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LETTER TO THE EDITOR

An inverse-photo-emission study on the photo-dissolution of Ag and Cu metals in amorphous GeSe₂

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Abstract. The conduction-band density of states of amorphous (a-) GeSe₂ photo-dissolved by Ag and Cu metals has been examined by means of inverse-photo-emission spectroscopy (IPES). The characteristic feature of the IPES spectrum of a-GeSe₂ rapidly smears out with the photo-dissolution of Ag or Cu metal, and each spectrum of the fully photo-doped samples is quite similar to that of a-GeSe_{1.5}. This result is consistent with a structural model in which the dopant atoms are surrounded by four Se atoms and many Ge-Ge bonds are induced by photo-dissolution. We also measured the change of the IPES spectra in the process of Ag photo-doping.

Photo-dissolution or photo-doping is one of the most interesting phenomena of photo-chemical 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 photo-dissolved amorphous materials [2].

Local structures around dopant Ag atoms in amorphous (a-) GeSe₂ have been investigated by x-ray scattering [3,4] and extended x-ray-absorption fine-structure [4,5] measurements. The established points are as follows. (i) The local structure of the photo-dissolved amorphous film is similar to that of the melt-quenched doped glass. (ii) Dopant atoms are surrounded by chalcogen atoms. There are no pronounced correlations of dopant-dopant or dopant-Ge. (iii) The coordination number of the dopant is most likely four.

The electronic states of the dopant have been examined by x-ray photo-electron spectroscopy for photo-doped a-Ge-Se mixtures [6]. The present author has compared the chemical shifts of the Ge, Se and Ag 3d levels in the photo-doped amorphous materials with those of reference crystals, such as Ag₂Se, and reported that the dopant is monovalent. Ultraviolet photo-electron spectroscopy (UPS) measurements were also performed for Ag- and Cu-photo-doped a-GeSe₂ using synchrotron radiation [7,8], and it was found that the network in pure a-GeSe₂ is partially preserved by the photo-doping of metals, though the spectral features become rather blurred. In particular, for the Cu-doped sample, they obtained the Cu 3d partial density of states (DOS) using the resonance photo-emission technique, and found that the dopant is in a monovalent state, and that the Cu 3d states are partially mixed with Se 4p states. Their results seem to have no inconsistency with a structural model described by Kastner [9] and Fischer-Colbrie *et al* [4] in which photo-doped Cu makes one covalent and three dative bonds with four surrounding Se atoms in a-GeSe₂, and many Ge-Ge bonds are induced.

The unoccupied electronic states in Ag-photo-doped a-GeSe₂ have been studied by Ge and Se 3d core-absorption measurements [7]. The spectra, however, only become broadened and seem to give no distinct information on the photo-doping. Reflectance measurements [7] were also performed in the wide photon-energy range from 1 to 36 eV. The spectral changes revealed that new Ag–Se bonds are induced by the photo-dissolution, but the roles of exciton effects as well as matrix elements were not sufficiently clear to analyse them further. Consequently, it was very difficult to deduce the unoccupied DOS from these two optical methods. On the other hand, inverse-photo-emission spectroscopy (IPES) is a powerful method to obtain directly the conduction-band DOS. We report the final results of IPES measurements for the Ag- and Cu-photo-dissolved a-GeSe₂ in the energy range up to 14.5 eV above the Fermi energy, E_F . In addition, we present the change of the IPES spectra in the process of the photo-dissolution of Ag, and discuss the progress of the photo-doping phenomenon appearing in the IPES spectra.

The IPES measurements were performed using two ultra-high-vacuum chambers: a sample preparation one and an analyser one, operating under base pressures of 4.0×10^{-10} and 7.0×10^{-11} Torr, respectively. A monoenergetic electron beam from an electron gun of Erdman–Zipf type with a BaO cathode was focused onto the sample. Light emitted from the sample was focused by an Al reflection mirror and detected using a band-pass photon detector of our own design [10]. The full width at half maximum of the detector was 0.47 eV, centred at 9.43 eV. The overall energy resolution of the spectrometer was 0.56 eV [11]. The energy calibration of the spectrometer was experimentally performed using the spectrum of the polycrystalline Au film.

The a-GeSe₂ film with a thickness of 40 Å was prepared *in situ* by evaporating a source material onto a clean surface of an Au substrate, and then an Ag or Cu film was evaporated on it (Ag or Cu/a-GeSe₂(40 Å)) under about 1.5×10^{-9} Torr in the preparation chamber. The sample was fully dissolved by strong light emitted from the evaporation source of Ag or Cu. Another amorphous film was prepared by evaporating a source material onto a fresh Ag or Cu film with a thickness of 500 Å evaporated onto a clean Au substrate (a-GeSe₂/Ag or Cu(500 Å)). In this case, noticeable photo-dissolution did not occur because a-GeSe₂ could be evaporated at relatively low temperatures. The gradual photo-dissolution was induced by weak light from a heater in the electron gun during the IPES measurements, which allowed us to observe a gradual change of the spectra on photo-doping. It took approximately 6 min for one cycle of the IPES measurement. In order to obtain well converged spectra, it was necessary to average the data of 20–50 cycles. The details of the experimental procedure have been described in our previous paper [12].

We used a commercial sample with purity of 99.9999% as a starting material for GeSe₂. The purity of the Ag, Cu and Au sources was 99.99% each. The sample thickness was measured by means of deviations of the frequency of a quartz oscillator located near the sample position, using the data of the density of a-GeSe₂ measured by Azoulay *et al* [13]. The sample was transferred into the analyser chamber *in situ* under the ultra-high vacuum below 2.0×10^{-10} Torr.

Figure 1 shows the IPES spectra of Ag/a-GeSe₂(40 Å) as a function of energy above E_F . The samples were fully photo-dissolved during the evaporation of Ag. The measurements were carried out in the energy range up to 14.5 eV above E_F . The thicknesses of Ag films were varied from 1.3 to 500 Å and are shown at the right-hand side of each spectrum. The spectrum of pure a-GeSe₂ is also shown at the bottom of figure 1, and is in good agreement with our previous data [12]. With increasing thickness of the Ag film, the characteristic feature of the spectrum for a-GeSe₂ changes rapidly; the heights of the first peak at 2.1 eV and the second one at 4.7 eV decrease. At about 6 Å, these peaks and the dip around

3.3 eV almost disappear, whereas the dip around 7 eV just remains. The spectra of Ag/a-GeSe₂(40 Å) with Ag thicknesses from 6 to 40 Å are all similar. The spectrum of 60 Å in Ag thickness, however, has a weak signal near E_F , and then the signal grows with increasing Ag thickness. Therefore, it is estimated that the saturated thickness of Ag photo-doping into a-GeSe₂ 40 Å in thickness is about 50 Å. This molar ratio of Ag to GeSe₂, 6.6, is much larger than that from the photo-emission measurement, 0.5 [7]. The spectrum for the Ag coverage of 500 Å suggests that the surface region of this sample is almost Ag, since the spectral shape is very close to that for a pure film shown in figure 3 later.

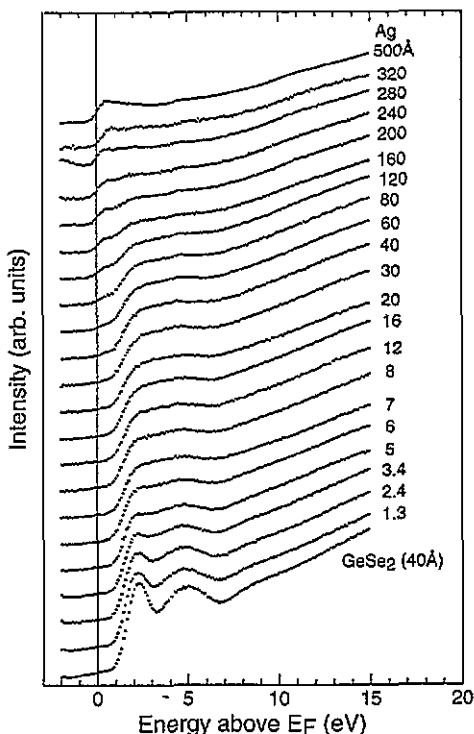


Figure 1. IPES spectra of fully photo-dissolved Ag/a-GeSe₂ in the energy range up to 14.5 eV above E_F . The thicknesses of Ag on the a-GeSe₂ film (40 Å) are shown at the right-hand side of each spectrum. The spectrum of pure a-GeSe₂ is also shown at the bottom of the figure.

Figure 2 presents the spectra of Cu/a-GeSe₂(40 Å). The thicknesses of the Cu films were from 2 to 720 Å and are shown at the right-hand side of each spectrum. With increasing thickness of Cu film, the characteristic feature of the spectrum for a-GeSe₂ changes rapidly, and the process of the change is quite similar to the Ag photo-doping case. At about 6 Å, the 2.1 and 4.7 eV peaks and the 3.3 eV dip almost disappear, while the 7 eV dip just remains. The spectra of Cu/a-GeSe₂ with Cu thicknesses from 6 to 40 Å are all similar. The spectrum for 80 Å Cu thickness, however, suddenly changes, and is similar to that for pure Cu, which is shown in figure 4 later. Therefore, it is supposed that the saturated thickness of Cu photo-doping into a-GeSe₂ 40 Å in thickness can also be evaluated to about 50 Å.

Figure 3 shows the spectra of a-GeSe₂/Ag(500 Å). The samples were fully irradiated by light from a W lamp, which was introduced into the sample preparation chamber through a viewing window. The thicknesses of a-GeSe₂ on Ag are from 5 to 2500 Å and are shown at

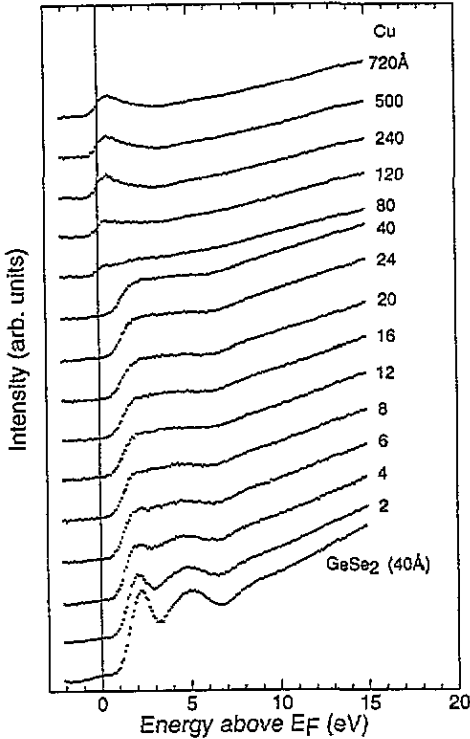


Figure 2. IPES spectra of fully photo-dissolved Cu/a-GeSe₂. The thicknesses of Cu on the a-GeSe₂ film (40 Å) are shown at the right-hand side of each spectrum. The spectrum of pure a-GeSe₂ is also shown at the bottom of the figure.

the right-hand side of each spectrum. The spectrum of the fresh Ag film is also presented in figure 3. The spectra of a-GeSe₂/Ag(500 Å) with a-GeSe₂ thicknesses less than 16 Å have weak signals around E_F . Since the spectra of a-GeSe₂/Ag(500 Å) with thicknesses from 31 to 500 Å are all similar, these spectra are regarded as those for the fully photo-dissolved sample. To represent these spectra, we use the data for 100 Å thickness of a-GeSe₂ for discussions below. The spectra of a-GeSe₂/Ag(500 Å) with a-GeSe₂ thicknesses more than 1500 Å, however, change their shapes. The spectrum of a-GeSe₂/Ag(500 Å) with an a-GeSe₂ thickness of 2500 Å closely resembles that for Ag/a-GeSe₂(40 Å) with 5 Å Ag thickness shown in figure 1, which suggests that the photo-dissolution reaches up to the surface region.

Figure 4 exhibits the spectra of fully photo-irradiated a-GeSe₂/Cu(500 Å). The thicknesses of a-GeSe₂ are from 1 to 3000 Å and are shown at the right-hand side of each spectrum. The spectrum of the fresh Cu film is also presented in figure 4. The spectra of a-GeSe₂/Cu(500 Å) with GeSe₂ thicknesses less than 10 Å have weak signals around E_F . Since the spectra with Cu thickness from 20 to 1000 Å are all similar, these spectra are regarded as that for the fully photo-dissolved a-GeSe₂. To represent these spectra, we use the data for 100 Å thickness of a-GeSe₂ for discussions below. With increasing a-GeSe₂ thickness, the spectra change in the same manner as those for a-GeSe₂/Ag(500 Å).

Figure 5 shows the spectra of fully photo-doped a-GeSe₂/Ag(500 Å) and a-GeSe₂/Cu(500 Å). We also present the IPES spectra of some undoped a-Ge-Se mixtures in the figure, which have been previously reported [12] except that of a-GeSe [14]. As clearly seen in the figure, the conduction-band states of a-GeSe₂ are strongly affected by

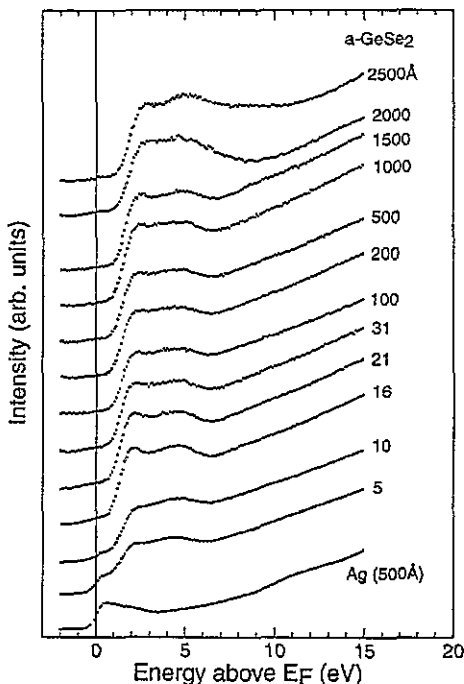


Figure 3. IPES spectra of fully photo-dissolved a-GeSe₂/Ag. The thicknesses of a-GeSe₂ on Ag(500 Å) are shown at the right-hand side of each spectrum. The spectrum of the fresh Ag film is also presented at the bottom of the figure.

the photo-doping of Ag and Cu metals. In addition, the spectra of Ag- and Cu-photo-doped a-GeSe₂ are quite similar to each other, in contrast to the UPS spectra [7, 8]. The most plausible speculation to explain these results is that the contributions of the dopant metals to the conduction-band states are small. By comparing the photo-doped spectra with those of the undoped a-Ge-Se mixtures, it is noticed that the characteristic shape of the spectra observed in the photo-dissolved a-GeSe₂ samples is quite similar to that of a rather Ge-rich mixture of a-GeSe_{1.5} containing many Ge-Ge bonds [15]. This result strongly supports the structural model proposed by Fischer-Colbrie *et al* [4], in which many Ge-Ge bonds are induced by photo-dissolution. The UPS measurements for Ag- [7] and Cu- [8] photo-doped a-GeSe₂ revealed that the Ag 4d or Cu 3d electrons are fairly localized at the valence band. According to the structural model [4], some of the Ag 5s (Cu 4s) states would become mixed into the conduction bands. In order to clarify the local structure and electronic states of the dopant atoms in a-GeSe₂ further, it is important to know the contribution of the dopant atoms to the conduction-band DOS. For this purpose, it is useful to compare the IPES spectra with the core-absorption spectra [12, 16]. Ag (Cu) core-absorption measurements for the photo-dissolved a-GeSe₂ are now in progress.

Finally, we present the change of IPES spectra in the process of photo-doping. Figure 6 shows the change of the spectra of a-GeSe₂(500 Å)/Ag(500 Å) with irradiation time of light emitted from the heater of the electron gun in the analyser chamber. The averaged irradiation time is shown at the right-hand side of each spectrum. Although the data points are rather scattered because of the limited data accumulation time, the feature of the spectral changes is clearly observed. The spectrum at 6 min is similar to that of undoped a-GeSe₂ shown in figure 1, but a slight smearing occurs, especially around the first peak and dip. With increasing irradiation time, the first peak rapidly damps, and then the structures in

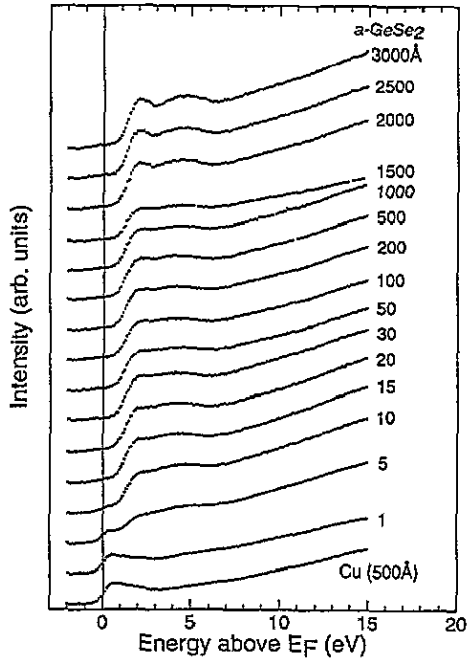


Figure 4. IPES spectra of fully photo-dissolved a-GeSe₂/Cu. The thicknesses of a-GeSe₂ on Cu(500 Å) are shown at the right-hand side of each spectrum. The spectrum of the fresh Cu film is also presented at the bottom of the figure.

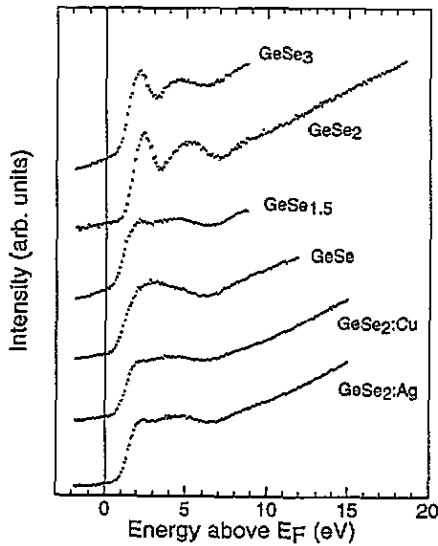


Figure 5. IPES spectra of fully photo-dissolved a-GeSe₂/Ag and a-GeSe₂/Cu, together with those of undoped a-Ge-Se mixtures.

the energy range up to the second peak smear out. The shift of the energy position of the conduction-band minimum is not clearly observed within the accuracy of the present

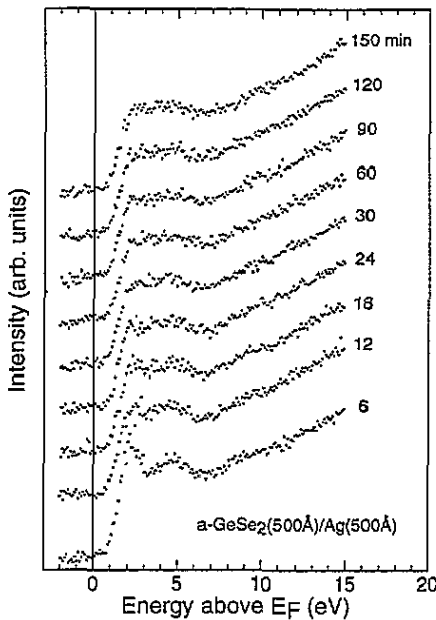


Figure 6. The change of the IPES spectra of a-GeSe₂(500 Å)/Ag(500 Å) with irradiation time of light emitted from the heater in the electron gun. The averaged irradiation times are shown at the right-hand side of each spectrum.

measurements. The feature of the spectral changes is essentially the same as that of the fully photo-dissolved sample with increasing Ag concentration shown in figure 1. This suggests that the photo-doping Ag atoms follow the structural model described by Fischer-Colbrie *et al* [4] at all times from the initial stage of the photo-dissolution.

We also measured the change of the IPES spectra of a-GeSe₂(500 Å)/Cu(500 Å) with light irradiation time. However, the photo-dissolution of Cu into a-GeSe₂ occurs rapidly within the first 6 min, and gradual changes could not be observed.

In conclusion, we have examined the conduction-band DOS of a-GeSe₂ photo-dissolved by Ag and Cu metals by means of IPES. The characteristic feature of the spectrum of a-GeSe₂ is rapidly smeared out by photo-dissolution of Ag or Cu metal, and each spectrum of the fully photo-doped samples is quite similar to that of a-GeSe_{1.5}. This result is consistent with the structural model described by Fischer-Colbrie *et al* [4], in which many Ge-Ge bonds are induced by photo-dissolution.

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