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Bismuth and antimony on InP(110): a comparison

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Abstract. Sb was reported to form an abrupt interface with ultrahigh-vacuum cleaved InP accompanied by anomalously low and high barriers on n- and p-type InP respectively. Since the structural and electronic properties of Bi are similar to those of Sb, the Bi–InP(110) interface may therefore play an important role in the discussion of the Schottky barrier models. Here, the adsorption of Bi at room temperature was studied *in situ* using x-ray photo-emission (XPS) and Raman spectroscopies up to almost 100 monolayers of Bi coverage. Current–voltage and capacitance–voltage measurements were performed at large coverages of several hundreds of monolayers. While Bi was also found to form an abrupt interface, the overlayer growth mode differs significantly from that of Sb on InP(110). The distinct growth mode is used to explain the higher and lower Schottky barriers for n- and p-type InP respectively. Metal-induced gap states are proposed to be responsible for the final barrier heights.

1. Introduction

Amongst the many metal–semiconductor combinations the Sb/III–V interfaces are exceptional since they are atomically abrupt and Sb forms an ordered monolayer when deposited at room temperature. Because of the absence of any chemical reaction at the interface the Sb/III–V systems may play an important role in the understanding of metal–semiconductor interfaces. Therefore Sb on InP(110), for instance, has been extensively studied using a number of experimental techniques such as LEED [1, 2], photo-emission spectroscopy [3, 4], Raman scattering [5, 6] and transport measurements [7]. In particular, the Raman results have shown a strong correlation of the Schottky barrier formation with the Sb growth mode [5, 6]. Furthermore, exceptional low and high barriers have been measured at high coverages of Sb on n- and p-type InP respectively. As a result, a modified metal-induced gap state (MIGS) model has been proposed for Schottky barrier formation which takes the bonding at the interface into account [8]. This model is likely to explain the anomalous Schottky barrier heights observed for Sb on InP(110).

The group V element Bi is very similar to Sb in its electronic and geometric structure. However, only the Bi–GaAs(110) interface has recently attracted some interest [9, 10], although the Bi/III–V combination may be another very important test case for the Schottky barrier formation. In this paper we present an extensive study of Bi on InP

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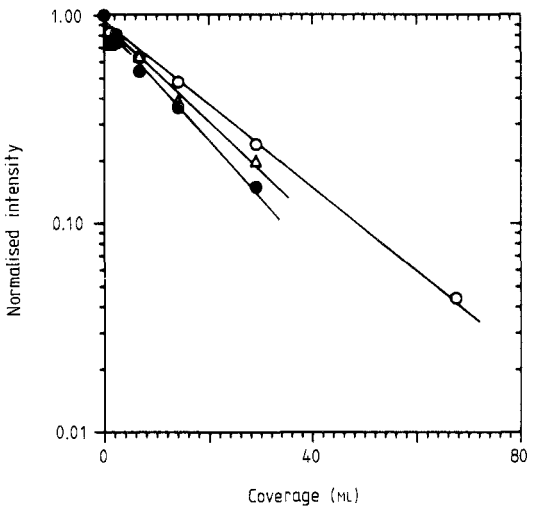

Figure 1. Bi/InP(110). Attenuation of the In 3d (●), In 4d (○), and P 2p (△) core level emission intensities as a function of Bi coverage.

using x-ray photo-emission spectroscopy (XPS), Raman spectroscopy and transport measurements, and we discuss the results in comparison with those previously obtained for Sb on InP.

2. Experimental

In this study InP crystals were cleaved in ultrahigh-vacuum (UHV) at base pressures below 2×10^{-10} mbar and Bi was deposited from a thermal evaporator. Details of this are given elsewhere [5]. The experimental set-ups for the Raman and the transport measurements were identical to those used previously for the Sb–InP(110) experiments and are also described elsewhere [5, 7]. The XPS measurements were performed using a VG ESCAlab Mark II. Monochromatic Al K_α radiation with a photon energy of 1486.6 eV was used as an excitation source and the photo-emitted electrons were detected by a hemispherical sector analyser. The resolution was approximately 0.8 eV.

3. Results

3.1. X-ray photo-emission

The high photon energy allows the emission from the In 3d, In 4d and P 2p as well as the Bi 4f core levels to be monitored. Spectra were taken of the clean cleaved surface and after each evaporation up to almost 70 ML of Bi coverage. The emission from the substrate core levels did not reveal any sign of chemically shifted components within the experimental resolution. The intensity attenuation (figure 1) follows an exponential decay in all three cases with different slopes according to the kinetic energies of the photo-emitted electrons. However, the escape depths evaluated from the slopes are greater (by a factor of 2.5) than the figures calculated using the empirical formula given by Seah [11]. A single pair of spin–orbit split Bi 4f core level emission lines were detected well below 1 ML. Upon deposition the FWHM of the Bi 4f emission line decreased gradually from 1.3 eV to 0.9 eV at the largest coverages.

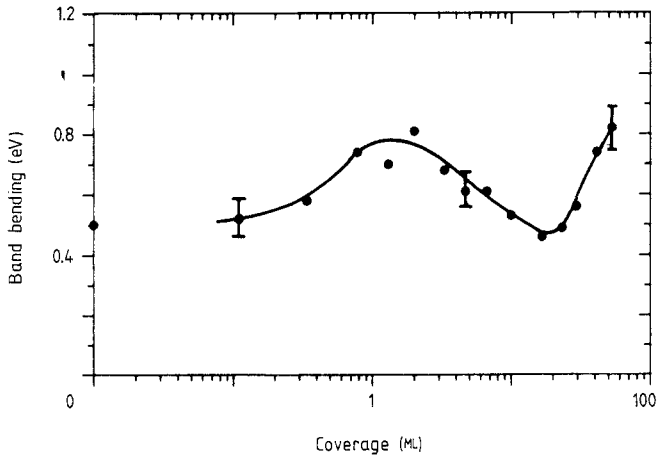

Figure 2. Bi/p-InP(110). Band bending as a function of Bi coverage on p-type InP(110). T = 300 K.

3.2. Raman spectroscopy

In previous publications [5, 6] we have demonstrated that the band bending at the Sb–InP(110) interface can be monitored by Raman spectroscopy, by measuring the ratio of the longitudinal optical (LO) to transverse optical (TO) phonon scattering intensities of InP. This technique of electric field induced Raman scattering (EFIRS) has also been applied for Bi on p-InP(110). Simultaneously, the scattering by the Raman-active Bi phonon modes provides information on the structure of the overlayer.

The band bending evaluated from EFIRS is shown in figure 2. After an initial increase up to 1 ML the band bending is diminished for intermediate coverages before a final value of approximately 0.8 eV is approached. Raman scattering by the lattice vibrational modes of Bi is detected beyond 10 ML (see figure 3). The observed features correspond to the E_g and A_{1g} lattice vibrations of bulk Bi.

3.3. Transport measurements

Current–voltage (I–V) measurements were performed on macroscopically thick >200 ML) Bi diodes on InP. A typical I–V characteristic of Bi on p-InP(110) is shown in figure 4. This characteristic was analysed using the thermionic emission theory [12] which was applicable because of the ideality factor of $n = 1.02$. The height of the Schottky barrier was calculated to be $\Phi_{SB} = (0.83 \mp 0.01)$ eV. Capacitance–voltage measurements provide a slightly higher value of 0.85 eV. Additional transport measurements on n-type InP reveal a Schottky barrier of 0.48 eV.

4. Discussion

The absence of shifted components in the core level emission lines of the substrate may indicate that there is no chemical reaction when Bi is deposited at room temperature. Therefore, Bi is likely to form an abrupt interface on InP. Further support for the abruptness is found in the attenuation plots of figure 1, since a simple exponential decay

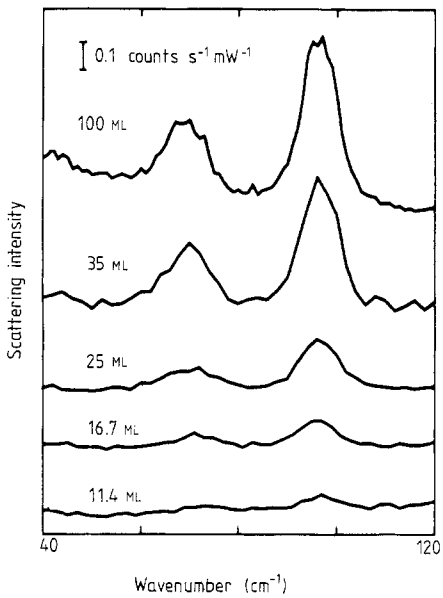

Figure 3. Bi/InP(110). Raman phonon spectra of Bi deposited onto InP(110); $h\nu = 3.06$ eV.

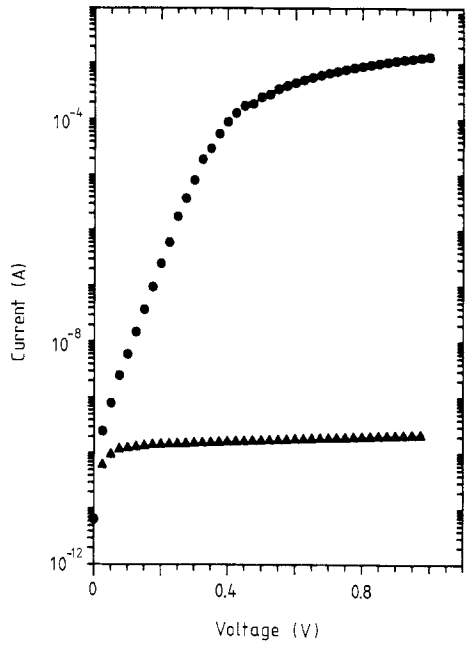

Figure 4. Bi/p–InP(110). *I–V* characteristics for a Bi diode on p-type InP(110). ●, forward bias; ▲, reverse bias.

is found for the In as well as the P core level emission intensities. However, the fact that the escape depths evaluated from the experimental data are considerably larger than the theoretical values which would be applicable in the case of layer-by-layer growth demonstrates island formation. Island formation was also found for Sb on top of the first monolayer [13]. However, the factor between the experimental and the theoretical figures of the escape depths is smaller (1.9), indicating a lower aspect ratio for Sb islands.

The appearance of a single pair of Bi 4f emission lines with a large FWHM at low coverage may indicate adsorption on random sites on the InP surface. In contrast, the ordered adsorption of Sb leads to two pairs of Sb 4d emission lines due to two distinct adsorption sites [13].

The Raman spectra of the Sb vibrational modes have also revealed the formation of an ordered monolayer, while subsequent deposited Sb has been found to be amorphous until a transition into the crystalline phase occurs around 10 ML of coverage [5]. The Raman spectra of the Bi vibrational modes, on the other hand, do not show any sign of an ordered monolayer or amorphous growth. The appearance of the bulk like Bi phonon modes is consistent with polycrystalline island formation.

The Schottky barrier as evaluated from the EFIRS data for large coverages is in excellent agreement with the value obtained from the *I–V* characteristic. The transport measurements for Bi on n-InP(110) reveal that there is a common pinning level of around 0.8 eV above the valence band. The pinning level for Sb on InP(110), on the other hand, is close to the conduction band which has recently been explained by a modified MIGS model [8]. This modified model takes the preferential bonding of Sb to In in the first ordered layer into account. If we consider Bi, which is likely to be adsorbed in random sites but still forming an abrupt interface, the unmodified MIGS model should be appropriate. Comparing the pinning level obtained experimentally with the theoretical value

(0.76 eV above the valence band) given by Tersoff [14], one finds a slight deviation. However, when the metal work function is also taken into account as described by Flores [15] the experimental value agrees even better with the theory.

While the initial band bending for thin coverages may be caused by defects and imperfections in the overlayer [16], the strong variations of band bending in the intermediate coverage range are likely to originate from a transition in the electronic structure. Thin Bi films have been reported to be semiconducting, whilst thick films are semimetallic [17]. A similar change in the electronic structure of Sb may be related to the phase transition from amorphous to crystalline, thus explaining the qualitatively similar band bending behaviour observed by EFIRS.

In summary we have shown that Bi forms an abrupt and chemically unreactive interface with InP. The detailed structure of the overlayer growth determines the difference in the Schottky barrier formation of Bi and Sb on InP. While the preferential bonding of Sb to In has to be considered, a simple MIGS model is appropriate to explain the Schottky barrier formation for Bi on InP.

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