Surface Analysis of InSb by X-Ray Photoelectron Spectroscopy (XPS)

R. G. Copperthwaite, O. A. Kunze, J. Lloyd, J. A. Neely, and W. Tuma

National Chemical Research Laboratory, and the National Physical Research Laboratory, Council for Scientific and Industrial Research, P.O. Box 395, Pretoria, 2000

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Surface compositions of single-crystal specimens of InSb have been investigated by XPS. A correlation between the degree of surface oxidation and the type of chemical etchant used has been found. This interpretation is based on chemical-shift data and argon-ion bombardment experiments, together with XPS results obtained on polycrystalline indium and antimony.

Introduction

The chemical nature of semiconductor surfaces can have a decisive bearing on the performance of these technologically important materials. In the case of InSb photoconductors, the low carrier concentration of the material used (approximately 10^{13} cm^{-3} at 77 K) means that its electrical properties can be adversely affected by the presence of surface space-charge layers. Control of the chemical state of the surface is therefore required and is usually achieved by a combination of mechanical polishing and chemical etching [1]. It is not always clear exactly what chemical modifications are introduced by such treatments, however, and the present work is directed towards producing information on this aspect. The results show significant differences in the chemical composition of surface regions of InSb after different etchants have been employed.

Previous work involving oxides on III-V semiconductors [2] has concentrated on relatively thick (ca. 500 Å) layers where conduction properties were found to be related to the chemical composition. In particular, InSb has been studied on the basis of line shape changes in the indium $N_{2,3}N_{4,5}N_{4,5}$ Auger transition [3]. The chemical shifts observed, however, were too small to identify unambiguously the nature of the indium oxide, whilst line-shape differences of any antimony Auger levels could not be detected.

In the present study X-ray photoelectron spectroscopy (XPS or ESCA) has been applied to the characterization of the surface layers. The chief advantage of XPS over Auger spectroscopy arises from the larger chemical shift of atomic core electron levels as a function of the electronic environment of the atom [4]. The photoelectric effect involves only one core level, whilst the Auger process [5] involves a transition between two core levels and therefore is much less sensitive to chemical changes, since both shift by similar amounts. Core electron binding energies have been measured for a number of III-V compound semiconductors by XPS [6, 7]. Comparison with the same levels for the pure elements has shown that levels associated with the (III) element generally increase in energy, whilst the corresponding levels for the (V) element decrease. The shifts suggest an appreciable charge transfer of the type $(III)^{\delta+}(V)^{\delta-}$ in these compounds and indicate the diagnostic value of the XPS technique. It must be borne in mind, however, that fairly large surface areas are irradiated in XPS (in our case 0.5 cm^2) and that, unlike Auger spectroscopy, we are observing an average sample surface composition only.

Reprint requests to Dr. R. G. Copperthwaite, National Chemical Research Laboratory, Council for Scientific and Industrial Research, P.O. Box 395, Pretoria 2000, Republic of South Africa.

Experimental

Specimens were examined in an AEI ES 200B photoelectron spectrometer using Mg(Kα) radiation (1254 eV), at a base pressure of 5×10^{-9} Torr. A physical Electronics 04-131 sputter ion gun using UHP argon gas at a pressure of 5×10^{-5} Torr with a beam energy of 850 eV and current of ca. 10 μA was used for ion bombardment.

Samples (dimensions $6 \times 12 \times 0.5$ mm) were made from InSb wafers cut normal to the [111] direction, mechanically polished with 1 μm alumina powder and washed with distilled water. Three of these were then subjected to different chemical treatments. Thus samples prepared in the following ways were investigated:

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(a) Mechanically polished,
(b) etched for 2 min in a 3:1:1 mixture (by volume) of H_2O, 48% HF and 30% H_2O_2 [8],
(c) etched for 2 min in a 1:3 mixture (by volume) of CP4A [9] and glacial acetic acid with 0.18 mol/l $InCl_3$ added,
(d) etched for 10 sec in CP4A.

The samples were mounted with conducting epoxy resin on a four-sided copper block and introduced via an intermediate pumping stage to the source chamber of the spectrometer; thus the four samples were investigated under the same physical conditions. Measurements were then repeated with two other sets of InSb samples which had been identically treated. Additional experiments showed that the p.e. spectra obtained were independent of the time of exposure to the X-ray beam and to subsequent exposure of samples to the laboratory atmosphere.

In a separate investigation the surface composition of samples treated with an etchant containing 0.03% by wt of gelatin, (a surface active polypeptide of MW $\simeq$ 150000) was studied.

Results and Discussion

Interpretation of XPS Spectra

The Sb(3d) region is shown for one series of treated InSb samples in Figure 1. It can be seen that at least two types of Sb are present, and further, that the relative contribution from each species depends on the chemical treatment used. The In(3d) region was much less informative in this respect, with spectra being obtained which contained only a weak asymmetry in the low binding energy tails of a single spin-orbit doublet. This indicates that any In chemical shifts are probably less than 0.5 eV, and we have therefore restricted the bulk of the discussion to the Sb levels.

A more detailed analysis of the Sb(3d) region is given in Fig. 2 for a sample treated by etch (d). The spectrum was obtained digitally and standard techniques [10] used to remove contributions from inelastically scattered electrons and $\alpha_{3,4}$ satellites. Resolution enhancement was achieved by a simple Lorentzian-Gaussian transformation on the Fourier transform [11], but, as can be seen, did not provide a complete separation of all components. By including a single peak for the O(1s) signal known

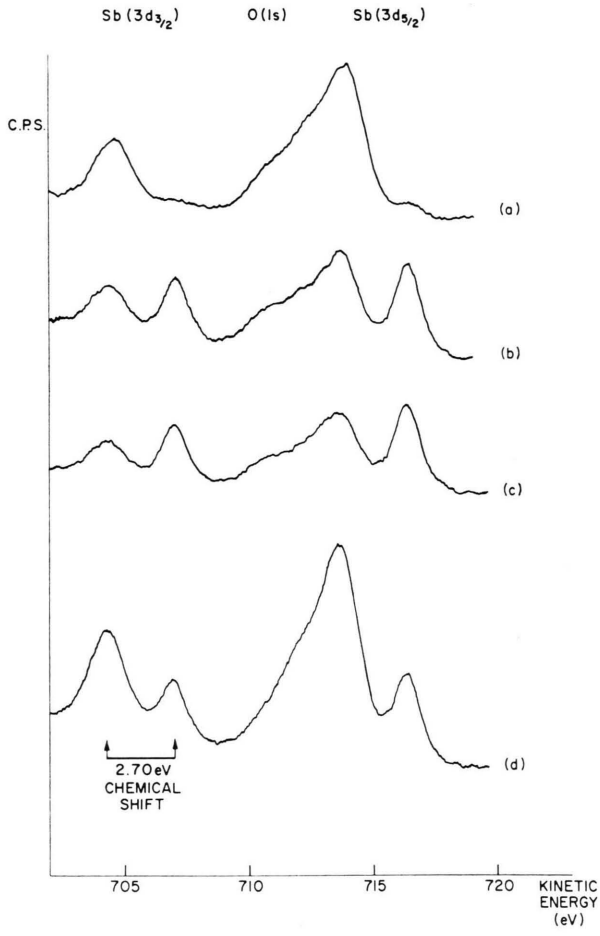

Fig. 1. Sb(3d) region of the photoelectron spectrum of InSb samples subjected to different surface treatments (a), (b), (c), (d) [see experimental section]. These spectra also contain an intense O(ls) signal at ~ 712 eV.

to be present in this region, however, it was possible to carry out an accurate least squares fit of the resolved spectrum which resulted in two spin-orbit Sb(3d) doublets having approximately the correct 2:3 intensity ratios.

The least squares analysis gave a spin-orbit ($d_{3/2}$, $d_{5/2}$) separation of 9.60 ± 0.05 eV for both components and a chemical shift of 2.60 ± 0.05 eV between them. These values were approximately reproducible: e.g. a similar analysis of an ion bombarded sample gave a spin orbit splitting of 9.40 ± 0.05 eV and a chemical shift of 2.35 ± 0.05 eV. No evidence was found in other samples to suggest that significantly different chemical shifts were present and the spectra shown in Fig. 1 can be considered to arise from a super-impostion of two

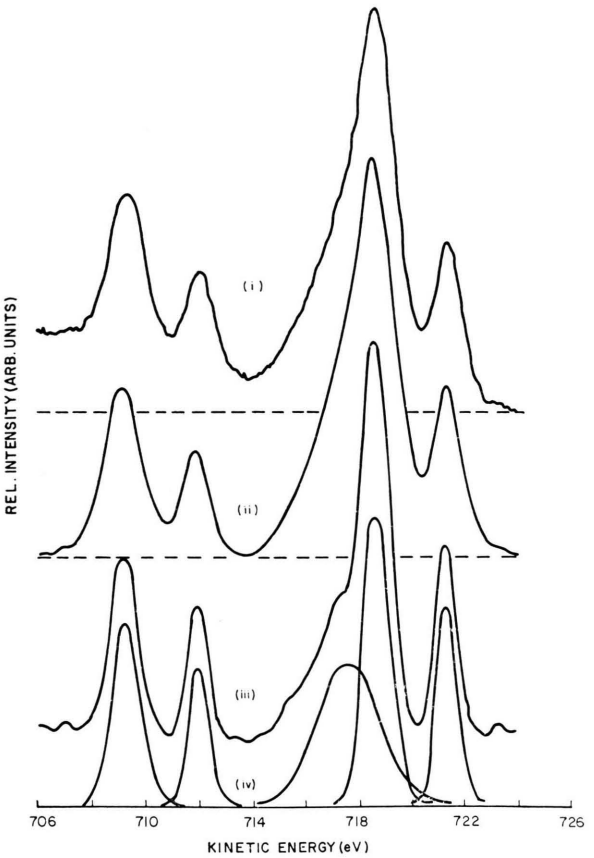

Fig. 2. (i) Typical photoelectron spectrum obtained for InSb treated with etch (d); Sb(3d) region. (ii) Smoothed spectrum, after background removal. (iii) Resolution-enhanced spectrum. (iv) Least-squares fit.

Sb species, plus an O(1s) signal whose relative intensities depend on the type of chemical treatment used.

A qualitative interpretation of these results shows that the surfaces of all the InSb samples studied are oxidised to a greater or lesser degree; the measured In, and Sb ($3d_{5/2}$) binding energies are shown in Table 1. Simple concepts of chemical shifts as a function of the type of bonding involved suggest that the doublet having the lower kinetic energy (higher binding energy) corresponds to an oxidised antimony species while the doublet at higher kinetic energy refers to "bulk" InSb. The generally intense O(1s) signal, coupled with the asymmetry of the In(3d) levels, support this interpretation. The data presented in Table 1 also suggest that the oxidised antimony layer corresponds closely to bulk Sb_2O_3.

Table 1. Measured binding energies (± 0.2 eV) relative to C(ls) = 285.0 eV.

	In($3d_{5/2}$)		Sb($3d_{5/2}$)	
InSb	(443.1)	444.5	(528.7)	526.0
In		444.0		
Sb				526.5
Sb_2O_3			528.4	

Further confirmation of an oxidised surface layer comes from the ion bombardment experiments. As can be seen in Fig. 3, the photoelectron peaks due to oxidised antimony and the associated O(1s) signal are gradually removed by the argon ion bombardment, with consequent increase in the Sb signal assigned to bulk InSb. After prolonged bombard-

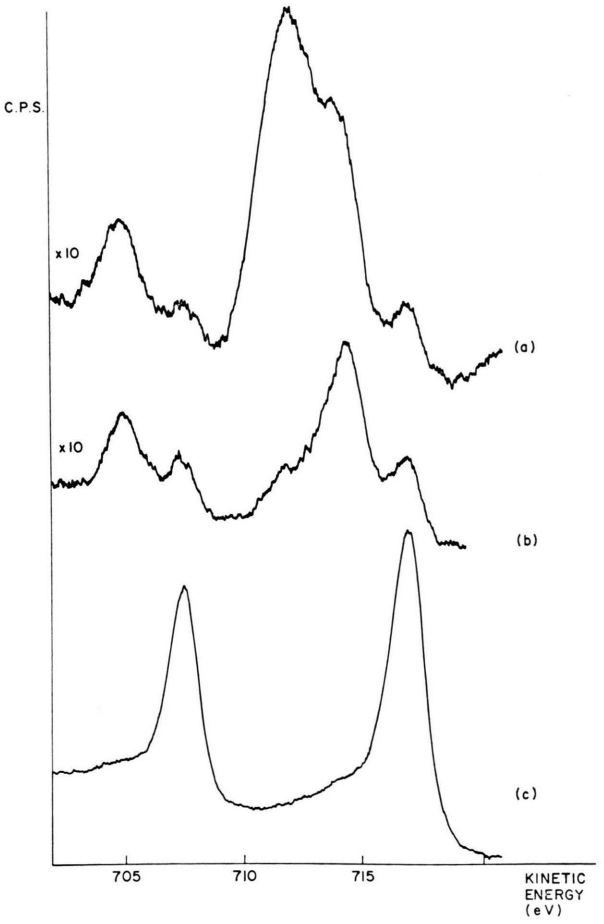

Fig. 3. (a) Initial photoelectron spectrum in the Sb(3d) region for a sample of InSb. (b) The same region, after a small amount of argon ion bombardment. (c) The same region after prolonged argon ion bombardment.

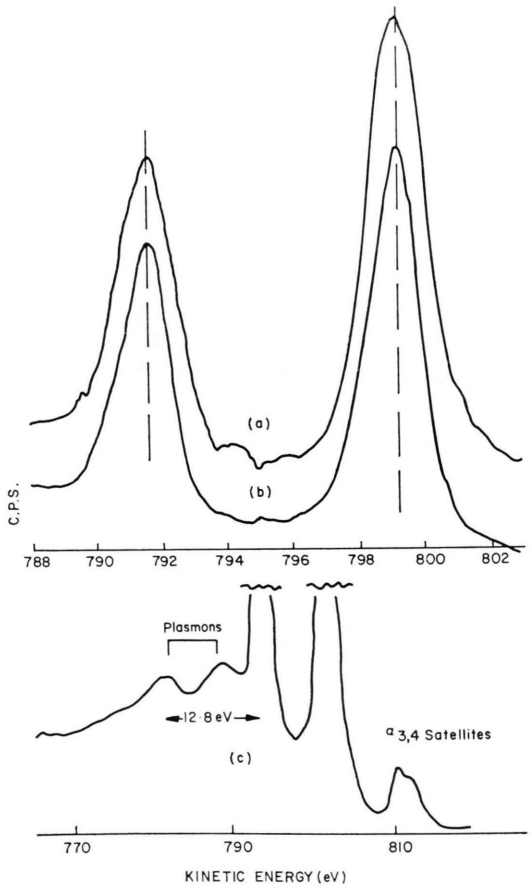

Fig. 4. (a) Initial photoelectron spectrum in the In(3d region for a sample of InSb. (b) The same region after a small amount of argon ion bombardment. (c) A wider scan of the In(3d) region after prolonged argon ion bombardment, showing bulk plasmons.

ment the surface begins to correspond to atomically clean InSb and plasmon peaks are seen to appear. An example of this is given in Fig. 4 for the In(3d) levels. This figure also shows that the asymmetry of the original peaks changes to the high binding energy side as bombardment times increase; again providing qualitative proof that the surface region is initially quite different from that of the bulk.

Correlation of XPS Data with Etchant

The relative ratios of oxidised antimony to unoxidised antimony are shown in Table 2 for the different types of surface treatment undergone by the InSb. These results have been obtained from three independent sets of samples. In case 1 and 3

Table 2. Sb($3d_{3/2}$) relative intensities for the InSb samples.

Sample series	Crystal face	Surface treatment *	Relative intensities "Oxidised Sb" Sb
1	111	a	< 28
		b	2.3
			0.8
		d	8.5
2	$\bar{1}\bar{1}\bar{1}$	a	6.5
		b	0.8
		c	0.5
		d	1.6
3	111	a	10.8
		b	1.0
		c	0.4
		d	7.3

* See experimental section.

the A (indium) face and in case 2 the B (antimony) face [12] was investigated. As might be expected, the mechanically-polished specimens have the highest degree of oxidation. Local heating during polishing in the presence of oxygen has led to a surface oxide of thickness which can be estimated to be greater than 100 Å. An intermediate degree of oxidation was found for the CP4A and the peroxide etches. They produce an oxidized surface layer with a thickness in the order of 20 Å or about three atomic layers. The least degree of oxidation, in the order of one atomic layer, occurred with the etch containing $InCl_3$. The use of this compound was part of an unpublished study to investigate the effect of Friedel-Crafts type catalysts in the etching of indium antimonide. $InCl_3$ is known to be a strong electron acceptor [13] and an interaction, especially with the Sb-(111) face having a high electron density, was expected. In addition to its effect on the surface oxidation it was found that increasing the concentration of $InCl_3$ in the etch increases the etch-rate. Both findings support the view that $InCl_3$ plays an active part in the dissolution process, although its exact rôle has not been established. No correlation between the intensity of the O(1s) signal and the degree of oxidation could be established; thus one sample treated with the $InCl_3$ etch and having a high proportion of unoxidised InSb, was found to have an intense O(1s) peak, which was attributed to adsorbed molecular oxygen.

The marked effect of gelatin — a wellknown surface active agent — in Allen's 111-etch [9] on

the resulting surface structure suggested that the polypeptide chains strongly coordinate to the Sb-(111) face [14]. These conclusions are supported by our XPS results on InSb samples treated with an etch containing gelatin and subsequently rinsed many times in de-ionised water. An intense N(1s) peak was observed on such samples, which also revealed a relatively low degree of surface oxidation. From the binding energy of the N(1s) signal and the large chemical shift for nitrogen [4] the presence of amine groups on the surface could be deduced. It would appear that the rôle of the gelatin in reducing surface oxidation is due to strong adsorption at the InSb surface.

The energy-loss features observed for ion-bombarded InSb are shown in Fig. 4(c) for the In(3d) region. These were also observed at the same energy (12.8 eV) in the Sb(3d) region. We believe this transition corresponds to a bulk plasmon excitation in InSb. The free-electron plasmon energy is readily calculated [15] to be 12.7 eV; the close correspondence between theory and experiment is probably due to the small band-gap of this material (<0.2 eV).

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