was found that the network in undoped a-GeSe$_2$ is partially preserved by the photodoping of metals, although the spectral features become rather blurred.

The unoccupied electronic states in Ag-photodoped a-GeSe$_2$ have been studied by the optical reflectance measurements in the wide photon energy range from 1 to 36 eV [7]. The

spectral changes revealed that new Ag–Se bonds are induced by the photodissolution, but the role of exciton effects as well as matrix elements were not sufficiently clear to analyse them further. Therefore it was very difficult to deduce the unoccupied density of states (DOS) from this optical method. Recently we have measured the inverse-photoemission spectra of Ag- and Cu-photodoped a-GeSe$_2$ [9] in order to obtain directly the conduction band DOS. The conduction band of a-GeSe$_2$ is strongly affected by the photodoping of Ag and Cu metals; the prominent two peaks in the unoccupied DOS of a-GeSe$_2$ smear out by the photodoping of Ag or Cu metals.

The core absorption spectroscopy also provides information on the conduction band DOS, especially including the selection rule of angular momentum on the optical transitions. By comparing core absorption spectra with inverse-photoemission spectra, we can extract the contribution of each orbital component from the DOS. In this paper we report the results of core absorption measurements for photodoped a-GeSe$_2$ in the soft-x-ray energy range and discuss the effect of photodoping on such partial DOSs.
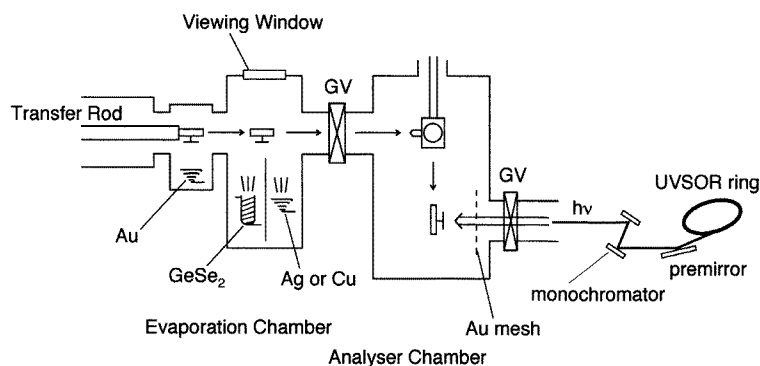

Figure 1.   Schematic view of the apparatus for the present soft-x-ray core absorption measurement. GV: gate value.

2. Experimental details

The Ge, Se and Cu $2p_{3/2}$ core absorption spectra for the Ag- and Cu-photodoped a-GeSe$_2$ were measured at the soft-x-ray beamline (BL-1A) of UVSOR at the Institute for Molecular Science. The diagram of the apparatus is schematically shown in figure 1. The storage ring was operated under conditions of an electron beam energy of 750 MeV and a stored current of 200–100 mA. A Pt-coated, elliptically bent cylindrical pre-mirror and beryl-double-crystal monochromator were used to provide soft x-rays from 830 to 1800 eV with an energy resolution $E/\Delta E$ of about 1500 [10]. The absorption spectra were measured in the total electron yield mode at room temperature. The intensity of the incident beam was monitored by the photoelectric current of an Au mesh placed in front of the sample and used for normalization.

The core absorption measurements were carried out using two ultrahigh-vacuum chambers; a sample evaporation chamber and an analyser chamber, operating under base pressures of 1.0×10^{-9} and 5.0×10^{-10} Torr, respectively. The undoped sample film of a-GeSe$_2$ with a thickness of 1000 Å was evaporated onto a clean Au substrate in the evaporation chamber. The photodoped samples were prepared by evaporating Ag or Cu metals onto the fresh a-GeSe$_2$ films. The concentrations of the dopant atoms were

determined by measuring the thickness of the corresponding metal films. Each photodoped sample was fully photodissolved by strong light emitted from the evaporation source of Ag or Cu and, in addition, from a 1000 W tungsten lamp through a viewing window of the chamber for more than 10 min. For the reference for the Cu $2p_{3/2}$ spectrum, a polycrystalline Cu film was prepared by evaporation onto a fresh Au substrate.

We used a commercial sample with a purity of 99.9999% as a starting material for $GeSe_2$. The purities of the Ag, Cu and Au sources were 99.99% each. The sample thickness was measured by means of deviations of the frequency of a quartz oscillator located near the sample position. The sample was transferred into the analyser chamber *in situ* under ultrahigh vacuum below 5.0×10^{-10} Torr.
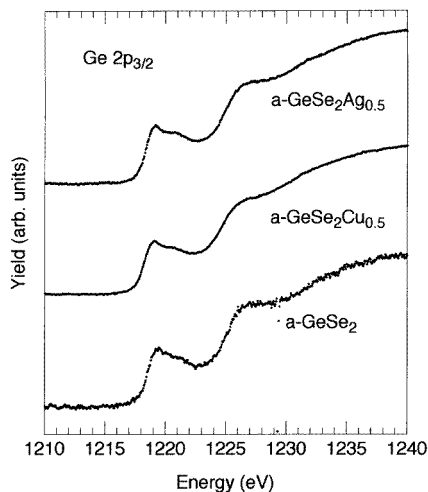

Figure 2. The Ge $2p_{3/2}$ core absorption spectra of photodoped a-GeSe₂Ag₀.₅, a-GeSe₂Cu₀.₅ and undoped a-GeSe₂.

3. Results

Figure 2 shows the Ge $2p_{3/2}$ core absorption spectra of photodoped a-GeSe₂Ag₀.₅, a-GeSe₂Cu₀.₅ and undoped a-GeSe₂. In the spectrum of undoped a-GeSe₂, a pronounced peak at around 1219 eV appears following a sudden threshold at around 1218 eV. Then, the spectrum has a minimum at around 1223 eV, and a shoulder at around 1226 eV. The spectrum is in good agreement with that measured in the laboratory by Belin *et al* [11], except that the first peak in the present spectrum is sharper than theirs. As clearly seen in the figure, the spectra of both the Cu- and the Ag-photodoped samples are very similar to that of undoped a-GeSe₂. The present result is very interesting because the Ge electronic states with s and d characters in the conduction bands are not affected by such heavy doping of the Ag or Cu metal.

Figure 3 shows the Se $2p_{3/2}$ core absorption spectra of photodoped a-GeSe₂Ag₀.₅, a-GeSe₂Cu₀.₅ and undoped a-GeSe₂. In the spectrum of undoped a-GeSe₂, a gradual increase appears above a threshold at around 1433 eV. Then a marked increase starts at around 1439 eV, a shoulder appears at around 1441 eV, and the yield saturates at around 1450 eV. Although the spectrum of a-GeSe₂ has not been measured yet, the spectra of a-Ge–Se mixtures with concentrations from pure a-Se to a-Ge₂Se show similar behaviours [11]. In
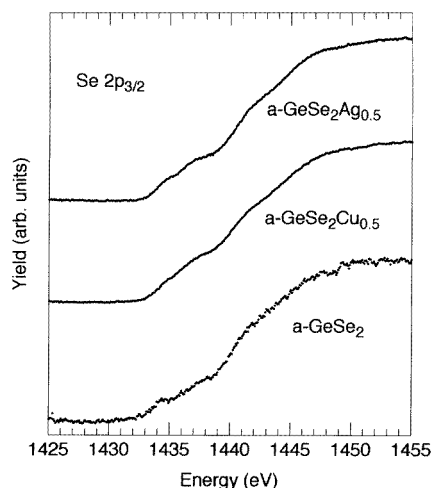
Figure 3. The Se $2p_{3/2}$ core absorption]spectra of photodoped a-GeSe$_2$Ag$_{0.5}$, a-GeSe$_2$Cu$_{0.5}$ and undoped a-GeSe$_2$.

this Se $2p_{3/2}$ spectrum, there is such a small doping effect that the yield at 1433–1439 eV becomes slightly large for each photodoped sample.
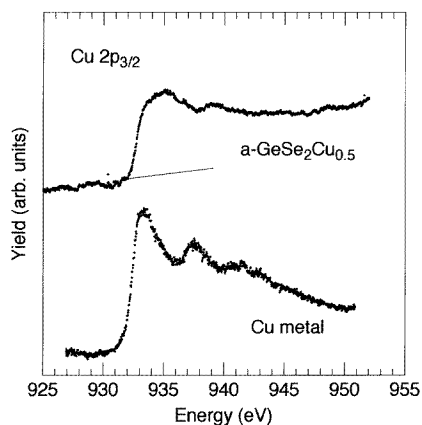

Figure 4. The Cu $2p_{3/2}$ core absorption spectra of photodoped a-GeSe$_2$Cu$_{0.5}$ and pure Cu metal.

Figure 4 shows the Cu $2p_{3/2}$ core absorption spectra of photodoped a-GeSe$_2$Cu$_{0.5}$ and pure Cu metal. The spectrum for a-GeSe$_2$Cu$_{0.5}$ has an edge at around 932 eV, and a broad peak at around 935 eV. Then the yield gradually decreases up to the Cu $2p_{1/2}$ edge at around 951 eV. On the other hand, the spectrum for pure Cu is completely different; the edge is about 0.5 eV lower and distinct peaks at 932, 937 and 941 eV appear. The difference in the threshold is induced by the formation of the band gap rather than the shift of the Cu $2p_{3/2}$ core level. As shown in textbooks [12], the conduction band of Cu near the Fermi energy is composed of 3d, 4s and 4p electrons, which become completely mixed each another. Mehta-Ajmani *et al* [13] calculated the energy bands for Cu and obtained both the total and the partial DOS where each partial DOS in the conduction bands has almost the same shape

as the total DOS. According to their results, the 932 eV peak in the $2p_{3/2}$ core spectrum indicates the unoccupied level near the X symmetry point in the Brillouin zone, and the 937 eV peak the level near the L point.
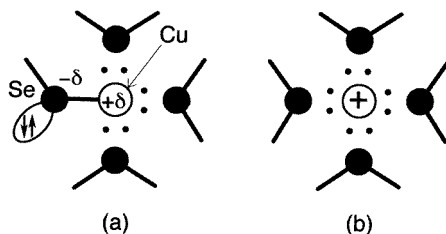

Figure 5. The schematic view of the local structure around the Cu atoms. The solid lines between atoms, two of the dots and two arrows in the oval attached to the Se atom indicate covalent bonds, dative bonds and the non-bonding lone-pair electrons, respectively.

4. Discussion

In 1978, Kastner [14] proposed some local configuration models for doped chalcogenide amorphous semiconductors around dopant atoms, such as Cu. Fischer-Colbrie *et al* [4] thought one of them preferable for Ag-photodoped a-GeSe₂ based on the results of their anomalous x-ray scattering and EXAFS measurements [4]. The model chosen was that photodoped dopant (Ag) atoms have one covalent and three dative bonds with four surrounding Se atoms in a-GeSe₂. The schematic view of the local structure around the dopant atoms in this model (model (a)) is shown in figure 5(a). Solid lines between atoms, two of the dots and two arrows in the oval attached to the Se atom indicate covalent bonds, dative bonds and non-bonding lone-pair electrons, respectively. A photodoped dopant atom breaks a Ge–Se bond in a-GeSe₂ and makes a covalent bond only to an Se atom using an electron in one of its sp³ hybrid orbitals. Because of the difference in the electron affinity, the dopant–Se bond has a partially ionic character ($\pm\delta$). The remaining three orbitals are used for the vessel to make dative bonds using the lone-pair electrons of the other three Se atoms. Although the model seemed to be established on their excellent structural experiments, it has no background of the electronic structure of the photodoped a-GeSe₂. Figure 5(b) exhibits another model (model (b)) of the local structure [14] which shows a similar atomic configuration. The dopant atom is fully ionized, and the correlations with four Se atoms are only dative bonds. The most different point between the models is the existence of Ge–Ge bonds in model (a). These homopolar bonds are induced by the Ge–Se bond breaks and satisfy the $8 - N$ rule around the Ge atoms.

For the Cu-doped sample, in particular, Inoue *et al* [8] obtained the Cu 3d partial DOS using the resonant photoemission technique and found that the dopant is in a positive state and that the Cu 3d states are partially mixed with Se 4p states in the valence band. Their results seem to have no inconsistency with structural model (a).

Figure 6 shows the previous results of the inverse-photoemission spectra for photodissolved samples as a function of the energy above the Fermi level E_F, together with those of undoped a-Ge–Se mixtures [9]. For undoped a-GeSe₂, the spectrum has two distinct peaks at 2.4 and 5.0 eV and a shoulder at around 8.5 eV. Since the initial state of this soft-x-ray absorption is the core level with p character, the final unoccupied states have s or d character near the bottom of the conduction bands because of the selection rule
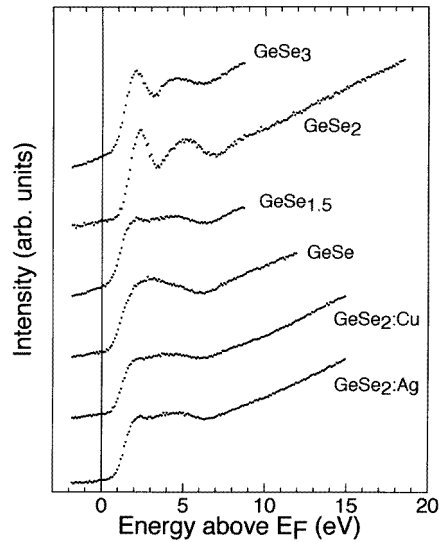
Figure 6. Inverse-photoemission spectra of Ag- and Cu-photodissolved a-GeSe$_2$ as a function of energy above E_F, together with those of undoped a-Ge–Se mixtures, reported in the previous paper [9].

on the optical transition. By adjusting the threshold of this inverse-photoemission spectrum with those of the Ge and Se $2p_{3/2}$ spectra shown in figures 2 and 3, respectively, the first sharp peak at 2.4 eV in the inverse-photoemission spectrum corresponds to the first peak of the Ge $2p_{3/2}$ core absorption spectrum at 1219 eV, the shoulder at 8.5 eV in the inverse-photoemission spectra, both the shoulders appearing in the Ge $2p_{3/2}$ core absorption spectrum at 1226 eV and the Se $2p_{3/2}$ core absorption spectrum at 1441 eV. The second peak in the inverse-photoemission spectrum at 5.0 eV, however, corresponds to no peak in each $2p_{3/2}$ core absorption spectrum, but to the dip between the first and second peaks. On the other hand, the Ge 3d core absorption spectrum [7] has a broad peak at the corresponding position of the second peak in the inverse-photoemission spectrum, and the Se 3d core absorption spectrum [7] has a prominent peak in the energy region around the first peak and a weak peak around the second peak in the inverse-photoemission spectrum. From such remarkable contrasts, one can easily speculate that the first peak of the conduction band DOS at 2.4 eV is mainly composed of the Ge 4s and Se 4p orbitals, the second peak at 5.0 eV of the Ge 4p and Se 4p orbitals, and the shoulder around 8.5 eV of both the Ge and the Se 4d and/or 5s orbitals [15]. In addition, a band calculation by Pollard [16] strongly supported our speculation.

As clearly seen in figure 6, the conduction band states of a-GeSe$_2$ are strongly affected by the photodoping of Ag and Cu metals; the prominent two peaks at 2.4 and 5.0 eV in the unoccupied DOS of a-GeSe$_2$ smear out by the photodoping of Ag or Cu metals. In addition, the spectra of Ag- and Cu-photodoped a-GeSe$_2$ are quite similar to each other. By comparing the inverse-photoemission spectra of the photodoped sample with those of the undoped a-Ge–Se mixtures, it can be seen that the characteristic shape of the spectra observed in the photodissolved a-GeSe$_2$ samples is quite similar to that of a rather Ge-rich mixture of a-GeSe$_{1.5}$ containing many Ge–Ge bonds [17, 18]. This result strongly supports structural model (a) shown in figure 5(a).

As mentioned above, it was established that the final states of the absorption for undoped

a-GeSe$_2$ in the energy range from 1218 to 1223 eV are mainly the Ge 4s states near the bottom of the conduction band, and those beyond 1223 eV mainly the Ge 4d and/or 5s states [15]. According to the structural model (a), the structural change around the Ge atoms by the photodoping is that many Ge–Ge bonds are induced to satisfy the $8 - N$ rule. Consequently, it can be supposed that the photodoping affects the electronic states of the Ge atoms a little.

The final states of the absorption for undoped a-GeSe$_2$ in the energy range from 1433 to 1439 eV in the Se 2p$_{3/2}$ spectrum are mainly the Se 4s states near the bottom of the conduction band, and those beyond 1439 eV are mainly the Se 4d and/or 5s states [15]. According to structural model (a), the local configuration around the Se atoms changes; some of the partners of the covalent bonds alter from Ge to Cu atoms, and then charge transfer occurs. Our experimental results revealed that the Se 4s partial DOS in the conduction bands changes a little by the photodoping. This would be induced by the bond partners from Ge to Cu atoms around Se atoms, and by charge transfer. On the other hand, the Se 3d core absorption spectra are strongly affected by the photodoping of Ag metal; the first prominent peak becomes very blurred [7]. Therefore, the prominent change in the conduction band DOS by Ag or Cu photodoping is caused through the Se 4p contributions.

The energy region of the broad peak around 935 eV in the Cu 2p$_{3/2}$ spectrum corresponds to the dip between the first and second peak in the inverse-photoemission spectrum for undoped a-GeSe$_2$. According to structural model (a), some of Cu 4s electrons would become mixed into the conduction bands because of the formation of Cu–Se covalent bonds using the sp^3 hybrid orbitals of Cu. The peak measured in the Cu 2p$_{3/2}$ core spectrum would originate from the antibonding states of the Cu–Se covalent bonds. It is easily supposed that the blurring of the conduction band DOS with the photodoping would occur partially by the formation of Cu–Se antibonding states, in addition to the newly induced Ge–Ge antibonding states speculated in the previous paper [9]. In the case of model (b) in figure 5, however, the assignment of the peak at around 935 eV is indefinable.

5. Summary

The conduction band electronic states of a-GeSe$_2$ photodissolved by Ag and Cu metals has been examined by means of soft-x-ray core absorption spectroscopy. Both the Ge and the Se 2p$_{3/2}$ spectra of the photodoped samples are similar to the corresponding spectra of undoped a-GeSe$_2$ in contrast with the Se 3d core absorption spectra, which suggests that the prominent change in the conduction band DOS by Ag or Cu photodoping observed in the inverse-photoemission spectra [9] is caused through the Se 4p contributions. The Cu 2p$_{3/2}$ core absorption spectrum has a clear peak which would originate from the Cu–Se covalent bonds. The results obtained do not contradict the structural model described by Fischer-Colbrie *et al* [4].

Acknowledgments

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