Passivation and reconstruction-dependent electron accumulation at sulphur treated InAs(001) surfaces

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Received 4 May 2002; accepted for publication 30 September 2002

Abstract

The effects of in situ sulphur passivation on the electronic properties of n-type InAs(0 0 1) have been studied using X-ray photoemission spectroscopy and high resolution electron energy loss spectroscopy coupled with space-charge layer calculations. Surfaces passivated by sulphur dosing followed by arsenic capping were annealed in vacuum to progressively remove the protective layers. For disordered surfaces with a sulphur coverage of almost 2 monolayers (ML), complex surface plasmon modes were observed due to strong electron accumulation at the surface, with downward band bending around 600 meV. For (2/1) reconstructed surfaces (sulphur coverage < 1 ML), the band bending dropped to 325 meV. A 375 °C anneal was sufficient to remove all sulphur and regain a clean (4/2) indium-terminated surface with 200 meV downward band bending. We discuss the reconstruction-dependent surface accumulation and some aspects of ‘electrical passivation’ of surfaces.

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Keywords: Indium arsenide; Electron energy loss spectroscopy (EELS); Plasmons; Electrical transport (conductivity, resistivity, mobility, etc.); Semiconducting surfaces

1. Introduction

The native oxides of III–V materials are generally unfavourable compared to those of silicon in terms of electronic device growth and performance. Since it was found that the performance of III–V based devices could be improved by sulphur passivation [1], there have been many studies of sulphur/III–V surface chemistry. Several methods of applying sulphur have been performed, including solution-based methods [1,2], gas-based methods [3], and by the use of an electrochemical cell [4]. Most studies have focused on the low index surfaces of GaAs [2,5] and InP [6,7]. For n-type material, these compounds exhibit native depletion layers in the near-surface region, and experiments have shown that sulphur acts to reduce the surface recombination velocity and Fermi level pinning at the surface [8]. However, there has been relatively little work on the surfaces of InAs [9,10].

Unlike GaAs, clean n-type InAs shows downwards band bending due to the presence of
donor-like states at the surface, giving rise to a 
native accumulation layer [11], with sheet density 
dependent on the surface reconstruction [12]. Pre-
vious studies of sulphur passivated InAs(001) have 
concentrated on studying the chemical and struc-
tural properties of the surface. Using an aqueous 
ammonium polysulphide solution [9], it was found 
that both S–As and S–In bonds form. Annealing to 
above 300 °C breaks the S–As bonds, leaving only 
S–In bonds at the surface, which are responsible for 
a (2 × 1) reconstruction as observed with LEED. A 
structural study of (NH₄)₂Sₓ-treated InAs(001) 
using coaxial impact collision ion scattering spec-
troscopy (CAICISS) [13] supported these findings, 
and further showed that when sulphur is adsorbed, 
it replaces some of the surface arsenic atoms, lead-
ing to a decrease in the quantity of near surface 
ar senic relative to indium. Annealing to 400 °C re-
moves all the sulphur from the surface, resulting in 
a clean InAs(001)-(4 × 2) surface. A study of sele-
nium-treated InAs(001) using synchrotron radia-
tion photoelectron spectroscopy [14] found that 
downward band bending was increased to approxi-
amately 500 meV for the (2 × 1) surface recon-
bstruction. Polysulphide treated InAs(1 1 1) surfaces 
also showed an increase in downward band bending 
of around 0.2 eV [10]. To date, there have been no 
high resolution electron energy loss spectroscopy 
(HREELS) studies of sulphur passivated InAs, and 
only a few on GaAs (e.g., [3]), focusing predomi-
nantly on adsorbates at the surface.

In the present paper, HREELS, X-ray photo-
emission spectroscopy (XPS) and LEED have been 
used to study the electronic and chemical prop-
ties of MBE-grown InAs(001) surfaces passivated 
by in situ molecular sulphur exposure and subse-
quently arsenic capping. By studying the conduction 
band surface plasmon losses in decapped and an-
nealed samples, surface state densities and band 
bending have been determined as a function of 
sulphur coverage. The chemical and electronic 
aspects of surface passivation are discussed.

2. Experimental details

Experiments were performed in two separate 
analysis chambers (University of Warwick, UK) 
while the samples were produced in a molecular 
beam epitaxy (MBE) chamber at the National 
Institute for Materials Science, Japan. InAs(001) 
samples were grown without intentional doping to 
thicknesses of around 0.5 μm with the growth 
monitored by reflection high energy electron dif-
fraction (RHEED). The samples were then trans-
ferred to an adjacent chamber and exposed at 
room temperature to sulphur vapour for 20 min at 
a pressure of ~2 × 10⁻⁵ mbar. The sulphur source 
was very simple: a gate valve to a stainless steel 
tube containing elemental sulphur. After sulphur 
dosing, the samples were capped with amorphous 
ar senic back in the MBE chamber before removal 
from the vacuum system. The samples were 
transported through air without any special pre-
cautions from Japan to the UK, providing a 
realistic test of passivation effectiveness. On in-
troduction to each of the analysis chambers, the 
ar senic cap and some amorphous sulphur were 
removed by slow annealing to 325 °C. This pro-
duced clean surfaces with oxygen and carbon 
contamination below the detection limit of XPS 
and HREELS. Subsequent 1 h anneals to higher 
temperatures were made to induce changes in the 
surface sulphur concentration and reconstruction.

HREEL spectra were obtained in a 45° specular 
geometry with typical instrumental resolution of 
7–10 meV. XPS measurements were carried out in 
a separate chamber using non-monochromated 
Al Kα radiation. Measurements were made at take 
off angles of 90° and 30° with respect to the sur-
f ace. The typical resolution was approximately 1.3 
eV. In both chambers, samples were heated radi-
atively, with temperatures measured by chromel– 
alumel thermocouples in direct contact with the 
samples.

3. Results

Typical LEED patterns obtained from the S– 
InAs(001) surface after different annealing stages 
are shown in Fig. 1. After annealing to 325 °C, 
only integer order LEED spots were observed. 
However, after a 350 °C anneal, a clear (2 × 1) 
reconstruction was observed, with a very low in-
tensity background (Fig. 1a). On further annealing
to 375 °C, the LEED pattern shows a “streaky” (4 × 1) reconstruction (Fig. 1b), evidence of a clean InAs(001) surface with disorder in the [110] direction [15]. It should be noted that under annealing conditions similar to those for producing the (2 × 1) surface after decapping, a (2 × 6) reconstruction could be observed by RHEED in the MBE chamber, with the sixth order diffraction streaks rather fainter than the rest of the pattern.

This reconstruction, as also observed on GaAs(001) after sulphur deposition, is closely related to the (2 × 1) reconstruction through a regular arrangement of missing dimers [16]. No sixth order diffraction spots were observed in LEED. This may reflect (1) better ordering of missing sulphur dimers between samples which do not leave the MBE system compared to the arsenic capped samples; and (2) differences between the sensitivity of RHEED and LEED to the ordering of missing dimers. We believe that the InAs(001)–(2 × 1)S surface observed in LEED is based on an incomplete coverage of sulphur dimers, with missing dimers showing no ordering in the [110] direction.

HREEL spectra obtained from the S–InAs(001) sample after annealing to 325 °C are shown in Fig. 2a. Solid lines represent dielectric theory simulations of the data (discussed in detail later) while symbols show experimental data, and three different probing electron energies are shown. Several features are immediately visible in the low energy phonon loss close to the elastic peak and in higher energy plasmon losses. Note that there are no vibrational energy loss modes in these spectra due to adsorbed sulphur, carbon, hydrogen or oxygen atoms. The phonon loss occurs at an energy of 33 meV, as opposed to the value of 29 meV expected for clean InAs [17]. Another striking feature is the width and complexity of the plasmon loss features (at around 100–200 meV). At lower electron energies the plasmon loss peak is extremely broad, making it difficult to determine a unique loss energy. This is indicative of large band bending near the surface, since the incident electrons are scattered by long range dipole interactions with sub-surface regions of different local plasma frequency.

Fig. 2b shows HREEL spectra obtained from the sample after annealing to 350 °C for 1 h to produce the ordered (2 × 1) surface. The phonon peak intensity is slightly increased compared to the case of 325 °C annealing, but now occurs at the expected loss energy of 29 meV. Again, the plasmon loss features are complex and actually show double peaks at higher electron energies. To our knowledge, this is the first time such complicated plasmon structures have been observed by
On annealing to 375 °C to produce the streaky (4 × 1) surface, phonon losses in the HREEL spectra do not change significantly (Fig. 2c) while all the plasmon features shift to lower loss energies.

The chemical state of the surface was monitored as a function of annealing temperature using XPS, and typical spectra are shown in Fig. 3. Note that it is not possible to observe any surface shifted components without using a synchrotron radiation source [9]. For the surface annealed to 325 °C (Fig. 3a–c), peak fitting of the indium spectra indicates two strong components at different energies, most likely due to bonding to both arsenic (bulk) and sulphur (surface) [9]. Examination of the O 1s region shows that the amount of oxygen on the surface is below the detection limit of the spectrometer, indicating that the higher binding energy component is indeed sulphur-related rather than due to a surface oxide. Observation of only one S 2p component (i.e. one spin–orbit integrated envelope) does not by itself indicate that only In–S bonding is present, since the S 2p peaks for both In–S and As–S bonding have been shown to occur at very similar energies in a higher resolution XPS study [9]. However, only one As 3d component is observed in our XPS data, implying that there is only In–As bonding and no As–S bonding.

For an annealing temperature of 350 °C (Fig. 3d–f), producing a (2 × 1) surface, the higher binding energy component of the In 3d_{5/2} peak is reduced in intensity, indicating the presence of less sulphur bound to indium. Approximate surface compositions were calculated using atomic sensitivity factors derived by Wagner et al. [18]. After annealing to 350 °C, the amount of sulphur at the (2 × 1) surface is somewhat less than 1 ML, about half that observed after annealing to 325 °C. The LEED results show that missing sulphur dimers have not formed an ordered array. It is also apparent that the In:As ratio also changes upon annealing. This ratio, using a take off angle of 30°, is approximately 2.2:1 after the 325 °C anneal, but is only 1.7:1 after the further anneal to 350 °C. These data are also in qualitative agreement with a previous CAICISS study [13], which reported a sulphur-for-arsenic exchange. On annealing to 375 °C, sulphur is desorbed from the surface (XPS spectra not shown here), leaving a surface identical to that found for clean InAs (In:As ratio of 1.4:1).

Fig. 2. Specular HREEL spectra from S–InAs(001) after annealing to (a) 325 °C, (b) 350 °C and (c) 375 °C, taken with incident electron energies of 10, 30, and 60 or 80 eV. All spectra are normalised to the specular elastic peak and the solid lines represent dielectric theory simulations.
4. Calculations and discussion

In Fig. 4, a summary is shown of the variations in plasmon loss frequency with incident probing energy for the sulphur treated InAs(001) surfaces after annealing to 325, 350 and 375 °C. Two trends are immediately apparent: firstly, the plasmon energy is smaller for higher temperature annealing; secondly, the plasmon energy drops for higher incident electron energy. The greatest variation in plasmon frequency comes after annealing to 325 °C. Over the incident electron energy range used,
the dispersion is more than 40 meV, while on annealing to higher temperatures the total dispersion drops to approximately 20 meV. The variation of plasmon energy with electron energy reflects the varying effective probing depth of specular HREELS [19]. The downward dispersion of the plasmon energy with increasing probing depth implies that the local plasma frequency drops deeper into the sample, i.e. that there is an electron accumulation layer. By comparison with the native accumulation layer at clean InAs(001) surfaces [12] the dispersion is very strong, especially for the 325 °C annealed samples, indicating a very high band bending and a large surface donor density.

One interesting and novel feature of the HREEL spectra (Fig. 2) is the appearance of a double plasmon feature. Both peaks decrease in energy with increasing incident probing energy, indicating plasmon behaviour. The more dominant peak, found at higher loss energies, decreases in intensity with increasing probing energy, while the lower energy plasmon increases slightly in intensity with increasing probing energy. These peaks are not multiple excitations of a single plasmon loss. For a given electron energy, the probing depth decreases with increasing excitation energy. The higher loss energy peak is associated with plasmon excitations at the surface due to electron accumulation. The lower loss energy peak is a consequence of plasmon excitations from both the electron accumulation region and the bulk, with the bulk contribution dominant. This is a direct result of extreme downward band bending.

The above considerations have been quantified by HREELS simulations based on dielectric theory and charge profile calculations based on the modified Thomas–Fermi approximation (MTFA). We have used this approach previously to successfully describe space-charge layers at the surfaces of narrow gap semiconductors [20,21]. The dielectric theory simulations shown in Fig. 2 were generated using the approach developed by Lambin et al. [22], modified for degenerate narrow gap materials [23]. Briefly, simulations are generated using a local dielectric function for each one of several uniform layers. The layer dielectric functions each contain a background term, a phonon term and a plasma term based on the hydrodynamic model. For simulations to be considered robust, all of the parameters are fixed over the entire incident probing electron energy range for a given anneal temperature. The only exceptions are the plasmon damping terms, which are allowed to vary with probing energy [24]. As can be seen, simulations reproduce the experimental data well with only a few deviations. It was necessary to use five or six layers in the simulations, more than previously necessary for satisfactory modelling of InAs accumulation layers [23]. This again indicates the rapidly varying charge profile near the surface due to extremely strong electron accumulation.

The plasma term in the local dielectric functions varies through the space-charge layer due to changes of Fermi level, local carrier density and carrier scattering rate. The most important parameter in the present case is the plasma frequency, which is related directly to the local Fermi level via an appropriate degenerate Kane band calculation [25]. To obtain a more accurate picture of band bending near the surface, along with information regarding surface state density, MTFA calculations were performed [20] in order to generate a smooth carrier concentration profile to

![Plasmon Energy vs Incident Electron Energy](image-url)
which layer structures from HREELS modelling could be compared. Fig. 5 shows the results of MTFA calculations together with the corresponding histogram profile used in the dielectric theory simulations, after the three annealing stages. All employ bulk carrier concentrations, in a semi-infinite base layer, of $1 \times 10^{17}$ cm$^{-3}$. Normally, a plasma free layer is included in the simulations of thickness 10–40 Å. This arises because the conduction band electron wave functions, which are constrained to be zero at the surface barrier, have non-zero wavelengths. For the most sulphur-rich surfaces (325 °C anneal), an uppermost carrier-free layer 6 Å thick with indium sulphide-like dielectric properties was needed in order to reproduce the altered phonon intensity and energy (Fig. 2a). Although it is not possible to make any firm claims about the phonon dielectric parameters of this layer, its presence is consistent with the XPS value of around 2 ML of sulphur at the surface.

The (2 × 1) surface with In–S bonding (350 °C anneal) shows a maximum carrier concentration of $8.3 \times 10^{18}$ cm$^{-3}$ in the accumulation layer, which is modelled by three layers, plus the bulk and carrier free surface layers (Fig. 5b). The carrier-free layer is of typical thickness (35 Å), although the band bending is much higher than for the clean surface at approximately 325 meV. The surface donor density is $9 \times 10^{11}$ cm$^{-2}$, similarly higher than for the clean surface. The surface atomic density of each atomic species in InAs is around $5.6 \times 10^{14}$ cm$^{-2}$ and so the fraction of surface sites associated with an ionised donor is around 0.16%. The downward band bending in this case is slightly smaller than that derived using photoemission from selenium-treated InAs(001), which showed a similar (2 × 1) reconstruction [14]. For the even more sulphur-rich disordered surface (325 °C anneal, Fig. 5a) the carrier concentration reaches a value of $3.3 \times 10^{19}$ cm$^{-3}$, the downward band bending is estimated at 600 meV and the surface donor density is $1.6 \times 10^{12}$ cm$^{-2}$ (0.29% of surface sites).

The sulphur-free (4 × 1) surface (375 °C anneal) shows the smallest carrier accumulation (Fig. 5c) and the native accumulation layer is accurately represented by two layers, plus the semi-infinite bulk and surface carrier-free layer. The accumulation layer has a peak carrier concentration of $3.5 \times 10^{18}$ cm$^{-3}$, the downwards band bending near the surface is 200 meV, and the surface state density is $4 \times 10^{11}$ cm$^{-2}$ (0.07% of surface sites). These values are typical for In-terminated InAs(001)-(4 × 1) surfaces [26]. For clean InAs(001) surfaces, the ionised surface donor density is known to be dependent on the reconstruction [12].

![Fig. 5. The MTFA electron density profiles for S-InAs(001) after annealing to (a) 325 °C, (b) 350 °C and (c) 375 °C, plotted as solid lines. Also shown are the corresponding histogram profiles used in the dielectric theory simulations (dotted lines).](image-url)
behaviour clearly extends to the sulphur- and selenium-induced reconstructed surfaces. Since the fraction of surface sites associated with an ionised donor is small (<0.3%) it appears that surface defects, whose density is reconstruction dependent, are responsible for the surface accumulation. The density of donor-like defects is highest for the disordered surface with high sulphur coverage (~2 ML).

Sulphide treatments can improve electrical characteristics of III–V surfaces over a timescale of several hours or more (e.g., [1,2]). It is also well known that polysulphide dipping of III–V materials provide sufficient chemical passivation to allow brisk transfer through air to a vacuum system without significant surface contamination occurring. Capping of III–V materials with amorphous group V layers is commonly used for longer transfers through air between an MBE machine and a separate surface analysis system. However, HREELS is highly sensitive to surface contamination, and it is quite often found that the spectra of Sb- or As-decapped III–V samples are marred by oxide vibrational modes, meaning that the capping/decapping procedure is not fully reliable [27]. However, the combination of sulphur termination and arsenic capping has allowed pristine and atomically clean surfaces to be regenerated even after a lengthy transit through air. It is suggested that this simple two-step method should protect III–V surfaces more reliably than group V capping alone, as well as allowing ordered sulphur-terminated surfaces to be regenerated after transit. This may be useful in multi-stage heteroepitaxial growth of widely different materials for which separate growth chambers may be used. For example, controlled nanocluster arrays can be grown on S- or Se-terminated III–V surfaces [28,29].

Achieving ‘electrical passivation’ of surfaces (or interfaces) depends primarily on reducing the density of surface (interface) states. This should result in a reduction of free carrier scattering or recombination by surface states as well as reducing the influence of the surface on the Fermi level. The lowest surface state densities for III–V materials are found on non-polar {110} surfaces freshly cleaved in a vacuum chamber, which display flat-band behaviour before contamination occurs [30,31]. At clean polar surfaces in ultra-high vacuum, the surface state density is typically $10^{11} - 10^{12}$ cm$^{-2}$. The states producing band bending at these surfaces are due to defects, since they occur at densities <1% of the surface atomic density. For most n-type III–V materials such as GaAs and InSb, the surface states act as acceptors and produce depletion layers near the surface, while on InAs they act as donors due to the unusual position of the conduction band minimum [12,17,32]. The density of ionised defect states on clean InAs polar surfaces is dependent on the reconstruction [12,24,27], although the exact nature of these defect states is unknown.

Turning to sulphur-terminated surfaces, the ionised surface states associated with sulphur adsorption on InAs also have defect character since the surface donor density is <1% of the surface density of sulphur atoms. These states are clearly donor-like and add to the electron accumulation. Ionised surface states on the sulphur-terminated surfaces of typical n-type III–V materials such as GaAs [8] and InSb [33] are also donor-like. However, since the native clean-surface defect states are acceptor-like for these materials, sulphur adsorption tends to reduce the overall surface charge density. In this sense, typical III–V material polar surfaces are indeed ‘electrically passivated’ relative to the clean surface by sulphur adsorption, whereas InAs surfaces are not. In all cases, the donor-like defects associated with sulphur-terminated surfaces are distinct from the native charged defects found on clean surfaces, although the precise nature of either defect type is unknown.

One result of changing the density of ionised surface states is that the scattering of conduction band electrons near the surface should be altered. In the present experiments, this is manifested in the apparent plasmon damping. The plasmon damping term varies as a function of both electron energy and depth and reflects a combination of electron scattering contributions from the bulk and surface as well as collisionless plasmon damping (Landau damping) [24]. The plasmon lifetimes in all layers of the present models are found to be substantially lower than those expected for undoped bulk InAs. This is due to the high con-
tribution of surface scattering and Landau damping over bulk scattering mechanisms throughout the wave vector and depth regime of the HREELS experiments. The plasmon lifetimes are about twice as long for the clean (4 × 1) surface as for both the (1 × 1)-S and (2 × 1)-S surfaces, which suggests that the combination of surface scattering and Landau damping is significantly higher for the sulphur-terminated surfaces. It is difficult to extract the precise contribution of Landau damping in the highly degenerate accumulation layer and so we are unable to distinguish between the two. However, the sulphur termination clearly does not lower the surface scattering rate relative to the clean surface: in this sense, no electrical passivation has occurred. This is expected given the increase of ionised surface state density after sulphur termination. There seems to be no significant difference in surface scattering between the (1 × 1)-S and (2 × 1)-S surface, despite the decrease of ionised surface state density.

5. Conclusions

It has been shown that the InAs(001) surface can be effectively protected from contamination using a combination of sulphur passivation and subsequent arsenic capping/decapping. Annealing at 325 °C removes the amorphous arsenic cap, leaving a disordered contamination-free sulphur-terminated InAs surface. This sulphur-rich surface (~2 ML sulphur) exhibits extreme downward band bending (up to 600 meV) and an ionised surface donor density of $1.6 \times 10^{12}$ cm$^{-2}$. The spectrum of surface plasmon excitations is complex. Annealing to 350 °C produces a (2 × 1) reconstructed surface with a surface donor density of $9 \times 10^{11}$ cm$^{-2}$ and a sulphur coverage of ~1 ML. A 375 °C anneal removes sulphur to produce a pristine InAs(001)-(4 × 1) surface with a typical native surface donor density of $4 \times 10^{11}$ cm$^{-2}$. This extends the previously reported reconstruction-dependent electron accumulation observed for clean InAs(001) surfaces [12]. The sulphur-terminated InAs(001) surfaces are not electrically passivated compared to the clean surface, in the sense of showing a reduced surface scattering rate or surface state density. This behaviour is different from typical n-type III–V material polar surfaces because of the different electrical behaviour of the native surface defects (normally acceptor-like) to that of the charged defects induced by sulphur termination (normally donor-like). For InAs, all such defects are donor-like.

Acknowledgements

The Engineering and Physical Sciences Research Council (UK) provided research studentships for MJL and TDV. GRB is grateful to the Royal Society (UK) for provision of a University Research Fellowship. This study was enabled through the Special Coordination Funds of the Ministry of Education, Culture, Sports, Science and Technology of the Japanese Government.

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