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Comparative x-ray-photoemission study of monoclinic, trigonal, and amorphous selenium

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X-ray-photoemission spectra of monoclinic, trigonal, and amorphous selenium have been first measured with the same photoelectron spectrometer in order to directly compare the valence electronic states of the three allotropes of selenium. It has been found that the 4*p* lone pair and the 4*s* band of monoclinic selenium (consisting of Se_8 ring molecules) are apparently narrower than those of trigonal and amorphous forms, reflecting the molecular character of the monoclinic crystal. This observation suggests that the Se_8 ring molecule is not a main constituent of amorphous selenium.

It is well known that solid selenium exists in three allotropes[1]: trigonal Se, the most stable form of Se, consisting of closely packed, infinite, and parallel hericoidal chains; monoclinic Se consisting of closely packed, slightly distorted, and puckered eight-membered rings; and amorphous Se whose structure has not been well established.[2] X-ray- (XPS) and/or ultraviolet- (UPS) photoemission spectra of trigonal and amorphous Se have been presented by Nielsen[3,4] and Shevchik *et al.*[5,6] Salaneck *et al.*,[7] on the other hand, have reported an XPS spectrum of monoclinic Se. Remarkable differences are found in the valence-band spectra among these three allotropes of Se. However, it has been very hard to directly compare these photoemission spectra because the photoemission measurements were performed using different experimental apparatuses; the resolution is different and the relative position of the abscissa of the spectrum is unknown between amorphous or trigonal and monoclinic Se. In this Brief Report, we present XPS (Mg *K*α) spectra of trigonal, monoclinic, and amorphous Se measured with the same photoelectron spectrometer in order to directly compare the valence electronic states of the three forms and discuss the possibility of the presence of Se_8 ring molecules in amorphous Se.

An amorphous Se film for the XPS measurements was prepared by vapor deposition onto a stainless-steel holder held at room temperature in a separate vacuum chamber. A polycrystal trigonal Se film was obtained by thermal annealing of an amorphous film in a nitrogen atmosphere at about 100 °C for 1 h. After a brief exposure to air, the sample films were inserted into the photoelectron spectrometer. Monoclinic Se crystallites were obtained from a saturated CS_2 solution. An XPS sample of monoclinic Se was prepared by crushing these crystallites onto a stainless-steel holder with a clean slide cover glass in an argon atmosphere immediately before inserting the sample into the spectrometer. Although the surfaces of the samples were initially contaminated with oxygen and carbon, the selenium samples were observed to be self-cleaning under the ultrahigh vacuum in the spectrometer, and reasonably clean samples could be obtained after a period of several hours.

XPS spectra were measured with a VG ESCALAB 5 photoelectron spectrometer (base pressure less than 1×10^{-10} Torr) with Mg *K*α (1253.6 eV) line as an exciting source. The total resolution of the spectrometer was about 1.0 eV in a full width at half maximum. A valence-band spectrum was obtained by a continuous scanning for abour 16 h. During the measurements, an electron flood gun was used in order to prevent the sample charging effect.

Figure 1 shows XPS (Mg *K*α) spectra of trigonal, monoclinic, and amorphous Se. The present XPS spectra of trigonal and amorphous Se are in good agreement with the previously reported ones[5,6]: (1) the triplet substructure is observed in the 4*p* lone pair band of trigonal form; (2) the upper 4*p* bonding band is apparently smaller than the lower 4*p* bonding band in trigonal form; (3) the 4*p* lone pair and bonding bands of amorphous form are rounded and structureless; and (4) a rectangular feature is observed in the 4*s* band of both amorphous and trigonal forms. As for monoclinic Se, the agreement with the previous data[7] is fairly good; the bandwidth of the 4*s* states is nearly equal between the present (about 3.0 eV) and the Salaneck *et al.* spectrum[7] (about 3.3 eV), although the relatively deep dip of the 4*s* band observed in the early data[7] is almost filled up in this study due to the lower-resolution power. The feature of the 4*p* bonding band of monoclinic Se is more clearly seen in the present spectrum probably because of the higher signal-to-noise ratio in this study. In the present XPS spectrum of monoclinic Se, the upper 4*p* bonding band is apparently larger than the lower 4*p* bonding band in contrast with trigonal Se.

When we compare the XPS spectrum of monoclinic Se with those of amorphous and/or trigonal form

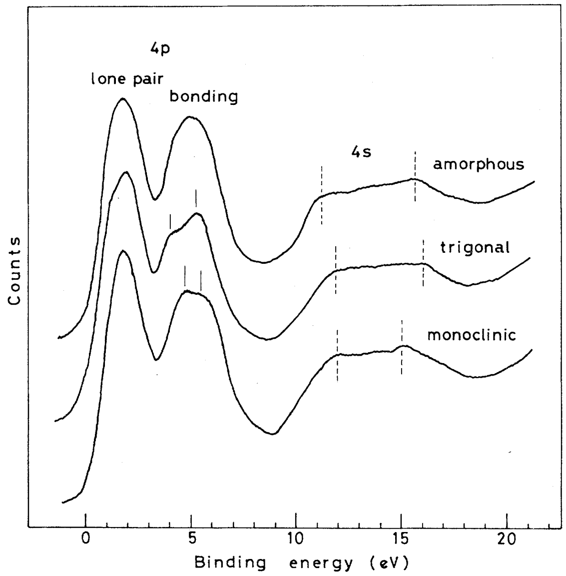

FIG. 1. XPS (Mg$K\alpha$) spectra of monoclinic, trigonal, and amorphous Se. The upper and lower 4p bonding bands are indicated by bars in the spectra of trigonal and monoclinic Se. The approximate bandwidths of the 4s band are indicated by dashed lines.

(Fig. 1), we notice several different points in the valence density of states among them: (1) the 4p lone pair band of monoclinic Se is sharper than those of amorphous and trigonal form; (2) the intensity ratio of the upper and lower 4p bonding band is reversed between monoclinic and trigonal form while the two bands are not resolved in amorphous form; and (3) the 4s band of monoclinic Se is apparently narrower than those of amorphous and trigonal form. The narrow feature of the 4p lone pair and the 4s band of monoclinic Se originates from the molecular character of the crystal; monoclinic Se is a molecular crystal consisting of eight-membered rings. The difference of the intensity ratio of the upper and lower 4p bonding bands between monoclinic and trigonal forms may be due to the difference in the sign of dihedral angles: the dihedral angle of trigonal Se is +102° while that of the monoclinic form is ±102°, and Bullett[8] calculated the density of states of Se in various structures and showed that the intensity ratio between the two 4p bonding bands is very sensitive to the fluctuations in the sign of the dihedral angle.

The presence of Se_8 ring molecules in amorphous Se has been proposed by Salaneck *et al.*[7] As is shown in Fig. 1, the 4s band of monoclinic Se (consisting of Se_8 ring molecules) exhibits a remarkably narrow feature compared with that of amorphous Se. This indicates that the Se_8 ring molecule is not a main constituent of amorphous Se, although the presence is not ruled out by the present study. The similarity of the width of the 4s band between amorphous and trigonal form (Fig. 1) suggests that amorphous Se may consist of relatively long disordered chains.

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