X-Ray Photoelectron Spectroscopic Studies of SbSI

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Synopsis. The binding energies of the core electron peaks suggest that SbSI has more ionic character than covalent character. The valence band spectrum was compared with the calculated density of states. XPS spectra of low temperature ferroelectric phase could not be obtained due to the inhomogeneous spontaneous polarization.

SbSI is the first substance which has been found to be ferroelectrics[1] with semiconductive and photoconductive properties.[2,3] It has a Curie point at 22 °C where it shows first-order phase transition between the high temperature paraelectric phase and the low temperature ferroelectric phase. The crystal structures of the both phases have been analyzed and it has been found that the atomic arrangement is nearly consistent with an ionic model of $Sb^{3+}S^{2-}I^{-}$.[4] However rather short distances among electronegative ions such as sulfurs and iodines suggest that there are tendencies of covalent bond formation.[4] The electronic band structures of SbSI have been calculated using CNDO approximation[5,6] and pseudo-potential method[7] for the ionic and/or covalent models. However more experiments are necessary for more precise calculations.

We measured X-ray photoelectron (XPS) spectra of SbSI and deduced bonding system in SbSI using the binding energies of the core electron peaks. We also compared the XPS valence band with the calculated density of states.[7]

Experimental

X-Ray photoelectron spectra were recorded with a McPherson ESCA 36 Electron Spectrometer, employing Al $K\alpha$ radiation (1486.6 eV). SbSI was kindly supplied by Professor Hideaki Chihara of Osaka University. Samples were single crystals, needle-like along the c axis, but they are not large enough for the measurement. Powdered samples were directly mounted onto Al or Pb plates. Binding energies of photoelectron peaks were calibrated by using the Au $4f_{7/2}$ peak (84.0 eV) of a thin gold film deposited on the sample surface. For the measurement of low temperature ferroelectric phase, samples were cooled with a Dry Ice–ethanol mixture or ice–water mixture.

Results and Discussion

High Temperature Paraelectric Phase. The binding energies of the various core electron peaks are shown in Table 1 with those of related compounds.

The binding energies of iodine peaks in SbSI agree with the corresponding binding energies of iodine peaks in KI. The binding energies of Sb peaks in SbSI are almost same with those of Sb peaks in Sb_2S_3. The binding energy of S peak in SbSI is 1.8 eV smaller than that of S peak in sulfur, and comparing it with the data by Siegbahn *et al.*[8] the state of S in SbSI seems to be S^{2-}. These results show that SbSI has more ionic character than covalent character.

The XPS valence band spectrum of SbSI is shown in Fig. 1 with the density of states obtained by band structure calculation using pseudopotential method.[7] In the calculated density of states, the valence bands separated into five groups and these are interpreted as

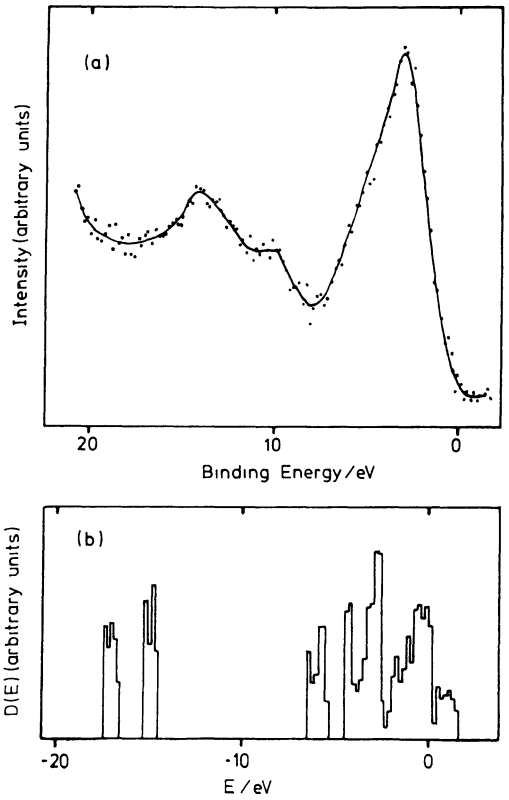

Fig. 1. (a) XPS valence band spectra of SbSI. (b) Calculated density of states of the energy bands of SbSI in the paraelectric phase.[7]

TABLE 1. BINDING ENERGIES/eV OF SbSI AND RELATED COMPOUNDS

	SbSI	KI	Thiourea	Sulfur	Sb_2S_3[a]	Sb_2S_5[a]
I $3d_{3/2}$	630.3	630.4				
I $3d_{5/2}$	618.8	618.9				
Sb $3d_{3/2}$	538.9				539.0	538.7
Sb $3d_{5/2}$	529.5				529.7	529.4
S 2p	161.2		162.0	163.0		

a) Data from Ref. 9.

the 5s-like bands of I atoms, the 3s-like bands of S atoms, the 5s-like bands of Sb atoms, the 5p-like bands of I atoms, and the 3p-like bands of S atoms as the energy increases. In the XPS spectrum of the valence band region, there are two main bands. On the higher binding energy band, there is a shoulder on the lower binding energy side. The overall shape corresponds well to the calculated density of states, but in the latter the distribution of the density of states is rather broader and the separation between two main bands is also larger than the observed one. Calculated intensities of the bands are rather different from the observed ones, but the difference of the cross section of various levels in XPS must be considered. SbSI has very complicated structure. Therefore, the calculated density of states seems to correspond to the observed XPS valence band rather well.

Low Temperature Ferroelectric Phase. XPS spectra of the ferroelectric phase show very anomalous behavior. When the samples were cooled through the Curie point, each core electron peak showed large shift, sometimes split into two or three peaks or gave a very broad peak. This behavior is similar to that due to large and inhomogeneous charging effect and the reproducible spectra could not be obtained. However when the samples were heated through the Curie point, the normal reproducible spectra of the paraelectric phase could be obtained. Several experiments under various conditions suggested that these behaviors could be explained by the spontaneous polarization which was characteristic of the ferroelectricity. Since samples are powder, the spontaneous polarization is not homogeneous throughout sample surface, then the spectra show the same behavior as that due to the charging effect. Anyway these anomalous behaviors of the XPS spectra are due to the ferroelectric property of SbSI and single crystals must be used to get the true spectra.

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