The electronic properties of Si(001)-Bi(2×n)

A. G. Mark†, J. A. Lipton-Duffin‡, J. M. MacLeod†, R. H. Miwa‡, G. P. Srivastava§ and A. B. McLean†

E-mail: mclean@physics.queensu.ca
† Department of Physics, Queen’s University, Kingston, Ontario, Canada, K7L 3N6
‡ Faculdade de Física, Universidade Federal de Uberlândia, C.P. 593, 38400-902, Uberlândia, MG-Brazil.
§ School of Physics, University of Exeter, Stocker Road, Exeter, EX4 4QL, UK.

Abstract. A Bi 2×n surface net was grown on the Si(001) surface and studied with inverse photoemission, scanning tunneling microscopy and ab initio and empirical pseudopotential calculations. The experiments demonstrated that Bi adsorption eliminates the dimer related \(\pi^*\) and \(\pi^*_2\) surface states, produced by correlated dimer buckling, leaving the bulk band gap clear of unoccupied surface states. Ab initio calculations support this observation and demonstrate that the surface states derived from the formation of symmetric Bi dimers do not penetrate the fundamental band gap of bulk Si. Since symmetric Bi dimers are an important structural component of the recently discovered Bi nanolines, that self-organize on Si(001) above the Bi desorption temperature, a connection will be made between our findings and the electronic structure of the nanolines.


PACS numbers: 73.20.Hb, 70.20.At, 71.20.Mq
1. Introduction

The Si(001)/Bi monolayer system (Fig. 1) is important because Bi can be used as a strain-relaxing surfactant in Si/Ge hetero-epitaxy (Sakamoto et al. 1993). Below the Bi desorption temperature of $T_d \approx 500^\circ C$, Bi forms a $2\times n$ surface net on Si(001) (Appelbaum et al. 1976, Rohlfing et al. 1995, Gay et al. 1998a, Gay et al. 1998b, Asahi et al. 2000). Whereas the $2\times$ periodicity is caused by Bi dimer formation, the $n\times$ periodicity is caused by the formation of ordered rows of Bi dimer vacancies (Naitoh et al. 1997, Park et al. 1994, Bowler & Owen 2002). The vacancy rows relax overlayer strain and the value of $n$ lies in the range 5-12, depending on both the Bi coverage and the annealing temperature (Park et al. 1994). The formation of the dimer vacancies is expected because the covalent radii of Bi (1.46 Å) and Si (1.17 Å) are very dissimilar.

In this paper we report the results of an investigation of the $2\times n$ phase using inverse photoemission, scanning tunneling microscopy (STM) and ab initio and empirical pseudopotential calculations. Interestingly, recent studies of Bi growth on Si(001) surfaces above $T_d$ have discovered a self-organized nanoline motif with an exceptionally high degree of structural order (Naitoh et al. 1997, Naitoh et al. 1999, Miki, Matsuhata, Sakamoto, Briggs, Owen & Bowler 1999, Miki, Bowler, Owen, Briggs & Sakamoto 1999, Naitoh et al. 2000, Naitoh et al. 2001, Bowler & Owen 2002, Owen, Miki, Koh, Yeom & Bowler 2002, Owen, Bowler & Miki 2002, Owen et al. 2003). These lines can be grown to lengths of up to 500 nm without breaks or kinks (Miki, Bowler, Owen, Briggs & Sakamoto 1999, Owen et al. 2003) and the growth of the lines is thought to involve the reconstruction of up to three silicon layers (Owen, Miki, Koh, Yeom & Bowler 2002). The aim of the present study is to provide a more complete understanding of the geometric and electronic structure of the $2\times n$ phase. The $2\times n$ overlayer phase is structurally simpler than the nanoline phase. In particular, we wanted to experimentally confirm the presence of the symmetric Bi dimers in the $2\times n$ phase because it is thought that the $2\times n$ phase and the nanolines share the symmetric Bi dimer as a common motif.

2. Experimental and Theoretical Details

The experimental studies were performed with an inverse photoemission system (Lipton-Duffin 2001, Lipton-Duffin et al. 2002, Lipton-Duffin et al. 2004) and also a beetle-type STM (MacLeod et al. 2003) using a Pt-Ir tip that was sharpened by field emission. The inverse photoemission system has a Stoffel-Johnson electron source (Stoffel & Johnson 1984) and two Geiger-Müller photon detectors (Johnson & Hulbert 1990) that are run concurrently to maximise the solid-angle of detection. Ethanol was used as a self-quenching detection gas in the photon detectors (Lipton-Duffin et al. 2002) and gating electronics were used to correct for the finite detector dead-time ($\approx 150 \mu s$) (Lipton-Duffin et al. 2002). The detectors have a mean detection energy of $\hbar \omega_d=(10.61\pm 0.07)eV$ and a bandpass of $\Delta \hbar \omega_d=(0.35\pm 0.05)eV$.

N-type Si(001) wafers, with resistivities in the range of 5.2-7.2 $\Omega cm$ (Virginia
The electronic properties of Si(001)-Bi(2×n) Semiconductors) were diced into rectangular samples with a width of 6 mm and a length of 17 mm. Following an overnight degas, atomically ordered surfaces were prepared by resistively heating the samples to 1260°C for 40 s while maintaining the chamber pressure below 5×10⁻¹⁰ Torr, annealing at 1000°C for 180 s, and then cooling the sample at a rate of ≈ 1°C/s. This procedure yielded sharp two-domain Si(001)(2×1) low energy electron diffraction (LEED) patterns, with a low background. High purity Bi was evaporated from a boron nitride crucible at rates that lay in the range 0.1-0.3 Å/min. During deposition the substrate was raised up to a maximum temperature of 400°C and after deposition the overlayers were annealed at this temperature for up to 15 min. Diffraction patterns had superlattice spots consistent with the formation of a double domain 2×n overlayer. Attempts were made to grow single domain Si(001)-Bi(2×1) overlayers on vicinal Si(001) surfaces (Cricenti A. et al. 1993). However, our studies did not provide surfaces with clear single domain structure and consequently we did not perform momentum-resolved studies off-normal.

Theoretical calculations were made by considering a full monolayer of Bi, forming the Si(001)-Bi(2×1) structure, shown in Fig. 2, characterized by the breaking of Si dimers and the formation of Bi dimers along the original Si dimer rows. The non-local pseudopotential method, together with the local density approximation (LDA), was applied to an artificially repeated supercell geometry. A plane wave basis set, up to a 12 Ryd kinetic energy cut-off, was used. This is 4 Ryd higher than used previously (Gay et al. 1998a) allowing us to expand the basis set. Details of the method, the atomic geometry and some previously published theoretical results for this system can be found elsewhere (Srivastava 1999, Gay et al. 1998a). We have not performed quasi-particle calculations in this study because we are primarily interested in the changes in the surface electronic structure that are induced by Bi adsorption. It has previously been shown that the major difference between quasi-particle bands and the LDA bands is that the unoccupied quasi-particle bands are rigidly shifted to higher energy. Consequently, a direct comparison of the Si(001)(2×1) and the Si(001)-Bi(2×1) DOS calculated using the LDA is sufficient for our purposes.

3. Results

A constant-current STM topograph collected from a Bi covered Si(001) surface that displayed clear 2×n order with \( n = 6 \pm 0.8 \) and some second monolayer Bi growth is shown in Fig. 3. The surface contains two 2×n domains that are separated by a single height step and related by a rotation of \( \pi/2 \). Areas of the surface that have dimer rows running approximately vertical have been labeled \( v \) and areas for the surface that have dimer rows running approximately horizontal have been labeled \( h \). The presence of two surface phases is expected because Si has the diamond crystal structure and a single height step (\( \frac{1}{4}a_0 \) where \( a_0 \) is the cubic lattice constant) rotates the tetrahedral bonding directions by \( \pi/2 \). In the STM image, the Bi-dimers within the rows appear to be symmetric. There are, for example, no pinned zig-zag dimer rows near surface defects.
that are frequently found on Si(001) surfaces. On Si(001) the $\pi$-like surface bands for a symmetric dimer configuration are half full and the surface can lower its energy by allowing the dimers in the surface layer to asymmetrically tilt. Although the geometric structure of the Si(001) and the Si(001)-Bi(2×1) systems are similar, the fact that Bi has one extra valence electron means the $\pi$-like surface bands are full and tilting the Bi dimers does not produce the same energy gain.

The image reproduced in Fig. 3 was taken with negative sample bias (full states). We found that the surface was difficult to image with positive sample bias (empty states). This observation is consistent with the results of the inverse photoemission study to be described below. In this particular case, 1.5 ML of Bi was deposited over 13 mins onto a Si(001) surface that was maintained at a temperature of 590°C. The surface was not post-annealed and regions of the surface, as might be expected from the temperature during deposition, also contained Bi nanolines (not shown). However, this part of the surface displays 2×n order with some additional second layer Bi growth.

In Fig. 4(a) an isochromat inverse photoemission spectrum collected at the center of the surface zone ($\Gamma$) from the two-domain Si(001)(2×1) surface is presented together with a spectrum that was collected at $\Gamma$ from an ordered Si(001)-Bi(2×n) overlayer (Fig. 4(b)). The lower spectrum has been shifted by 0.35 eV, to line up the feature marked $\beta$ and, to first order, 0.35 eV is the Bi-induced band bending shift. The sign and magnitude of the band bending shift is in good agreement with the results of recent core-level photoemission studies of Bi adsorption on Si(001) using synchrotron radiation (Corradini et al. 1999). The $\pi_1^*$ and $\pi_2^*$ surface states were probed at $k_{||} = 0$ ($\Gamma$). Although only one unoccupied state is expected on the 2×1 surface, two states are observed with inverse photoemission (Cricenti et al. 1995, Johansson & Reihl 1992). This is consistent with the presence (Cricenti et al. 1995, Johansson & Reihl 1992) of correlated dimer buckling at room temperature (Wolkow 1992, Northrup 1993, Cricenti et al. 1995, Johansson & Reihl 1992). The two occupied, $\pi_1$ and $\pi_2$, and the two unoccupied, $\pi_1^*$ and $\pi_2^*$, bands of surface states are derived from the four dangling bonds of the Si(001)-c(4×2) surface net (Northrup 1993) and Fig. 4(a) demonstrates that c(4×2) order is still present at room temperature. Fourteen n-type surfaces were studied and estimates for the state positions were obtained by averaging the results from all surfaces. The $\pi_1^* - E_F$ splitting, where $E_F$ is the Fermi level, was found to be (0.51±0.1) eV. This value is larger than previous inverse photoemission estimates (Cricenti et al. 1995, Johansson & Reihl 1992) that placed $\pi_1^*$ closer to the Fermi level (0.35-0.4 eV). However, our lowest estimates for this splitting do lie in this range. Furthermore, we resolved the $\pi_2^*$ state at $\Gamma$ on all samples, consistent with the predictions of ab initio calculation (Northrup 1993). The $\pi_2^*$ state was also present on single-domain vicinal Si(001) surfaces (4°) that we studied that are not included in the above averages. The $\pi_2^*$ band does overlap the conduction band continuum at $\Gamma$ and so it is possible (see later) for the $\pi_2^*$ surface state band to be obscured by the conduction band states. Our estimate of the $\pi_2^* - \pi_1^*$ splitting (0.73 ± 0.08) eV is in excellent agreement with the value obtained previously using inverse photoemission (0.75 eV), averaging over the $\Gamma\Gamma$
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direction (Johansson & Reihl 1992), and slightly lower than a value determined recently in a two photon photoemission study (0.82 eV) (Kentsch et al. 2002).

In contrast to the results presented here, we note that previous inverse photoemission studies of single-domain Si(001)(2×1) surfaces (Cricenti et al. 1995, Johansson & Reihl 1992) did not resolve π\textsuperscript{*} at Γ. To resolve the state, they had to go into the second surface Brillouin zone to Γ\textsubscript{2}. The most natural explanation for this difference is that the overlap with the conduction band continuum (Northrup 1993) obscured π\textsuperscript{*} at Γ in the earlier experiment. The experimental geometries and also the detection energies in the two experiments are different. Consequently, it is unsurprising that the experimental spectra are not identical.

The curve in the lower portion of Fig. 4 is a difference spectrum, generated by subtracting (b) from (a). This curve clearly illustrates that the growth of the overlayer eliminates both of the unoccupied surface states without producing intense new adsorbate-induced unoccupied states at Γ. We note that although relatively few studies of epitaxial growth on Si(001) have been performed with inverse photoemission (Reihl B. et al. 1989, P. & B. 1989, Himpsel 1990, Cricenti A. et al. 1993, n.d.), studies of epitaxial overlayer growth on Si(111) (e.g. Cu (Reihl B. et al. 1989), Ag (Reihl B. et al. 1989), Au (Reihl B. et al. 1989), B (Himpsel 1990, Himpsel 1990a), Al (Reihl B. et al. 1989), Ga (Reihl B. et al. 1989), In (Reihl B. et al. 1989, Himpsel 1990a) and Ge (Reihl B. et al. 1989, P. & B. 1989)) find clear adsorbate induced levels between the Fermi level and the vacuum level. The exception to this rule being elements from group V (e.g. As (Himpsel 1990b, Himpsel 1990a)) that act as dopants in bulk Si and fill the unsaturated dangling bond on Si(111) producing an occupied lone pair state. Bismuth acts in a similar fashion on Si(001).

For the full monolayer coverage of Bi, the Si dimer is broken and Bi dimers are formed along the original Si dimer rows. Theoretical considerations leads us to believe that the Bi dimers are symmetric, leading to the formation of the Si(001)-Bi(2×1) structure. Experimental evidence for symmetric dimers, or more accurately the lack of asymmetric dimers, can be found from Fig. 3, published STM images (Hanada & Kawai 1990, Hanada & Kawai 1991, Park et al. 1993, Park et al. 1994) and from the fact that the Bi5d core-level is found to have only one spin-orbit split component up to Bi coverages of one monolayer (Corradini et al. 1999). Asymmetric dimers would produce two spin-orbit split components because there would be two in-equivalent surface sites. The Si dimer related states π\textsubscript{2}, π\textsuperscript{1}\textsuperscript{*} and π\textsuperscript{2}\textsuperscript{*} are replaced by the Bi dimer related π, π\textsuperscript{*} and pπσ\textsuperscript{*} states, as shown in Fig. 5 and also Fig. 10 (b,c,d) in Ref (Gay et al. 1998a). As mentioned above, due to the availability of a sufficient number of electrons from the Bi atoms, the π and π\textsuperscript{*} states are occupied and lie inside the bulk valence band region. The application of the local density approximation indicates that the pπσ\textsuperscript{*} state lies close to the conduction band edge. (It is well known that the energies of unoccupied states are generally pushed upwards when a proper quasi-particle calculation is performed. Such an upward shift of unoccupied states is usually more pronounced for surface states than bulk states (Srivastava 1999).) The density-of-states calculations (Fig. 5) were
performed using 12 special k-points distributed throughout the surface Brillouin zone and by including all states in the supercell. Although only the region around the zone center is probed in the inverse photoemission spectrum (± 0.05 Å⁻¹) we have calculated the DOS averaged over the entire surface Brillouin zone because the surface bands have a fairly shallow dispersion. However a detailed comparison of experiment and theory requires the surface energy bands (Gay et al. 1998a). From these we infer that the \( p p \sigma^* \) band overlaps the bulk continuum at the zone center, The experimental curve obtained from the Si(001)-Bi(2×n) system (Fig. 4) does contain a weak shoulder 1.5 eV above the Fermi level that could be the \( p p \sigma^* \) band obscured by the bulk transition. From the calculated surface energy bands we also infer that the \( p p \sigma^* \) band splits off from the bulk continuum as it approaches the surface Brillouin zone boundary (\( \mathcal{J} \)). Consequently \( \mathcal{J} \) would be the most natural place to probe this state if it were possible to grow single domain Si(001)-Bi(2×1) overlayers.

An assumption that has been made in these calculations is that the electronic structure of the Si(001)-Bi(2×1) system is representative of the electronic structure of the Si(001)-Bi(2×n) system. Another way of stating this is that we have have assumed that the rows of missing Bi dimers that appear in the Bi overlayer do not have an appreciable effect on the electronic structure. This seems reasonable based on our theoretical and experimental studies of the GaAs(110)-Bi(1×1) system (McLean & Himpsel 1989, McLean et al. 1991). This system contains discommensurate misfit dislocations that are not dissimilar to the Bi dimer vacancy rows. We found that rows of Bi vacancies in the Bi(1×1) structure on GaAs(110) produced no noticeable effect on the surface electronic structure of the system; the surface bands were measured using angle-resolved photoemission and compared with the calculated surface bands. However, we are currently testing this assumption using a larger surface unit-cell and explicitly including the vacancy dimer rows. The results of this study will be reported in a future publication.

The large peaks located at 2.86 and 4.14 eV above the Fermi level, that dominate both inverse photoemission spectra, have previously been attributed to transitions between unoccupied bulk energy bands of Si (Johansson & Reihl 1992, Ortega & Himpsel 1993). To identify the energy bands involved in the transitions, the band structure of Si was calculated along the \( \Gamma - X \) and the \( \frac{2}{3} \Sigma - L \) lines (Fig. 6 and Fig. 7). The conduction band results presented in Fig. 7 were obtained by employing the empirical pseudopotential method, using the atomic form factors presented in Ref. (Chelikowsky et al. 1989). The valence and conduction band results obtained from this method are in agreement with optical transition measurements, and thus the higher conduction bands are the best predictions available. The latter peak can be reached by a surface umklapp process involving the \( \vec{g} \left( \frac{1}{2}, 0 \right) \) vector (or equivalently, the \( \vec{g} \left( 0, \frac{1}{2} \right) \) vector in the rotated domain). This reciprocal lattice vector is associated with the \( 2 \times \) dimerization induced, translational symmetry of the (2×1) overlayer. All possible transitions along these two lines, involving a photon equal to our isochromat detection energy (\( \hbar \omega_d = 10.61 \text{eV} \)), were calculated from the bulk bandstructure and the
two transitions that match the experimental initial energies are shown on the Fig. 7. Previously, a similar approach has been used to analyze normal incidence inverse photoemission spectra collected in the initial energy range, measured relative to the vacuum level, from 14.5 to 21.5 eV (Ortega & Himpsel 1993). These authors also identified a radiative transition from the primary cone to the $\Delta_2$ band. This is the transition labeled $\alpha$ in Fig. 7. It is interesting to note that the shape of the spectrum, in the energy range that contains the two bulk transition, changes when Bi is adsorbed; the transition that has been labeled $\beta$ loses intensity relative to the $\alpha$ transition. Although this could be due to a suppression of surface related features, that are not resolved in the spectrum, it is also possible that the formation of the ordered Bi overlayer affects the two transitions differently, because one involves a surface umklapp process. Although the latter possibility is intriguing, it is impossible for us to differentiate between these two scenarios in the experiment.

4. Conclusions

We have studied the Si(001)-Bi(2×n) monolayer system using inverse photoemission, STM and a combination of ab initio and empirical pseudopotential calculations. The experimental spectra collected from the Si(001) system have four peaks that can be clearly resolved with inverse photoemission. They have been labeled $\pi_1^*$, $\pi_2^*$, $\alpha$ and $\beta$. For the Si(001)-Bi system, the two most intense peaks ($\alpha$ and $\beta$), although translated by the band bending shift, remain largely unaltered by Bi deposition. Based on the calculated band structure results, the peaks $\alpha$ and $\beta$ are identified as Si bulk transitions, in excellent agreement with our inverse photoemission results and previous experimental studies of the Si bulk bandstructure using inverse photoemission (Ortega & Himpsel 1993). Our calculations demonstrate that the unoccupied $\pi_1^*$ and $\pi_2^*$ surface state bands on Si(001) are replaced by the $\pi$ and $\pi^*$ surface state bands associated with the symmetric Bi-dimer structure. The latter lie below the valence band maximum and are therefore invisible to inverse photoemission. The lack of unoccupied states close to the Fermi level near the zone center could also explain why it is difficult to image Si(001)-Bi(2×n) with STM at positive bias (empty states). Since symmetric Bi-dimers are known to be a basic building block of the Bi nanolines (Owen, Miki, Koh, Yeom & Bowler 2002), we would expect the electronic structure of the nanoline to be semiconducting. This conjecture is confirmed by ab initio calculations of the nanoline electronic structure that will be presented in a future publication.

Acknowledgments

Acknowledgments This research was supported by the Natural Sciences and Engineering Research Council of Canada. RHM was supported by CNPq and CAPES, Brazil.
The electronic properties of Si(001)-Bi(2\times n) n.d. The inverse photoemission cross-section of Si(001) is approx. a factor of 3 times smaller than that of Si(111) at the electron and detector energies used in this study.


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Figure 1. A side view of a Bi overlayer on Si(001). The ×2 order is due to Bi dimers and the ×n order is due to missing Bi dimers.
Figure 2. (a) Schematic, side view, structural models of the Si(001)(2×1) surface with asymmetric Si-dimers and (b) the Si(001)-Bi(2×1) surface with symmetric Bi-dimers and calculated total charge densities. The white spheres represent Si atoms and the black spheres represent Bi atoms. On flat Si(001) surfaces there are two equally populated 2×1 domains rotated by π/2 w.r.t. one another. Correlated dimer buckling produces locally a c(4×2) surface net.
Figure 3. STM constant-current topograph of the double domain Si(001)-Bi(2×n) surface. Regions of the surface that have Bi-dimer rows running approx. vertical are labeled \( v \) and regions that have Bi-dimer rows running approx. horizontal are labeled \( h \). Areas labeled \( v \) are separated by a single height step from areas labeled \( h \). The step rotates the dimerisation direction by \( \pi/2 \). In this image there is some second layer Bi growth (bright spots). Image area = (30 nm)\(^2\). Image bias = -1.50 V (full states).
Figure 4. Inverse photoemission spectra collected at $\Gamma$ of (a) the Si(001) surface showing the $\pi_1^*$ and the $\pi_2^*$ unoccupied surface states and (b) the Si(001)-Bi(2×n) epitaxial monolayer system. The curve in the lower portion of the figure is a difference spectrum, generated by normalizing spectrum (b) to (a) at $\beta$ and subtracting (b) from (a).
Figure 5. Calculated density of states (DOS) for Si(001) (shaded) and the Si(001)-Bi(2×1) epitaxial overlayer system. All surface and bulk states in the surface Brillouin zone are included. The energy zero is the Si valence band maximum. The growth of the Bi overlayers eliminates the $\pi_2$, $\pi_1^*$ and $\pi_2^*$ states. They are replaced by $\pi, \pi^*$ and pp$\sigma^*$ states associated with the symmetric Bi dimer structure in the epitaxial overlayer. Although the pp$\sigma^*$ band overlaps the bulk continuum at the zone center, it splits off from the bulk energy bands as it approaches the surface Brillouin zone boundary ($\mathcal{J}$). Due to the state’s strict localization on the surface plane, the cross-section for an inverse photoemission transition into this state may be weak.
Figure 6. Side view of the Si bulk Brillouin zone. When the incoming electrons are antiparallel to the (001) surface normal, the bulk transitions are located along the $\Gamma - X$ line. The dotted line, $\frac{2}{3}$ of the way from $\Gamma$ to $K$ along the $\Sigma$ high symmetry line, can also be accessed by a surface umklapp process involving the $\vec{g}(\frac{1}{2},0)$ vector.
Figure 7. In the left panel, the bulk Si energy bands along Γ − X are shown together with a possible transition involving a photon with an energy equal to our detection energy: $\hbar\omega_d = 10.61\text{eV}$. Surface umklapp scattering via $\vec{g}(\frac{1}{2}, 0)$ also makes the $\frac{2}{3}\Sigma - L$ line accessible (right panel). The $\alpha$ and $\beta$ transitions were selected out of the many possible transitions, that conserve energy, by matching the initial energies to the experimental values.