Extreme band bending at MBE-grown InAs(001) surfaces induced by in situ sulphur passivation

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Abstract

The passivation of InAs(001) surfaces by exposure to sulphur in ultra-high vacuum (UHV), followed by capping with amorphous arsenic, has been studied by high resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED). Samples grown and passivated at NIMS were transferred to Warwick for analysis, through air and without special precautions. Well ordered and clean InAs surfaces were recovered simply by thermal annealing in UHV. A series of reconstructions were investigated using LEED and XPS by increasing the anneal temperature: a disordered S-rich (1\textup{\texttimes}1\textsuperscript{C2}), ordered S-terminated (2\textup{\texttimes}1\textsuperscript{C2}), and finally a S-free (4\textup{\texttimes}2\textsuperscript{C2})/c(8\textup{\texttimes}2) In-terminated surface. The evolution of the HREEL spectra with annealing was also measured, and observations of the surface plasmon mode indicated a very strong surface electron accumulation layer. The downward band bending was largest for the S-rich surfaces with the surface Fermi level as high as 600 meV above the conduction band minimum.

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1. Introduction

The surface passivation of III–V materials such as InAs and GaAs is a subject of wide interest and significant technological relevance. In recent years, the use of sulphur as a passivating agent has been extensively studied, both with ex situ wet chemical treatments [1–3] and in vacuo sulphur vapour or atomic beam exposure [4–6]. The latter methods avoid the etching effect of the wet chemical treatment [4]. As well as providing chemical passivation, S treatment can improve the electrical properties of GaAs-based structures [7–8] and provide novel templates for crystal growth [9]. In the case of the GaAs(001) surface, a well-ordered (2\textup{\texttimes}6) reconstruction has been observed and characterised for in vacuo S treatment [4,5,10]. This reconstruction also appears on polysulphide etched GaAs [4], although the comparative roughness of the surface makes it more difficult to discern; a diffuse (2\textup{\times}1) diffraction pattern is commonly observed. On InAs(001) treated by

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polysulphide etching, a clear \((2 \times 1)\) structure has been observed after annealing to 350°C [1]. X-ray photoelectron spectroscopy (XPS) indicated that S bound to As atoms desorbed at \(\sim 300^\circ\text{C}\), while S remained bonded to In with a single chemical state [1]. For GaAs(001), S termination has been shown to reduce the upward band bending (depletion layer) normally present at the surfaces of n-type GaAs by 0.3–0.45eV [6]. Unlike GaAs(001), InAs-free surfaces show downward band bending and the presence of an electron accumulation layer. On the In-terminated (001) surface, the density of donor-like surface states is around \(5 \times 10^{11} \text{cm}^{-2}\) [11,12]. Depending on the bulk Fermi level (determined by doping level and temperature) the resulting downward band bending can result in surface Fermi levels up to \(~300\text{meV}\) above the conduction band minimum (CBM) [13]. Selenium passivation of InAs(001) surfaces has been shown to promote even stronger downward band bending with a surface Fermi level up to 500meV above the CBM [14].

In the present paper, we report on surface studies of in vacuo sulphur treated InAs(001) using XPS, low energy electron diffraction (LEED), and high resolution electron energy loss spectroscopy (HREELS). A sharp \((2 \times 1)\) reconstruction was found after annealing to 350°C while a disordered \((1 \times 1)\) pattern was found for lower temperature anneals. On annealing to 375°C, the S desorbed to leave a typical In-terminated \((4 \times 2)\)/c(8 \times 2) reconstruction. The band bending inferred from the surface plasmon excitations observed in HREELS, correlated to the amount of S on the surface, with the most S-rich surfaces showing the highest surface charge.

2. Experimental details

InAs(001) samples were grown at NIMS, Japan, by molecular beam epitaxy (MBE) without intentional doping, at 520°C. The surface reconstruction was monitored throughout by reflection high energy electron diffraction (RHEED). After completion of a 50 nm thick layer, samples were transferred in vacuo to a side chamber where they were exposed to S vapour from an elemental source at room temperature at a pressure of \(2 \times 10^{-5} \text{mbar}\) for 20 min. After S exposure, they were returned to the MBE chamber where an amorphous As cap was deposited (thickness \(\sim 1 \mu\text{m}\)). Thus passivated, they were transferred through air to Warwick without special precautions. On insertion into one of two analysis chambers (XPS or HREELS, both equipped with LEED) the samples were annealed gently to remove the As cap. Experiments were performed as a function of increasing annealing temperature (up to 375°C) with fixed anneal times of 1h.

3. Results and discussion

On annealing up to \(~325^\circ\text{C}\), the LEED pattern showed mainly integer order spots, with rather weak fractional order features. The sharpness of the pattern improved as the temperature was increased to 350°C and showed a clear \((2 \times 1)\) by 350°C. The \((2 \times 1)\) LEED pattern is illustrated in Fig. 1(a), and this structure is in agreement with a previous study of polysulphide etched InAs(001) [1]. However, it should be noted that it was possible to observe a \((2 \times 6)\) reconstruction using RHEED when the S–InAs(001) samples were annealed in situ in the MBE chamber. This latter reconstruction has been observed for S–GaAs(001) prepared by similar means [4,5,10]. Scanning tunnelling microscopy would be useful in clarifying the nature of the InAs(001)–S–GaAs(001) \((2 \times 1)/\(2 \times 6)\) surfaces, as for S–GaAs(001) [4]. Nonetheless, the LEED patterns were sharp and bright, and contamination levels were below those detectable by XPS and HREELS. This demonstrates the effectiveness of the combined S-passivation and As-capping procedure in protecting the sample surface during a long transit through air. On heating the samples further, the LEED pattern evolved from a \((2 \times 1)\) to a ‘streaky’ \((4 \times 1)\). The LEED pattern after annealing to 375°C is shown in Fig. 1(b) and is typical for a clean In-terminated c(8 \times 2) surface with one-dimensional disorder along the \([1 1 0]\) direction. XPS scans showed that all the S had been desorbed at this temperature, in agreement with a previous study of polysulphide etched InAs(001) [1].
XPS spectra of the S 2p, As 3d and In 3d$_{5/2}$ regions are shown in Fig. 2 for the (2 x 1) surface after annealing at 350°C. For brevity, neither the dependence of the spectra on take-off angle nor the spectra for S-free surface are shown. Fitting of the XPS spectra indicated bonding of S to In only...
(a single spin–orbit split peak), while In is bound to both As and S. The dominant In peak relates to In–As bonding while a small chemically shifted peak (≈0.8 eV to higher binding energy) relates to In–S bonding at the surface. There is no evidence for a chemically shifted As feature in addition to the dominant bulk-like As peaks of InAs. This is consistent with a $(2 \times 1)$ structure in which S dimers are bound to In atoms in the second layer \[5,10\] and there is no elemental S or S–As bonding \[1\]. The S peak is best fitted with a single 2p doublet (1.18 eV splitting) for all annealing temperatures and there is no evidence for elemental S at the surface. Despite this, there is evidence for S desorption even at 300–350 °C from the integrated intensity of the S XPS peak during and after the development of the $(2 \times 1)$ LEED pattern. This implies the presence of missing S dimers \[5\] the density of which increases as the thermal load is increased. However, for the samples studied ex situ the ordering of these missing dimers is never good enough to produce a $(2 \times 6)$ LEED pattern.

The electronic properties of the near-surface region, in particular surface space charge layers, can be probed by examining plasmon excitations in HREELS \[11–13\]. For a bulk electron density of \(\sim 1 \times 10^{17} \text{cm}^{-3}\), the expected plasmon frequency is around 20 meV. The plasmon frequencies obtained from S–InAs(001) are shown in Fig. 3 for three different annealing temperatures (and hence three different S surface concentrations). All the plasmon energies are much higher than that expected from bulk doping alone due to the presence of an accumulation layer at the surface \[11–13\]. The plasmon energies also vary strongly with incident electron energy (Fig. 3). This is due to both the native spatial dispersion of the plasmon excitation, and to the inhomogeneous spatial structure of the accumulation layer. At higher electron energies, regions of lower plasma frequency deeper into the bulk are probed, and so the overall surface plasmon energy drops \[13\]. Both the plasmon frequency and the dispersion are highest for the largest S coverage (lowest anneal temperature), consistent with stronger band bending. At high electron energies, the plasmon frequency drops from \(\sim 120\) to \(\sim 50\) meV as the S layer is desorbed. This corresponds to band bending values of around 600 and 300 meV respectively, the latter being typical for clean InAs(001)-(4 \(\times\) 2). \[11,13\]. The surface donor density in the two extreme cases is estimated to be \(\sim 1 \times 10^{12}\) and \(\sim 5 \times 10^{11} \text{cm}^{-2}\), respectively. \[1\] The additional surface donors and extreme band bending clearly arise from the presence of S at the surface, and a similar strong band bending effect has been measured on Se-terminated InAs(001) \[14\]. This behaviour contrasts with that of GaAs(001)–S only in that clean n-type GaAs(001) shows a depletion layer due to the presence of native surface acceptors. Termination with group VI atoms adds surface donors and reduces the band bending in this case \[6\]. It would be interesting to examine the effect of surface ordering (e.g. missing dimers and \(2 \times 1\) versus \(2 \times 6\) structures) on the donor density for a fixed S coverage, since clearly only a fraction of the surface atoms are able to donate an electron to the bulk conduction band.

Footnote:\footnote{Amore detailed analysis of the HREEL spectra via full dielectric theory simulations will be presented elsewhere.}

Fig. 3. Plasmon frequencies obtained from HREELS measurements as a function of probing electron energy, for S–InAs(001) after anneal temperatures of (a) 325°C, (b) 350°C and (c) 375°C.
4. Conclusions

The effectiveness of S-passivation and subsequent As-capping/decapping in protecting the InAs(001) surface from contamination has been demonstrated. A clean S-terminated surface showing $(2 \times 1)$ symmetry in LEED is recovered by annealing to $350 \pm 1^\circ$C in UHV. XPS results are consistent with a basic $(2 \times 1)$ structural unit comprising S dimers bound to second layer In atoms, with some missing S dimers. Annealing to $375^\circ$C removes all the S dimers to leave a $c(8 \times 2)$ In-terminated surface with typical one-dimensional disorder. All surfaces show downward band bending and the presence of an electron accumulation layer, with the band bending greatest for the S-terminated surfaces. The surface Fermi level lies $\sim 600 \pm 100$meV above the CBM for the most S-rich surfaces, in agreement with the Fermi level behaviour of Se-terminated InAs(001) [14]. A fraction of the group VI species present act as surface donors, adding to the surface charge already present at clean InAs polar surfaces.

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