Surface electronic properties of clean and S-terminated InSb(001) and (111)B

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The electronic properties of clean and sulfur-terminated surfaces of InSb(001) and (111)B are investigated using x-ray photoemission spectroscopy and high-resolution electron energy loss spectroscopy. The clean surfaces exhibit upward band bending (electron deplation) consistent with the charge neutrality level in InSb lying at the valence band maximum. The surface Fermi level to valence band maximum separation is increased for the S terminated compared with the clean surface, leading to flat bands and downward band bending (electron accumulation) for the (001) and (111)B surfaces, respectively. This is discussed in terms of compensation of native acceptor surface states. © 2008 American Institute of Physics. [DOI: 10.1063/1.3000567]

I. INTRODUCTION

Following the discovery that the electronic properties of devices can be improved by coating the surface with sulfur-containing compounds, chemical and electronic passivation of III–V semiconductors by sulfur has been intensively investigated. Chemically, sulfur passivation aims to provide and maintain a surface free from atmospheric contaminants. This is important for device applications as the native oxides of III–V materials are generally considered unsuitable dielectrics. However, potentially more important is the electronic passivation. The breaking of the translational crystal symmetry at a surface or interface allows evanescent states to exist within the semiconductor band gap. These states act to pin the Fermi level at the surface/interface, largely independent of the bulk doping level or the properties of a contact made to the semiconductor. This Fermi level pinning prevents control of the barrier height of metal-semiconductor contacts, and the high density of surface states leads to high surface recombination. Electronic passivation aims to reduce (ideally to zero) the density of surface states within the semiconductor band gap, hence unpinning the surface Fermi level so that it occurs near to the value found in the bulk.

Sulfur can be chemisorbed at the surface by treating the samples in aqueous sulfur containing compounds, or in vacuo by gas-based methods, ultraviolet photosulphidation, or by depositing sulfur from an electrochemical cell. The influence of sulfur on the surface electronic properties of III–V materials to date has largely focused on GaAs, InP, InAs, and related alloys are favorable materials for use in long wavelength optoelectronic devices. Despite this technological importance, few investigations have been performed into sulfur passivation of these materials. Weiguo grew a thick (~300 Å) sulphide-oxide film on InSb and reported almost flat-band conditions to result. Ichikawa et al. observed a 6–7 monolayer (ML) sulphide layer formed following immersion of InSb in \((\text{NH}_3)_2\text{S}\) solution for 60 min. Annealing was observed to result in a breaking of Sb–S bonds (310 °C) and In–S bonds (400 °C) with a reduction in the unoccupied surface state density for S terminated in comparison to clean InSb inferred from inverse photoemission spectroscopy measurements.

In this paper, the surface chemical and electronic properties of InSb(001) and (111)B surfaces, following initial preparation by atomic hydrogen cleaning (AHC) and after S dosing from an electrochemical cell and various annealing treatments, are investigated. X-ray photoemission spectroscopy (XPS) provides information on the bonding of the sulfur atoms at the surface. High resolution electron energy loss spectroscopy (HREELS) is utilized to investigate the band bending at the surface of the material by probing the variation in near-surface conduction band plasmon energy. For the clean surfaces, depletion layers were found to occur with flat bands ([001] surface) and electron accumulation ([111]B surface) resulting following deposition of sulfur and annealing to break the Sb–S bonds. Upon desorption of all sulfur from the surface, depletion layers were recovered, restoring the upward band bending present for the clean surface prepared by AHC.

II. EXPERIMENTAL DETAILS

n-type Te-doped InSb(001) and undoped InSb(111)B wafers obtained from WaferTech, U.K. were grown by the Czochralski method and mechanically polished and chemically etched before being loaded into the vacuum chambers. The carrier concentration and electron mobility measured by the single-field Hall effect were \(5.3 \times 10^{17} \text{ cm}^{-3}\) and 12 800 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}, respectively, for the InSb(001) and 1.9 \times 10^{16} \text{ cm}^{-3}\) and 49 900 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}, respectively, for the InSb(111)B samples.

Room temperature XPS measurements were performed using a VG Scientific ESCALAB Mk I spectrometer. Al Kα x-rays of energy \(h\nu=1486.6\) eV were produced using a non-monochromated dual anode x-ray source. The ejected photoelectrons were analyzed by a 100 mm mean radius 150° spherical-sector electron energy analyzer. The effective instrumental resolution is \(~1.1\) eV derived from the Gaussian
convolution of the analyzer broadening and the natural line-
width of the x-ray source (~0.85 eV). Satellite peaks due to
the nonmonochromatic nature of the x-ray source are also
observed in the spectra. The predominant satellite observed
is from Al K\(\alpha_1\) x-rays, giving rise to an additional peak
located at a binding energy of 9.7 eV below each Al K\(\alpha_1\)
peak with an intensity of 7.3% of that of the main peak.\(^{18}\)
This was accounted for in the peak fitting.

Room temperature HREEL measurements were per-
formed using a VSW HREELS spectrometer in the specular
scattering geometry with incident electron energies in the
range of 7–60 eV. The spectrometer consisted of a fixed
monochromator and rotatable analyzer, both of the 180°
hemispherical deflector design with four-element entrance
and exit lens systems.

Initial surface preparation was achieved via AHC. The
AHC consisted of annealing the sample at \(\sim 125 \, ^\circ C\) under
exposure to a 5 kilo-Langmuir (kL) dose of molecular hy-
drogen passed through a thermal gas cracker with a cracking
efficiency of approximately 50%, followed by a further 20
kL hydrogen dose, while the sample was annealed to
\(\sim 200 \, ^\circ C\). XPS core level spectra for as-loaded and AHC
treated InSb(001) are shown in Fig. 1. Before AHC, two
components are required to fit the In 3d\(_{5,2}\) peak, attributed to
In–Sb and In–O bondings, in addition to satellite features
arising from the In 3d\(_{5,2}\) peak. Three main components were
required to fit the Sb 3d\(_{5,2}\) region of the spectrum, attributed to
Sb–In and Sb–O bondings, as well as an O 1s core-level com-
ponent (~531 eV), which overlaps the Sb 3d\(_{5,2}\) region of the
spectrum. Additionally, a large C 1s peak was ob-
served. Upon AHC, the O- and C-related components are
quenched.

An electrochemical sulfur cell based on the design of
Heegemann \textit{et al.} \(^{19}\) held at a temperature of \(\sim 275 \, ^\circ C\) was
used for deposition of sulfur on the clean InSb(001) and
(111)B surfaces. Dosing times were 30 min. Following dos-
ing, the (001) [(111) B] sample was annealed successively
for 1 h at 200, 300, 350, and 400 \(^\circ C\) (200, 300, 400, and
450 \(^\circ C\)).

![FIG. 1. In 3d\(_{5,2}\), Sb 3d\(_{5,2}\), and C 1s XPS core level spectra from InSb(001)
before [(a)–(c)] and after [(d)–(f)] surface preparation by AHC. The In 3d\(_{5,2}\)
and Sb 3d\(_{5,2}\) peaks have been fitted using a Shirley background and Voigt
(mixed Lorentzian–Gaussian) line shapes, shown vertically offset for clarity.](image1)

FIG. 1. In 3d\(_{5,2}\), Sb 3d\(_{5,2}\), and C 1s XPS core level spectra from InSb(001)
before [(a)–(c)] and after [(d)–(f)] surface preparation by AHC. The In 3d\(_{5,2}\)
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(mixed Lorentzian–Gaussian) line shapes, shown vertically offset for clarity.

![FIG. 2. In 3d\(_{5,2}\), Sb 3d\(_{5,2}\), and S 2p XPS core level spectra from InSb(001)
after AHC [(a) and (b)], sulfur dosing and annealing to 300 \(^\circ C\) at normal
emission [(c)–(e)] and at an emission angle of 30° [(f)–(h)], and at normal
emission after sulfur dosing and annealing to 400 \(^\circ C\) [(i)–(k)]. All peaks
have been fitted using a Shirley background and Voigt (mixed Lorentzian–
Gaussian) line shapes, shown vertically offset for clarity. Peak assignments
are indicated by dashed vertical lines.](image2)

FIG. 2. In 3d\(_{5,2}\), Sb 3d\(_{5,2}\), and S 2p XPS core level spectra from InSb(001)
after AHC [(a) and (b)], sulfur dosing and annealing to 300 \(^\circ C\) at normal
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are indicated by dashed vertical lines.

### III. RESULTS, ANALYSIS, AND DISCUSSIONS

#### A. InSb(001)

Core level XPS spectra from InSb(001), following sur-
face preparation by AHC and after S dosing and annealing to
300 and 400°C, are shown in Fig. 2. All peaks have been
fitted using a Shirley background and Voigt (mixed
Lorentzian–Gaussian) line shapes.

After AHC, a single component due to In–Sb bond-
ing was observed in the In 3d\(_{5,2}\) and Sb 3d\(_{5,2}\) core levels at 444.3
and 527.9 eV, respectively. Additionally, satellite peaks due
to the In 3d\(_{5,2}\) and Sb 3d\(_{5,2}\) core levels were observed. The
lack of oxide or carbon components in the XPS spectra indi-
cates the preparation of a clean surface, as discussed
above.

HREEL spectra for a variety of incident electron ener-
gies from the clean surface are shown in Fig. 3(a). The
Fuchs–Kliewer surface phonon mode occurs at \(\sim 23 \, meV\) in
InSb (Refs. 20–22) and, for the bulk carrier concentration of
the InSb(001) sample used in this work, a bulk conduction
band plasmon frequency of \(\sim 40 \, meV\) would be expected.
Due to the proximity of these energies, the phonon and plas-
mon couple resulting in a plasmon mode, which is ob-

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observed in the HREEL spectra with a loss energy of ~35 meV. A slight dispersion of the plasmaron mode to higher loss energies is observed with increasing incident electron energy, indicating an increase in the carrier concentration with increasing depth below the surface, suggesting the presence of a depletion layer at the surface, as has previously been observed by HREELS at clean InSb surfaces.  

To obtain a more quantitative analysis of the variation in carrier concentration in the near-surface region, the HREEL spectra were simulated using semiclassical dielectric theory, as developed by Lambin et al. A multilayered dielectric function (DF) model is utilized to describe the variation in electronic properties with depth normal to the surface, with the DF of each layer described in the hydrodynamic model used here by

\[
\epsilon(q, \omega) = \epsilon(\infty) \left[ 1 + \frac{\epsilon(0) - \epsilon(\infty)}{\omega_p^2} \frac{\omega_{\text{TO}}^2}{\omega_{\text{TO}}^2 - \omega^2 + i \Gamma \omega} \right]
\]

where \( q \) and \( \omega \) are the wave vector and frequency of the excitation, \( \epsilon(0) [\epsilon(\infty)] \) is the static [high frequency] dielectric constant of the material, \( \omega_{\text{TO}} \) is the frequency of the transverse optical phonon, \( \omega_p \) is the frequency (lifetime) of the conduction band plasmon, and \( \beta \) is the spatial dispersion coefficient. The plasma frequency is related to

\[
\alpha = \frac{n e^2}{\varepsilon_0 \epsilon(\infty) \langle m^*(E) \rangle^{1/2}},
\]

where \( \langle m^*(E) \rangle \) denotes the density of states averaged momentum effective mass

\[
\langle m^*(E) \rangle = \frac{\int_{-\infty}^{\infty} g(E) m^*(E) f(E) dE}{\int_{-\infty}^{\infty} g(E) f(E) dE},
\]

where \( g(E) \) is the density of states and \( f(E) \) is the Fermi–Dirac factor and the momentum effective mass

\[
m^*(E) = \hbar^2 \left| \frac{dE(k)}{dk} \right|^{-1}.
\]

The effective mass is energy dependent due to the distinct nonparabolicity of the conduction band, which is described here in the Kane formalism. The InSb material parameters used are listed in Table I.

A two-layer DF model consisting of a carrier-free layer atop a semi-infinite layer representing the bulk of the semiconductor was found to be sufficient to reproduce the measured HREEL spectra. The dielectric theory simulations resulting from such a two layer model are shown in Fig. 3(a) and exhibit good agreement with the experimental HREEL spectra for all excitation energies. The plasma frequency layer profile is converted into a carrier concentration histogram profile, shown in Fig. 4(a), using Eqs. (2)–(4) and consists of a carrier-free layer of 185 Å thickness, followed by a semi-infinite layer of carrier concentration \( 4.6 \times 10^{17} \text{ cm}^{-3} \), very close to the bulk carrier concentration measured by the single field Hall effect. The large thickness of the carrier-free layer required to simulate the HREEL spectra confirms the presence of a depletion layer at the semiconductor surface.

Realistic charge profiles calculated by solving Poisson’s equation within a modified Thomas–Fermi approximation (MTFA) (Refs. 28 and 29) as described elsewhere were compared to the histogram charge profiles in order to determine the band bending, position of the Fermi level at the surface, and the surface state density for the clean InSb(001) surface. From this, an upward band bending of 0.15 ± 0.05 eV is determined at the clean surface, corre-
band bending present, the surface Fermi level is determined by the background positively charged donor ions in the electron conduction band. Negatively charged acceptor ViGS are compensated by the Fermi level upward at the surface leading to a depletion of electrons in the conduction band minimum (CBM) at the surface. The ViGS are specific to a given surface reconstruction and are affected by the presence of any adatoms on the surface. In the theoretical estimates of the Fermi level at the VBM upon irradiation\(^{32}\) indicates that the CNL lies at the VBM in InSb.

If the Fermi level is located above the CNL at the surface, a number of acceptor ViGS will be occupied, and hence negatively charged, although the exact density of acceptor ViGS is specific to a given surface reconstruction and is affected by the presence of any adatoms on the surface. In the presence of a negative surface charge, the bands must bend upward at the surface leading to a depletion of electrons in the near surface region, maintaining charge neutrality—the negatively charged acceptor ViGS are compensated by the background positively charged donor ions in the electron depletion region. From the bulk Fermi level and the upward band bending present, the surface Fermi level is determined to lie 0.11 ± 0.05 eV above the VBM, and hence below the conduction band minimum (CBM). The depletion layer observed here indicates that the Fermi level at the surface must be pinned slightly above the CNL and is consistent with the CNL lying at the VBM. This rather low location of the CNL relative to the band edges in InSb can be understood by considering the high energy of the Sb 5\(p\) atomic orbital, \(p\) \(-d\) repulsion due to the occupied In 4\(d\) orbitals and the large spin-orbit splitting, which all push the \(p\)-like VBM to high energies on an absolute energy scale.\(^{33}\)

Sulfur was deposited on the clean surface. XPS core-level spectra (not shown) revealed the formation of In–S and Sb–S bonds, in addition to In–Sb bonds, and also some carbon contamination (attributed to residual contamination from the electrochemical sulfur source). C–H vibrational modes and a broadening of the elastic peak were also observed in the HREEL spectra of the S-dosed surface (not shown), indicating some carbon contamination and a reduction in the degree of surface order, respectively, following S dosing.

Annealing the sample to 200 °C resulted in the breaking of Sb–S bonds, revealed by core-level XPS spectra (not shown), although some carbon was still present on the surface. Further annealing to 300 °C was sufficient to remove this carbon and also resulted in a slight increase in the In:Sb ratio determined from the XPS core levels, attributed to the formation of In–S bonds at the expense of In–Sb bonds at the surface. The XPS core-level spectra following this annealing treatment are shown in Fig. 2.

A clear S 2\(p\) peak is evident, indicating the presence of S at the surface. The In 3\(d_{\text{ill}}\) core-level peak is well described by two components in addition to satellite features from the In 3\(d_{\text{ilv}}\) core-level peak. The lower binding energy component at 444.6 eV is attributed to In–Sb bonding. The higher binding energy component at 445.3 eV is attributed to In–S bonding. The separation of these components is of the order of that previously observed for In–Sb and In–S bonds.\(^{34,35}\) Additionally, the area of the In–S component increases relative to that of the In–Sb component on moving to more grazing (and hence more surface sensitive) emission angles [Figs. 2(e) and 2(f)], supporting the assignment of In–S bonding at the surface. The Sb 3\(d_{\text{ill}}\) peak consists of only a single Sb–In component at 528.3 eV binding energy (and a satellite of the Sb 3\(d_{\text{ilv}}\) peak), indicating that no S is bonded to Sb after a 300 °C anneal. The In–Sb bonding components of the In 3\(d_{\text{ilv}}\) and Sb 3\(d_{\text{ilv}}\) core-level peaks are shifted to higher binding energies by ~0.3 eV following the S dosing and 300 °C annealing compared with after the AHC treatment. This suggests that the surface Fermi level is located higher above the VBM following the S dosing and annealing than for the clean surface, although accurate quantification of the shift via XPS would require high resolution valence band photoemission to directly determine the VBM to surface Fermi level separation in each case.

After a further annealing treatment at 350 °C, very similar XPS spectra were obtained although the elastic peak of the HREEL spectra showed a reduction in width with successive annealing treatments, indicating an improvement in surface order. The sulfur coverage was estimated as 1.4 ML using the inelastic mean free path of the photoelectrons calculated using the TPP-2M predictive formula of Tanuma et al.\(^{36}\)

HREEL spectra following the 350° anneal are shown in Fig. 3(b). Very little dispersion is observed in the plasmon
peak as a function of incident electron energy, indicating that the charge profile varies much less in the near surface region than for the clean surface. Three-layer dielectric theory simulations were required to simulate the HREEL spectra. The first layer is a thin (2 Å) carrier-free layer with the dielectric constants modified to represent the differing properties of an InS surface layer. A further 20 Å carrier-free layer (with InSb properties) followed by a semi-infinite InSb layer with a carrier concentration \( n = 4.87 \times 10^{17} \text{ cm}^{-3} \) were required to simulate the spectra. This carrier concentration is slightly higher than the bulk carrier concentration used to simulate the clean surface spectra, and this may be due to a small amount of sulfur diffusing into the subsurface region and acting as an \( n \)-type dopant.

The carrier-free layer thickness is much smaller than for the clean surface, as shown in Fig. 4, indicating a drastic reduction in the band bending compared with the clean surface. Calculated charge profiles and band bending at the surface for a small band bending of \( \pm 0.01 \) eV are shown in Figs. 4(b) and 4(e), respectively. As the surface acts as an almost infinite potential barrier, the wave functions of the carriers must have zero amplitude at the surface, and hence the carrier concentration tends smoothly to zero, requiring a “dead layer” at the surface regardless of the type of space-charge layer.\(^3\) It is therefore difficult to distinguish between the flat band condition (where there is no band bending at the surface) and small amounts of accumulation or depletion at the surface, as evident from Fig. 4(b). However, the band bending is clearly very small in this case resulting in approximately flat band conditions with a band bending at the surface from 0.00 \( \pm 0.01 \) eV. Thus, the sulfur effectively passivates the electron depletion.

The Fermi level is located significantly higher at the surface (0.09 \( \pm 0.01 \) eV above the CBM) and is thus located further above the CNL than for the clean surface. As acceptor-like VIGS are the dominant species above the CNL, this would be expected to lead to a higher density of occupied (and hence negatively charged) VIGS than for the clean surface, and hence a higher (more negative) surface state density resulting in a greater depletion width. However, the band bending is reduced to zero here, resulting in an approximately zero space charge. Two mechanisms are possible to maintain charge neutrality. First, sulfur bonded to indium at the surface acts as a donor donating an electron into the depletion layer, hence reducing the depletion. A positive S ion is therefore left at the surface, which passivates the negative surface charge. Second, the intrinsic surface state distribution may be modified by the dosing of S on the clean surface. A diffuse (1 \( \times \) 1) low-energy electron diffraction (LEED) pattern was observed here at 45 eV incident electron energy on the S-terminated surface, which may be a slightly disordered version of the (2 \( \times \) 1) surface reconstruction, which has previously been observed on an ammonium sulphide treated InSb(001) surface following annealing to 310 °C.\(^{17}\) This is in contrast to the (4 \( \times \) 2)/\( c(8 \times 2) \) reconstruction commonly observed at clean InSb(001) surfaces, which was also observed by LEED here following AHC and following the desorption of all sulfur from the surface. A reduction in the density of unoccupied dangling bond states was reported from inverse photoemission measurements for the (2 \( \times \) 1) reconstruction;\(^3\) such a change could be partly responsible for the reduction in band bending at the surface of S-terminated InSb(001).

Further annealing of the sample to 400 °C breaks the In–S bonds, and the S is completely desorbed from the surface, indicated by the quenching of the S 2p and In–S component of the In 3d XPS core level peaks [Figs. 2(k) and 2(i)]. The In–Sb components are also located at very similar binding energies as for the AHC surface (444.3 and 528.0 eV for the In 3d\( \_2 \) and Sb 3d\( \_2 \) core levels, respectively), suggesting the surface electronic properties are like those of the AHC surface. Indeed, the HREEL spectra following this anneal [Fig. 3(c)] are very similar to those of the AHC surface and are well simulated assuming a carrier-free layer of thickness 160 Å at the surface and a semi-infinite layer with a carrier concentration \( n = 5.27 \times 10^{17} \text{ cm}^{-2} \). The slightly higher “bulk” carrier concentration compared with after the previous treatments is again attributed to additional subsurface diffusion of S. The slightly smaller depth of the carrier-free layer compared with the AHC surface may also be due to this higher bulk carrier concentration reducing the screening length for the space-charge region.

Again, realistic smooth charge profiles were calculated to determine the band bending at the surface, and good agreement with the HREEL histogram charge profile was achieved for an upward band bending of 0.15 \( \pm 0.05 \) eV as for the AHC surface, corresponding to a surface state density of \( (10.5 \pm 2.6) \times 10^{11} \text{ cm}^{-2} \), very similar to that of the AHC surface. Once the sulfur is desorbed from the surface, the surface states will no longer be compensated by the sulfur ions, leading to the reformation of a depletion layer as for the AHC surface. Additionally, a \( (4 \times 2)/c(8 \times 2) \) surface reconstruction was observed by LEED after desorption of the sulfur as for the AHC surface, and so any reconstruction related change in the distribution of intrinsic acceptor surface states between the clean surface and the surface following desorption of the sulfur would not be expected.

B. InSb(111)B

The chemical nature of the (111)B surface after AHC, S dosing, and various annealing stages was very similar to the (001) surface, revealed by core-level XPS measurements (not shown), although In–S bonds remained on the surface with annealing treatments up to 400 °C. This indicates that the S-terminated surface is slightly more thermally stable for the (111)B surface than the (001) surface with a breaking of the In–S bonds and desorption of sulfur from the surface being achieved only after annealing at 450 °C. After annealing to 400 °C, the sulfur coverage was estimated to be \( \sim 2 \) ML.

HREEL spectra for an excitation energy of 10 eV after AHC, S dosing, and annealing to 400 °C and 450 °C are shown in Fig. 5. The bulk carrier concentration for the (111)B sample was low, resulting in the loss-related features in the HREEL spectra consisting of a shoulder on the elastic peak. The shoulder becomes much more pronounced after S dosing and annealing at 400 °C, indicating the presence of a higher electron concentration in the near surface region for
the S-terminated surface, although further qualitative analysis of the HREEL spectra is limited due to the low carrier densities involved. Dielectric theory simulations of the HREEL spectra have been performed for five excitation energies ranging from 8 to 60 eV, enabling quantitative analysis.

The HREEL spectra for the clean (111)B surface prepared by AHC were well reproduced using a two-layer model: a 160 Å carrier-free layer followed by a semi-infinite layer with a carrier concentration \( n = 2.4 \times 10^{16} \text{cm}^{-3} \), similar to the bulk carrier concentration determined by the single field Hall effect. Although lower than for the (001) sample, the bulk Fermi level in the (111)B sample still lies above the CNL. Consequently, the surface Fermi level will also lie above the CNL and a number of acceptor ViGS will still be occupied, hence negatively charged, leading to an upward bending of the bands and electron depletion at the surface, as for the (001) surface. Poisson-MTFA charge profiles have again been calculated, and those showing the best agreement with the HREELS histogram charge profiles are shown in Fig. 6. For the clean (111)B surface, an upward band bending (surface state density) of \( 0.03 \pm 0.02 \text{eV} \) \((-8.0 \pm 3.6 \times 10^{10} \text{cm}^{-3}\)) has been determined, resulting in the Fermi level at the surface being pinned above the CNL, as required for acceptor ViGS to be occupied. The smaller amount of band bending in the depletion layer observed here than for the (001) sample is predominantly due to the lower bulk Fermi level in this case.

Sulfur dosing and annealing to 400 °C resulted in a S-terminated surface with S-In bonds but no S-Sb bonds present, as identified by XPS measurements. Dielectric theory simulations of the HREEL spectra following this treatment required a four-layer model consisting of a 3 Å InS carrier-free layer, a 15 Å InSb carrier-free (dead) layer, a 225 Å layer of carrier concentration \( n = 2.3 \times 10^{17} \text{cm}^{-3} \), and a semi-infinite layer of carrier concentration \( n = 2.4 \times 10^{16} \text{cm}^{-3} \). The third layer having a significantly higher carrier density than that of the bulk indicates the presence of an electron accumulation layer at the S-InSb(111)B surface.

Comparison of Poisson-MTFA charge profiles with the HREELS histogram charge profile indicates a downward band bending of \( 0.12 \pm 0.02 \text{eV} \) for the S-terminated InSb(111)B surface.

This pronounced downward band bending results in the Fermi level at the surface being located substantially above the CBM and a large accumulation of electrons in the near surface region as shown in Fig. 6. The absolute shift in the surface Fermi level position between the AHC and S-treated surface after annealing to 400 °C is similar to that for the (001) surface between AHC and S dosing and annealing to 350 °C \((-0.15 \text{eV}\) ), suggesting a similar mechanism is responsible for the shift in both cases. Considering the difference in bulk Fermi levels, a similar shift in the surface Fermi level as for the S-InSb(001) surface is sufficient to induce a pronounced electron accumulation at the S-InSb(111)B surface. The Fermi level lies significantly above the CNL at the S-terminated (111)B surface suggesting that acceptor ViGS will be occupied and hence negatively charged. These will be compensated by S donors at the surface, as was proposed for the (001) surface. This mechanism is supported by the plasmon lifetime values required in the dielectric theory simulations of the HREEL spectra, which were higher for the clean surface (both AHC and after sulfur desorption) than for the S-terminated surface. This suggests that the presence of the sulfur increases the carrier scattering; the sulfur is charged, acting as an ionized impurity at the surface. The ionized sulfur therefore acts to compensate the acceptor surface states. However, as for the (001) surface, a change in the intrinsic distribution of surface states with surface recon-

![Fig. 5](image1.png)

**Fig. 5.** (Color online) InSb(111)B HREEL spectra (open circles) normalized to the elastic peak intensity after (a) AHC, (b) sulfur dosing and annealing to 400 °C, and (c) sulfur dosing and annealing to 450 °C for an excitation energy of 10 eV and corresponding semiclassical dielectric theory simulations (solid lines). The spectra are vertically offset for different S dosing and annealing treatments for clarity.

![Fig. 6](image2.png)

**Fig. 6.** (Color online) (a) InSb(111)B Poisson-MTFA carrier concentration profiles and (b) corresponding band bending profiles following AHC, sulfur dosing and annealing to 400 °C, and sulfur dosing and annealing to 450 °C.
struction for the S-terminated surface cannot be ruled out as a possible cause of some changes in surface Fermi level pinning position.

Annealing of the sample to 450 °C to desorb the sulfur resulted in a depletion layer very similar to that of the AHC surface. A slightly higher bulk Fermi level was required to simulate the HREEL spectra (2.9 × 10^16 cm^-3 as opposed to 2.4 × 10^16 cm^-3 for the AHC preparation), which is attributed to the diffusion of a small amount of sulfur into the near-surface region, acting as an n-type dopant, as was observed for the (001) surface.

The HREELS analysis presented above for the (111)B surface is consistent with the positions of the XPS core level peaks, which show, as for the (001) surface, a shift of ~0.3 eV to higher binding energies for the S terminated compared with the clean surface. This indicates that the VBM to surface Fermi level separation is greater for the S terminated than the clean surface, as found from the analysis of the HREELS spectra.

Following preparation of the (111)B surface by AHC, a (√3 × √3)R30° reconstruction was observed by LEED, as shown in Fig. 7(a). This reconstruction is believed to be Sb-rich by analogy with the As-rich GaAs(111)B (√3 × √3)R30° reconstruction and is likely observed here due to the low-temperature AHC procedure used to prepare the clean surface. In contrast, following desorption of sulfur from the surface, a (3 × 3) reconstruction was observed [Fig. 7(c)]. The very similar surface electronic properties observed for the two different clean-surface reconstructions indicate that the distribution of intrinsic surface states may not be especially sensitive to the surface reconstruction in this case.

IV. CONCLUSIONS

The clean and sulfur-terminated surfaces of InSb(001) and (111)B have been investigated using x-ray photoemission spectroscopy and high-resolution electron energy loss spectroscopy. Depletion layers were observed at the clean (001) and (111)B surfaces prepared by AHC. This was explained within the theory of VIGS and is consistent with the CNL in InSb lying at the VBM.

Dosing with sulfur from an electrochemical cell resulted in In–S and Sb–S bond formation, although after annealing to 350 °C (400 °C) for the (001) [(111)B] surface, an ordered S-terminated surface remains with only In–S bonds present. The S termination caused an increase in the surface Fermi level for both surface orientations of ~0.15 eV, resulting in approximately flat band conditions for the (001) surface and a pronounced electron accumulation for the (111)B surface. This was attributed to compensation of intrinsic acceptor surface states above the CNL by ionized sulfur. Annealing to 400 °C (450 °C) resulted in desorption of sulfur from the (001) [(111)B] surface. Depletion layers very similar to those found on the clean surface prepared by AHC were recovered, even for the (111)B surface where a (√3 × √3)R30° reconstruction was observed following the AHC treatment, in comparison to a (3 × 3) reconstruction for the S-desorbed surface.