

## Oxidation States of In in $\text{Pb}_{1-x}\text{In}_x\text{Te}$

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According to AES and XPS results, the oxidation state of In in  $\text{Pb}_{1-x}\text{In}_x\text{Te}$  ( $x = 0.056$ ) is lower than in  $\text{In}_2\text{Te}_3$ , corresponding to  $\text{In}^+$  as the major state. The bond valence sum calculations show that In atoms more readily occupy the octahedral sites, substituting for lead. © 1995 Academic Press, Inc.

### I. INTRODUCTION

Dopants such as In, Ga, Cr with variable oxidation states drastically change semiconducting properties of narrow-gap PbTe (1). One of the distinguishing features of In-doped PbTe ( $\text{Pb}_{1-x}\text{In}_x\text{Te}$ ) is chemical stabilization of the Fermi energy, which ensures a high level of spatial uniformity of the physical properties. At  $x > 0.004$  the carrier concentration appears to be constant ( $\cong 7 \times 10^{18} \text{ cm}^{-3}$ ) and does not depend on In content, other impurities, or point defects created by deviation from stoichiometry or by radiation. Another specific feature is the formation of a barrier at the defect, which substantially changes the rate of carrier transition between the center and the band. The barrier is in particular the reason for very high photosensitivity, and for the existence of long-lived electronic states. Unfortunately, the chemical nature of the states is not clear. One of the models assumes the presence of two different states of In atoms,  $\text{In}^+$  and  $\text{In}^{3+}$ , that may be induced by the dissociation process  $2\text{In}^{2+} = \text{In}^+ + \text{In}^{3+}$ . From magnetic susceptibility measurements (2) it is evident that the In impurity has no unpaired spin in the ground state. Taking into account the complicated shape of In core spectra at low  $x_{\text{In}}$  (2, 3) and the nonmonotonic dependence of carrier density on  $x_{\text{In}}$  (1) it can be assumed that very likely both  $4d^{10}$  and  $4d^{10}5s^2$  ground state configurations do coexist, but their ratio should vary depending on the doping level. Reported here are the results of the Auger (AES) and X-ray photoelectron spectroscopic (XPS) investigations on the In states in InTe,  $\text{In}_2\text{Te}_3$ , and  $\text{Pb}_{1-x}\text{In}_x\text{Te}$ . It has been shown that in  $\text{Pb}_{1-x}\text{In}_x\text{Te}$  ( $x = 0.056$ ) the oxidation state of In is lower than in  $\text{In}_2\text{Te}_3$ , corresponding to the presence of  $\text{In}^+$  as a major state. XPS results and bond va-

lence sum calculations (BVS) are used to discuss the mechanism of In incorporation.

### II. EXPERIMENTAL

Crystals of InTe,  $\text{In}_2\text{Te}_3$ , PbTe (standards for XPS and AES), and  $\text{Pb}_{1-x}\text{In}_x\text{Te}$  with  $x = 0.056$  were grown from melts with the compositions InTe,  $\text{In}_2\text{Te}_3$ , PbTe, and  $\text{Pb}_{0.75}\text{In}_{0.25}\text{Te}$ , respectively, by the directional freezing technique. The starting components In (99.999%), Pb(99.9999%), and Te(99.999%) were melted and homogenized in evacuated and sealed quartz ampules at temperatures 20 K above the melting points. The phase composition was identified using X-ray diffraction ( $\text{CoK}\alpha$  radiation). The lattice parameters of InTe ( $a = b = 8.435 \pm 0.002 \text{ \AA}$ ,  $c = 7.132 \pm 0.002 \text{ \AA}$ ) and  $\text{In}_2\text{Te}_3$  ( $a = b = c = 18.472 \pm 0.02 \text{ \AA}$ ) are similar to those reported in (4). The crystal composition  $\text{Pb}_{0.944}\text{In}_{0.056}\text{Te}$  was established using the measurements of lattice constants (5).

The XPS measurements were performed on a KRATOS XSAM-800 instrument at a pressure of  $8 \times 10^{-11}$  Torr using a  $\text{MgK}\alpha$  source ( $h\nu = 1253.6 \text{ eV}$ ). The energy scale of the spectrometer was calibrated from the binding energy of  $\text{Ag}3d_{5/2}$  electrons ( $368.20 \pm 0.02 \text{ eV}$ ). The resolution of the photoelectron energy analyzer was set at 0.8 eV; all of the core-level binding energies have been referenced to the  $\text{C}1s$  peak at 284.8 eV to account for the surface charge-up. In order to remove surface contaminants and oxides, prior to XPS characterization each sample was cleaned *in situ* by mild (0.8 kV)  $\text{Ar}^+$  sputtering. The binding energies of  $\text{In}3d$ ,  $\text{Te}3d$  and  $\text{Pb}4f$  electrons were often checked during the cleaning procedure and any evidence of surface reduction has not been found.

### III. RESULTS AND DISCUSSION

X-ray photoemission spectra from the  $\text{In}3d$  core level in  $\text{Pb}_{0.944}\text{In}_{0.056}\text{Te}$  and in the reference compounds  $\text{In}_2\text{Te}_3$  and InTe are shown in Fig. 1. In general, the core level binding energy (BE) of a cation becomes larger in the higher oxidation state, while for kinetic energies (KE) of

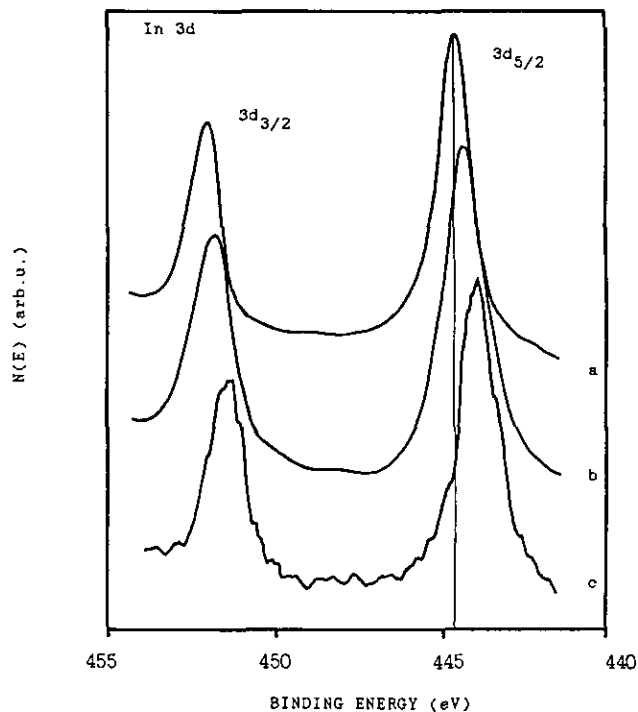


FIG. 1. In3d photoelectron spectra measured from  $\text{In}_2\text{Te}_3$  (a), InTe (b), and  $\text{Pb}_{0.944}\text{In}_{0.056}\text{Te}$  (c). The spectra are approximately normalized to the  $3d_{5/2}$  peak height in  $\text{In}_2\text{Te}_3$ .

Auger transitions the opposite is true. In  $\text{In}_2\text{Te}_3$ , where all In cations are considered to be trivalent, the doublet  $\text{In}3d_{3/2,5/2}$  is shifted toward higher binding energies by 0.3 eV compared with InTe. A different type of local chemical environment of indium in these two compounds is also evident from the shift of the  $M_{45}N_{45}N_{45}$  Auger spectra ( $\Delta\text{KE} = -0.4$  eV) shown in Fig. 2. The experimental data are summarized in Table 1. From a careful analysis of the In3d lines in InTe (Fig. 1) it can be observed that an increase occurs in the full width at half maximum (by  $\sim 0.35$  eV) originating, possibly, from the two crystallographically inequivalent In sites in the tetragonal unit cell of InTe: one In atom is tetrahedrally coordinated with four Te atoms while the second In atom is surrounded by a cage-like system of eight Te atoms [6]. Both components of the 3d spin-orbital doublet can be deconvoluted into pairs of Gaussians separated by  $\approx 0.4$  eV, which might be assigned to  $\text{In}^+$  and  $\text{In}^{3+}$  states. As stated by several authors (9, 10), the chemical shift of the In3d line between monovalent and trivalent states measured for different compounds is less than 1 eV, though the difference of 0.4 eV at the present resolution is too small for distinctive separation of these peaks.

The XPS spectra of the  $\text{Pb}_{0.944}\text{In}_{0.056}\text{Te}$  solid solution are quite different. In contrast to the XPS data for  $x_{\text{In}} = 0.01$  reported in (2), there is only one In3d doublet at

TABLE 1  
Photoelectron Binding Energies and Kinetic Energies (eV) of the Strongest Auger Lines for In, Te, and Pb Measured in This Work

	In	InTe	$\text{In}_2\text{Te}_3$	PbTe	PbTe(In)
In $3d_{5/2}$	443.5	444.0	444.3	—	443.8
Te $3d_{5/2}$	—	572.2	572.3	571.6	571.9
Pb $4f_{7/2}$	—	—	—	137.0	137.1
In $M_4N_{45}N_{45}$	410.4	409.4	409.0	—	409.7
Te $M_4N_{45}N_{45}$	—	491.6	491.7	492.6	492.2
Pb $N_6O_{45}O_{45}$	—	—	—	95.5	95.3

markedly lower binding energy than in  $\text{In}_2\text{Te}_3$  (Fig. 1). The data obtained for  $\text{In}3d_{5/2}$  and  $\text{In}M_4N_{45}N_{45}$  (Table 1) appear to lie closer to the respective values for  $\text{In}^0$  and, therefore, can be assigned to the  $\text{In}^+$  state. Also, no broadening of the In3d spectra was observed. The indium incorporation leads to a slight positive shift of the  $\text{Te}3d_{5/2}$  spectrum relative to its position in PbTe (Fig. 3), while no changes in the core lines of lead was detected. However, the presence of the  $\text{In}^{3+}$  state in  $\text{Pb}_{1-x}\text{In}_x\text{Te}$  must be assumed, considering its electroneutrality. The lack of a clear signal from  $\text{In}^{3+}$  implies that at  $x = 0.056$  their concentration is significantly lower than the concentration of  $\text{In}^+$ .

Since the changes in the core level binding energies of an atom in a solid reflect the changes of such factors as the coordination number, the type of ligands, and the interatomic distances, it is interesting to analyze the relationship between these factors and the shift of photoelec-

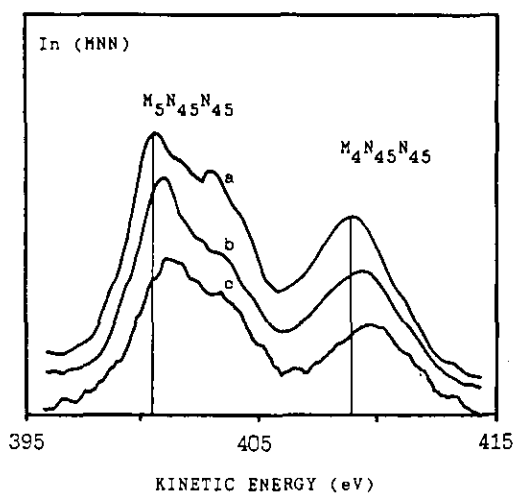


FIG. 2. In  $M_{45}N_{45}N_{45}$  Auger spectra excited by  $\text{MgK}\alpha$  in  $\text{In}_2\text{Te}_3$  (a), InTe (b), and  $\text{Pb}_{0.944}\text{In}_{0.056}\text{Te}$  (c) single crystals. The spectra are approximately normalized to the height of the most intense feature of In  $M_{45}N_{45}N_{45}$  in  $\text{In}_2\text{Te}_3$ .

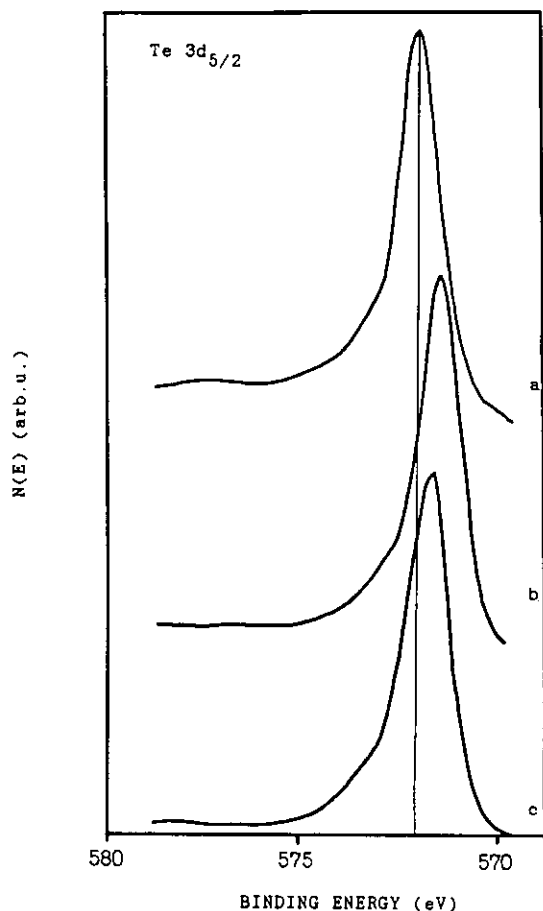


FIG. 3.  $\text{Te}3d_{5/2}$  photoelectron spectra measured from InTe (a), PbTe (b), and  $\text{Pb}_{0.944}\text{In}_{0.056}\text{Te}$  (c).

tron lines as the system is altered by substitution. For this purpose the bond valence sum (BVS) calculation method, which gives information about local charge distribution as a function of species and bond lengths (7), is most promising. The BVS or effective charge of the  $i$ th cation (anion) can be determined from the empirical expression

$$\text{BVS}_i = \sum_j \exp \left[ \frac{r_0 - r_{ij}}{0.37} \right], \quad [1]$$

where  $r_0$  is an empirical parameter specified for each cation-anion pair, and  $r_{ij}$  is the length of the  $i$ - $j$  bond (7). The effective valence can be derived as the sum of the effective charges in the single  $i$ - $j$  bond over  $j$  similar bonds within the first coordination sphere.

Based on the interatomic distances evaluated from the lattice constant and the  $r_0$  parameter derived from "size" parameters of species and electronegativity coefficients tabulated in (8), a bond valence sum calculation was per-

formed for two possible types of indium ordering in the PbTe lattice. The results for the octahedral and tetrahedral indium sites are shown in Table 2. It should be noted, however, that it is impossible to obtain accurate BVS values, since no detailed structural data on this system is available. Nevertheless, the present estimate might be useful in qualitative explanation of spectroscopic results. As shown in Table 2, the effective valence of tetrahedral In would be as large as 2.936, which should lead to a higher binding energy of  $\text{In}3d_{3/2,5/2}$  lines than was observed (see for comparison the  $\text{In}_2\text{Te}_3$  spectrum in Fig. 1), while for octahedral indium sites the calculated BVS value appears to be in better agreement with our Auger and XPS data.

In an earlier study of  $\text{Pb}_{1-x}\text{In}_x\text{Te}$  for  $x \approx 0.01$  (3), two sets of  $\text{In}(M_{45}N_{45}N_{45})$  lines were observed. The intensity of the lower-kinetic-energy  $M_{45}N_{45}N_{45}$  spectrum, which we can now associate with the  $\text{In}^{3+}$  state, was found to be independent of indium content in the sample, in contrast to the higher-energy Auger spectrum. On the other hand, it is well known that  $\text{Pb}_{1-x}\text{In}_x\text{Te}$  at  $x > 0.004$  shows  $n$ -type conduction at nearly constant carrier density. Such unusual behaviour of In in heavily doped PbTe can be explained by the formation of weakly bonded electrically neutral molecular complexes of tellurium with octahedral indium atoms. A second possible mechanism is the segregation of surplus In atoms into microdefects (clusters) when indium concentration goes above a certain threshold, while the  $\text{In}^{3+}$  donor centers in tetrahedra should be responsible for electron conduction.

## CONCLUSION

The Auger and XPS characterization of the chemical state of indium in  $\text{Pb}_{0.944}\text{In}_{0.056}\text{Te}$  was performed using InTe and  $\text{In}_2\text{Te}_3$  as reference compounds. It has been found that the dominant state of the indium impurity is monovalent. On the basis of bond valence sum calculation for different In sites in PbTe one can draw the conclusion that at the impurity concentration used (5.6 at.%), In atoms more readily occupy the octahedral sites, substituting for lead.

TABLE 2  
Effective Valence of In Cations in  
 $\text{Pb}_{0.944}\text{In}_{0.056}\text{Te}$  (Space Group  $Fm\bar{3}m$ ,  
 $a = 6.454$ )

Cation site	$r_{ij}$	BVS
In-Te ( $r_0 = 2.6806$ )		
In (octahedral)	$6 \times 3.227$	1.370
In (tetrahedral)	$4 \times 2.795$	2.936

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