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Abstract. We have used the self-consistent tight-binding method in the extended Hückel approximation to calculate the electronic band structure and surface dielectric function of three Sn/Si(111) reconstructed surfaces. We show that the anisotropy in the imaginary part of the surface dielectric function and the corresponding reflection spectra as determined from the self-consistent wavefunctions for the three surfaces are quite different. This suggests that the recently developed technique of reflection anisotropy spectroscopy can be used in studying the change in surface reconstruction with increased Sn deposition.

1. Introduction

Over the last twenty years there has been a growth in the range of powerful techniques used for probing structural and electronic properties as well as the chemistry of surfaces. As most of these involve the use of electron and ion beams forbidding their use in high-pressure growth chambers, there have been major efforts by many groups to develop simple optical techniques which can be used to probe solid surfaces particularly during the growth phase. For example, it has been demonstrated that changes in the dielectric function resulting from an epilayer as thin as one monolayer on a substrate can be measured using ellipsometry [1]. Reflection anisotropy spectroscopy (RAS) is another optical technique that has been shown to be very useful in the monitoring of growth of semiconductors by MBE and MOVPE [2]. RAS examines the difference in reflectivity for light of two orthogonal polarizations incident on a surface. The differences in these reflectivities are a consequence of the anisotropy of the surface electronic structure which in turn is influenced by the surface atomic configuration and chemistry. It has been shown that the RAS signal depends on the photon energy and can be used to 'fingerprint' particular surface structures. Thus, for example, the GaAs (2×4) As-rich reconstructed surface has particularly identifiable camel-shaped RAS spectra, whereas the (4×2) Ga-rich surface has an altogether different shape [3]. It has further been shown that some of the features in the spectra may be ascribed to the presence of dimers on these surfaces [4]. It is quite clear then, that information relating to the detailed nature of the surface bonds may be extracted from the RAS data by correlating the data with detailed calculations of the surface states and corresponding optical response. However, to fully exploit the potential of this technique, it is important to study a few selected test systems both experimentally and theoretically. The Si and GaAs reconstructed surfaces are examples of such systems which have been studied [5, 6] to date. Near-monolayer coverages of Sn on Si provide another such system and are the subject of this paper.

Sn on Si(111) is an example of an abrupt, chemically inert surface. For 0.33 monolayer (ML) coverage, the Sn atoms order on the T_4 sites of the (111) surface forming a $(\sqrt{3} \times \sqrt{3})$ reconstructed surface, hereafter referred to as the R3 surface. When the coverage is increased to just over a monolayer, the LEED pattern shows a $(2\sqrt{3} \times 2\sqrt{3})$ reconstructed surface (2R3) with the Sn forming an incomplete double layer on the silicon substrate. We have already performed self-consistent electronic structure calculations using the tight-binding method in the extended Hückel approximation (TBEHA) [7]. The atomic positions were determined from scanning tunnelling spectroscopy studies [8] combined with molecular dynamics simulation [6]. Both occupied and unoccupied surface-state energies thus calculated were found to be in very good agreement with photoemission data suggesting that the electronic structure of the surface is well described. We have therefore used the results of the electronic structure calculation to determine the linear optical response of these reconstructed surfaces and in particular the anisotropy of the surface dielectric function.

2. Theory of the optical response

The TBEHA is an empirical self-consistent method which takes into account charge transfer at the surface and provides a good description of the surface electronic structure. We had previously applied the TBEHA to calculate the imaginary part of the dielectric function for the Si(100) (2×1) and As/Si(100) (2×1) reconstructed surfaces [5]. The results for the calculated difference in ε_2 for these two surfaces were found to be in excellent agreement with experiment giving confidence in the validity of the approximations used and in the suitability of the approach to such calculations. The approach has therefore been employed to determine the optical absorption (reflection) of the reconstructed Sn/Si(111) surfaces. For large wavelengths compared to the interatomic spacing, the imaginary part of the dielectric matrix can be derived from standard perturbation theory [9]:

$$\varepsilon_2 = (e^2/\pi m^2 \omega^2) \sum_{cv} \sum_{BZ} \left| \int \mathrm{d}\boldsymbol{r} \ \psi_c(\boldsymbol{k}, \boldsymbol{r}) \boldsymbol{e} \cdot \boldsymbol{p} \psi_v(\boldsymbol{k}, \boldsymbol{r}) \right|^2 \delta(E_c(\boldsymbol{k}) - E_v(\boldsymbol{k}) - \hbar\omega) \tag{1}$$

where c refers to unoccupied conduction band and v to an occupied valence band with energies E_c and E_v respectively. $\boldsymbol{e}$ gives the direction of polarization of light and $\boldsymbol{p}$ is the momentum operator. Following the analysis and notation of [5], it can be shown that within the TBEHA, the dipole matrix elements take the simple form

$$\boldsymbol{P}_{cv} \propto \sum_{\alpha\beta} \sum_{s} C_{\alpha s}^{v} C_{\beta s}^{c*} (E_{\beta}^{s} - E_{\alpha}^{s}) \int \phi_\alpha(\boldsymbol{r} - \boldsymbol{R}_s) r \phi_\beta(\boldsymbol{r} - \boldsymbol{R}_s) \, \mathrm{d}\boldsymbol{r} \tag{2}$$

which is the expression used to calculate ε_2. $\phi_\alpha(\boldsymbol{r} - \boldsymbol{R}_s)$ represents atomic orbitals of type α centred on the basis atoms labelled s, and the Cs are the mixing coefficients in the construction of the Bloch functions from the atomic orbitals.

3. Results

To determine the surface dielectric function, we first require a knowledge of the electron wavefunctions and their corresponding energies at k-points in the Brillouin zone. These were obtained by performing electronic structure calculations treating the surface structure as a periodically repeating slab consisting of a few layers of atoms and a few 'vacuum' layers. To ensure that the results of the calculation were sensible, we first examined the Si(111) (1×1) relaxed but unreconstructed structure. In this instance, the slab had 16

layers of Si with an equivalent of 8 layers of vacuum region. These dimensions were found to be adequate to avoid surface–surface interactions. As each layer in the unit cell comprised only one atom, the total number of atoms in the hexagonal cell was sixteen. The placements of these atoms in the cell were taken to be the relaxed positions as determined by an energy minimization using a valence force field. As the two surfaces in the slab were made identical, with dangling bonds in a hexagonal arrangement, there were no artificially induced anisotropies. The imaginary surface dielectric function was then calculated using the expression

$$\varepsilon_2^s = (\varepsilon_{2xx} + \varepsilon_{2yy})/2 \tag{3}$$

and equation (2). The surface dielectric function anisotropy is given by

$$\Delta\varepsilon_2^s = (\varepsilon_{2xx} - \varepsilon_{2yy})/2 \tag{4}$$

and can be related to the experimentally measured reflection anisotropy. This is achieved by first performing a Kramers–Kronig transformation to give the real part of the dielectric function, ε_1, from a knowledge of ε_2. The complex dielectric function is related to the real and imaginary parts of the refractive index, n and k respectively, through the relation

$$\sqrt{\varepsilon} = n + \mathrm{i}k \qquad \varepsilon = \varepsilon_1 + \varepsilon_2. \tag{5}$$

The reflection coefficient is defined as

$$r = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{6}$$

and the reflection anisotropy is then given by

$$\frac{\Delta r}{r} = \frac{r^x - r^y}{r^x + r^y}. \tag{7}$$

Aspnes *et al* [3, 10] have shown that the energies of the features in the experimentally derived dielectric anisotropy and RAS spectra are virtually the same. This is only to be expected as an analysis of the linear optical response within a three-phase model yields the result

$$\frac{\Delta r}{r} \propto (\varepsilon_{2xx} - \varepsilon_{2yy}). \tag{8}$$

In deriving the expression for the dipole matrix elements, an approximation that only single-centre integrals were important was employed. The validity of this approximation was tested by performing the two-centre integrations and examining their effect on the bulk dielectric function. It was observed that ε_2 was affected only in the region >6 eV with an enhancement of the amplitude. In common with previous work [5], we employed the tetrahedron method to perform the integration over 1/24 of the Brillouin zone (BZ). Although this is adequate for most purposes, in some cases it can introduce some artificial asymmetry in the surface dielectric function depending on the symmetry of the BZ points chosen. The dielectric functions on the Si(111) (1 × 1) surface along the $x = [110]$ and $y = [11\bar{2}]$ directions were found to be almost identical, giving confidence that the calculational approach used is a valid one and, in particular, that the k-point mesh does not induce any spurious asymmetry.

Similar calculations were then performed on the (1 × 1), R3 and 2R3 reconstructed Sn/Si(111) surface structures. The geometry for the (1 × 1) Sn/Si structure was the same as that used for the Si (1 × 1) surface. The top (and bottom) silicon layers of the slab were replaced by tin layers, the positions of which were obtained by an energy minimization. The surface dielectric function for the Sn/Si and Si (1 × 1) surfaces were found to be almost identical in shape, with the only difference being a shift in energy. This is because

for the two surfaces, the surface states are found at similar energies, although for the Sn surface, the occupied and unoccupied states near the Fermi level, E_F, are shifted slightly in energy towards each other [7]. There is, however, very little difference in the dispersion and in the nature of the wavefunctions associated with these states. It is therefore the shift in the surface states that gives rise to the larger transition amplitude at ~2 eV for the Sn/Si surface. The difference in surface dielectric functions between the Sn- and Si-terminated (1×1) surfaces, though different in shape from that found for the As/Si system, is of similar magnitude, suggesting that ellipsometry measurements can be used to differentiate between the Sn/Si and Si surfaces. However, unlike for the case of As/Si(111), Sn does not form an ordered monolayer with a (1×1) reconstruction.
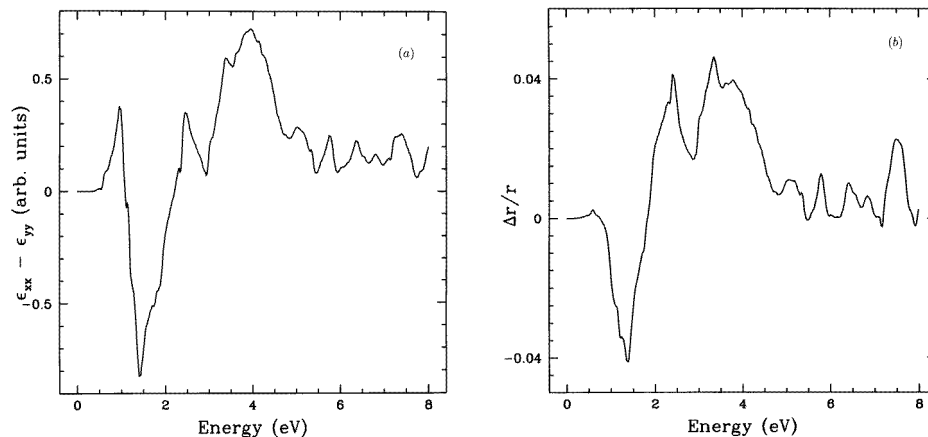

Figure 1. (*a*) The anisotropy in the surface dielectric function for the R3 reconstructed Sn/Si surface shown as a function of energy. *x* and *y* refer to the (110) and (11$\bar{2}$) directions respectively. (*b*) The RAS spectrum for the R3 reconstructed Sn/Si surface.
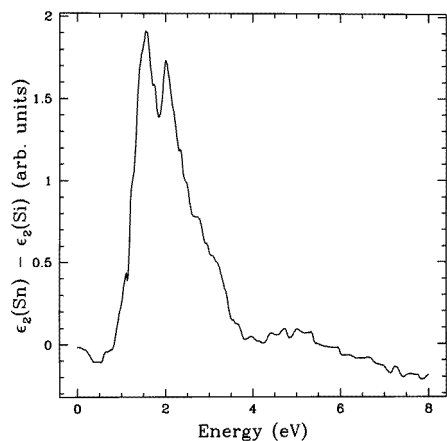

Figure 2. The difference between the surface dielectric function for the R3 reconstructed Si and Sn/Si surfaces shown as a function of energy.

We now turn our attention to the commonly observed reconstructed Sn/Si surfaces. For the R3 reconstructed surface, the unit cell was such that there were two Sn layers (top and bottom) comprising one atom and sixteen Si layers of three atoms, making a total of

50 atoms. As a consequence of the increase in unit-cell size, the number of bands and, therefore, the number of matrix elements in the calculated dielectric function scale as the square of the number of bands. The surface anisotropy in the surface dielectric function $(\varepsilon^{110} - \varepsilon^{11\bar{2}})$ thus calculated is shown in figure 1(*a*). The reflection anisotropy calculated from equations (5)–(7) is shown in figure 1(*b*). As may be observed, the energies of the features in the dielectric anisotropy are the same as that in the RAS. The main features in the spectrum are found to occur between 1 and 5 eV and, from an analysis of the various matrix element contributions, can be attributed to transitions from occupied to unoccupied surface states arising from silicon atoms in the layer below the surface [7]. Surprisingly although these atoms suffer very small displacements of the order of 0.01 Å, they appear to have quite a significant contribution to the RAS signal. For comparison, we have also calculated the difference in the surface dielectric function for the Sn/Si ($\sqrt{3} \times \sqrt{3}$) and the Si ($\sqrt{3} \times \sqrt{3}$) surfaces and the results are displayed in figure 2. As these surfaces are almost identical in structure, a direct comparison between the two is possible. The peak in $\Delta\varepsilon_2$ at 2 eV is similar to that found for the (1 × 1) structure. There is, however, an extra broad feature between 4 and 7 eV.
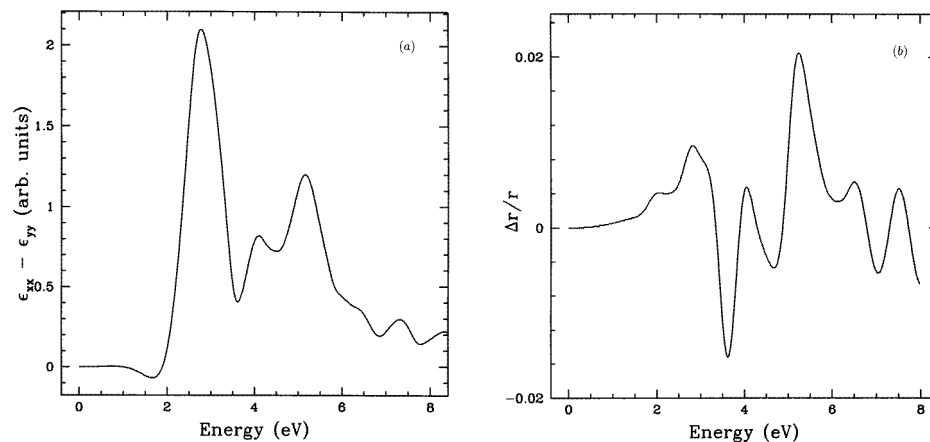

Figure 3. (*a*) The anisotropy in the surface dielectric function for the 2R3 reconstructed Sn/Si surface shown as a function of energy. *x* and *y* refer to the (110) and (11$\bar{2}$) directions respectively. (*b*) The RAS spectrum for the 2R3 reconstructed Sn/Si surface.

As the atomic configuration of the 2R3 reconstructed Sn/Si surface [7] appears to be more anisotropic than that of the corresponding R3 surface, it might be expected that the anisotropies in the ε_2-spectra would be correspondingly large. For calculations involving this structure, the periodic slab considered comprised 8 Si layers with 12 atoms per layer and 2 sets of Sn bilayers each with 14 atoms, making a total of 124 atoms. Because of the large number of atoms in the unit cell it is not helpful to examine the band structure in detail. From the calculated bands [7] the dielectric function was obtained in the manner described above and the results for the surface dielectric and reflection anisotropy are shown in figure 3. The characteristic features are two peaks at 3 eV and 5 eV; the former results from transitions from the occupied states 1 eV and 2 eV below E_F (coming from the topmost Sn layer) to unoccupied states $\sim$2 eV above E_F. The asymmetry of the occupied orbitals of these Sn atoms results in the calculated difference in the surface dielectric function.

4. Conclusion

The main purpose to this study was to show that optical probes like ellipsometry and RAS can be used as tools in the identification of even such complex surfaces as in the differently reconstructed surface structures of Sn on Si and need not be confined to studying well studied systems like the GaAs surface. The R3 surface is found to display significant anisotropy with a spectrum similar to that found for the c(4 × 4) GaAs(001) surface and different to that found for the 2R3 surface which in turn is more like that seen in the (2 × 4) reconstructed GaAs(001) surface. The 2R3 surface does not have a discernible anisotropy in the energy region where the R3 surface does, and so by analysing the RAS signal in this energy region it should be possible to identify the proportions of the two reconstructions with increasing Sn deposition. Such calculations can therefore be used in conjunction with experiment to study other surfaces which are not directly accessible to other techniques.

Acknowledgments

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