Sensitivity of Reflectance Anisotropy Spectroscopy to the Orientation of Ge Dimers on Vicinal Si(001)

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Reflectance anisotropy spectroscopy (RAS) is employed to follow the initial room temperature growth of Ge dimer layers on clean vicinal Si(001)-(1×2). The experimental data show structure in the region of 2.5 eV which changes sign depending on Ge dimer orientation. Comparison with microscopic calculations for one monolayer and two monolayer Ge coverages reveals excellent agreement with experiment, demonstrating that surface states localized on Ge dimers are responsible for the RA response in the region of 2.5 eV. This provides the first clear and unambiguous proof that a dimer related transition can be responsible for the RAS sensitivity to dimer orientation. [S0031-9007(98)05779-2]

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An important and fundamental question concerning the optical response of surfaces is whether the techniques employed are sensitive to the bonding geometry at the surface. As a result of a significant body of work on GaAs(001) surfaces, it was found that one of these techniques, reflectance anisotropy spectroscopy (RAS) is sensitive to the orientation of surface dimer bonds. Wassermeier *et al.* [1] found that the sign of the RA response from the GaAs(001)-$c(4 \times 4)$ and GaAs(001)-(2×4) surfaces could be related to the orientation of surface As dimer bonds. However, the exact origin of the transitions giving rise to this sensitivity could not be explained. It has been suggested recently that many of these surface related features observed by RAS can be explained by a surface termination of the bulk dielectric function [2]. In this Letter, we use the initial growth of up to two monolayers of Ge on vicinal Si(001) as a model system and provide the first unambiguous demonstration that transitions involving overlayer states are responsible for the RAS sensitivity to dimer orientation in this system.

RAS was developed in its present form by Aspnes and Studna [3] and has proven to be a powerful tool for observing surface-related optical anisotropy and growth transience under both ultrahigh vacuum (UHV) [4–6] and atmospheric pressure [7,8] conditions. The technique derives its surface sensitivity from measurements of the difference in normal incidence reflectance for light polarized along two major orthogonal axes in cubic crystals which have isotropic bulk optical properties. Some progress has been made in the theoretical understanding of the origins of the RAS signal [5,9–12].

The growth of Ge on Si(001) proceeds in a similar way to Si homoepitaxy for the first few monolayers producing a layer-by-layer growth mode with Ge dimers oriented orthogonally on subsequent layers [13–16]. Scanning tunneling microscopy (STM) reveals that dimer vacancy rows are formed to alleviate strain at Ge coverages of approximtely 1.5 monolayer (ML), producing a $(2 \times n)$ rather than a (2×1) reconstruction, where $n(\geq 3)$ refers to the separation between adjacent dimer vacancy rows [17]. Above approximately 3 ML growth, the increased strain causes breakdown of the layer-by-layer growth mode in favor of islanding [18]. It is also found that diffusion of Ge into the Si bulk occurs upon annealing above 623 K destroying the interface abruptness [15,19,20]. To minimize this effect and retain an abrupt interface upon Ge deposition, we grow Ge on Si(001) at room temperature followed by gentle annealing to 473 K.

The experiment was carried out in an UHV chamber with a base pressure of 4×10^{-11} mbar. The vicinal Si(001) substrate was n type, lightly phosphorus doped with a resistivity in the range 2200 Ω cm and was polished 3° off the [001] direction towards [110]. The vicinal Si samples were degassed for 8 h at 873 K before being cleaned by sequential direct heating to 1273 K while maintaining the system pressure below 5×10^{-10} mbar. All temperatures above 523 K were monitored by optical pyrometry, while lower temperatures were obtained by extrapolation.

After cleaning, low energy electron diffraction (LEED) revealed a split-spot single domain (1×2) pattern indicative of a dimerized surface with a regular arrangement of

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double-atomic height steps. A (1×2):(2×1) domain ratio of 4:1 was estimated from intensity analysis measurements of the LEED half order spot intensities. Ge was deposited from a well calibrated miniature Knudsen cell at a deposition rate of 1 ML every 37 min. RA dynamical spectra were recorded during Ge deposition. After deposition of 1 ML, the cell shutter was closed, and the samples were annealed. Upon cooling to room temperature, a Ge-induced (2×1) LEED pattern was observed along with no change in split-spot separation indicating that the double-height step structure of the clean surface is maintained upon Ge deposition and that the primary mechanism reducing strain in this system is the formation of dimer vacancy lines on the Ge-induced terraces rather than a change in step structure [21]. The LEED domain ratio is reversed and reduced to 1:1.5. This result is expected since STM work has shown that in this coverage regime some disorder exists and new Ge layers begin forming before the underlying layers are complete [13]. Along with this, some intermixing of Ge with Si occurs [20]. Upon deposition of a further ML of Ge, a (1×2) LEED pattern was observed, with no change in split-spot separation but with indications from the LEED 1/2-order spot intensities of a further reduction in domain ratio. No evidence of a $(2 \times n)$ reconstruction, reported by Chen *et al.* [17] for either coverage, was observed by LEED, probably due to the nonperiodic separation n between adjacent dimer vacancy rows.

The RAS experimental arrangement used in this work is similar to that described by Aspnes and co-workers [22]. The reflectance difference signal, ΔR, is normalized to the average reflectance, R, and is related to the surface and bulk dielectric function components by

$$\frac{\Delta R}{R} = \frac{8\pi d}{\lambda} \mathrm{Im}\left[\frac{\epsilon_x - \epsilon_y}{\epsilon_b - 1}\right], \tag{1}$$

where d is the thickness of the overlayer, λ is the wavelength of the light, ϵ_x and ϵ_y are the surface dielectric function components, and ϵ_b is the isotropic bulk dielectric function. In the present geometry, the x crystallographic axis is the surface $[\bar{1}10]$ direction (parallel to the step edges) while the y crystallographic axis is $[110]$ (perpendicular to the step edges). It follows from Eq. (1) that when ϵ_b is predominantly real, a positive signal here indicates preferential absorption in the x direction. Equation (1) is strictly valid only for $d \ll \lambda$.

Figure 1(a) shows the experimental RA spectra for the 1 and 2 ML coverage (2×1)-Ge and (1×2)-Ge LEED structures, respectively. Two features dominate both spectra. For (2×1)-Ge, which contains an excess of Ge-Ge dimers oriented in the $[110]$ direction, two positive features (i.e., in the $[\bar{1}10]$ direction) exist, one at 2.4–2.5 eV and the other at 3.6 eV, indicating their origin must involve optical transitions that are stronger for light polarized perpendicular to the Ge-Ge dimer bonds. Upon the formation of the (1×2)-Ge structure, which even after the reduction in domain imbalance contains

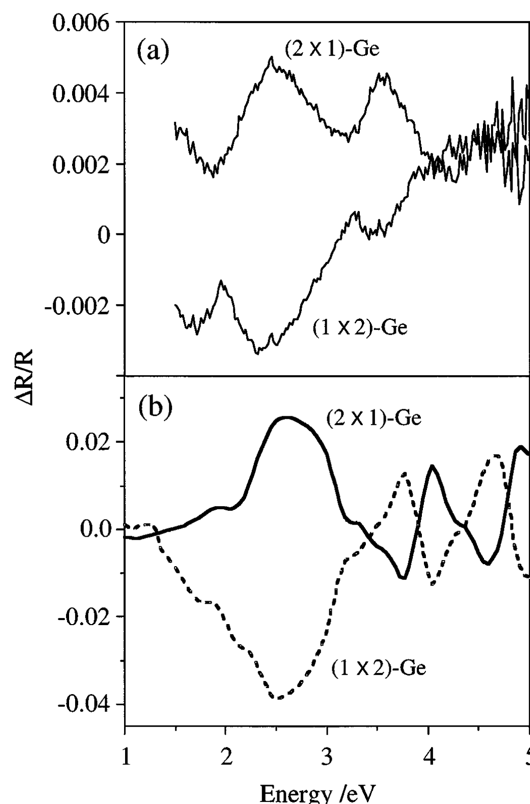

FIG. 1. (a) The experimental RA spectra for the 1 ML Si(001)-(2×1)-Ge and 2 ML Si(001)-(1×2)-Ge structures grown on 3° off-cut Si(001)-(1×2). Ge was deposited onto a room temperature sample and annealed to 473 K. The samples were cooled prior to data acquisition and (b) calculated RA spectra for the 1 ML (2×1)-Ge (solid line) and 2 ML (1×2)-Ge (dashed line) structures.

an excess of Ge-Ge dimer bonds oriented in the $[\bar{1}10]$ direction, both peaks change sign and shift slightly down in energy. These two features are clearly dependent on the orientation of the Ge-induced surface bonding. Interpretation of the higher energy peak is complicated by the fact that it occurs above the onset of the direct optical gap of Si which occurs at 3.1 eV [23]. The difficulty in interpreting such features is made clear by recent work showing that certain RAS features, previously assigned to surface dimer features from GaAs surfaces, can now be explained by a surface termination of the bulk dielectric function [2]. However, the peaks in the region of 2.5 eV for both 1 and 2 ML Ge coverages must be Ge induced as the imaginary part of the dielectric function of Si is zero and the real part is only slowly varying in this region.

Figure 1(b) shows the results of microscopic calculations of the RA spectra for the 1 and 2 ML Ge-induced structures. The details of the calculation can be found elsewhere [24,25]. To calculate the spectra, the tight binding approach with a sp^3s^* basis [26] has been used for a 20-layer slab. The structural input for the optical calculation has been obtained from extensive *ab initio* molecular dynamics simulations of a number of different Ge overlayer (from 1 to 3 ML) structures obtained by

total energy minimization, ranging from the $c(4 \times 2)$ and $p(2 \times 2)$ asymmetric dimer structures to the symmetric and asymmetric (2×1) structures, together with various intermixed structures [27]. Modeling of symmetric dimer geometries was found to be completely unstable, converting practically immediately into asymmetric dimers during energy minimization, and so was not considered. The optical spectra shown in Fig. 1(b) are obtained using an asymmetric dimer terminated (1×2) and (2×1) geometry for each of the Ge terminations on Si(001) whose coordinates were obtained using density functional theory within the local density approximation (LDA-DFT).

The overall shapes of the RA spectra for theory and experiment show excellent agreement (see Fig. 1). For the 1 ML (2×1) -Ge structure, two positive features are present in the calculated spectra; a broad positive peak at 2.5 eV and a smaller narrower peak near 4.0 eV, with a shallow negative trough between them at 3.7 eV. The lower energy peak at 2.5 eV is observed experimentally, while both the 3.7 eV trough and the 4.0 eV peak are shifted in energy by approximately 0.4–0.5 eV with respect to the experimental positions of 3.25 and 3.6 eV. For the 2 ML (1×2)-Ge structure similar agreement is obtained, with a trough at 2.4–2.5 eV being observed by both theory and experiment. The trough at 3.6 eV, seen by experiment is also observed in the calculated spectra, although shifted upwards in energy to 4.0 eV. Such shifts in energy between calculated and experimental spectra (of approximately 0.3–0.5 eV) are common in tight-binding calculations.

From Fig. 1, it can be seen that the calculated RA spectra are larger than the experimental spectra by a factor of 5 for the 1 ML structure and by a factor of 20 for the 2 ML structure. These differences in RA intensity clearly have two origins. First, increased Ge deposition reduces the imbalance in domain occupation which determines the amplitude of the RA response from these Si systems. For example, a clean flat Si(001) surface contains no dimer imbalance, and hence no RA signal is observed. For the (2×1)-Ge structure, a domain ratio of 1:1.5 exists yielding a 20% domain imbalance. The calculations assume the presence of only one domain, so the actual domain structure will reduce the theoretical amplitudes by a factor of 5, reconciling the difference between theory and experiment for the 1 ML (2×1)-Ge structure and reducing the disagreement to a factor of 4 for the 2 ML (1×2)-Ge structure (see Fig. 1). Second, disorder in the Ge structures due to defects and dimer vacancies, especially above 1 ML coverage will further reduce the RA intensity bringing the 2 ML structure into the range of accuracy usually obtained in calculations of this kind.

Figure 2 shows the surface to surface, bulk to bulk, surface to bulk, and bulk to surface contributions to the overall calculated RA spectrum shown in Fig. 1(b). All contributions can be seen to change sign depending on Ge dimer orientation. From the figure, it can be seen that surface to surface and bulk to surface transitions involving surface dimers must dominate the overall RA line shape in the region of the lower energy feature at 2.4–2.5 eV, both contributions changing sign depending on the orientation of the surface Ge dimers. For the 1 ML structure, there is a sharp surface to surface contribution at 2.5 eV which dominates the total calculated RA response and arises from transitions localized on Ge dimers. We can exclude transitions involving Ge dimer dangling bonds alone as for the 1 ML structure; for example, these should be stronger for light polarized along the dimers in the [110] direction. Also, inspection of the surface band structure shows that transitions between dangling-bond-like surface states occur below 1 eV, while the overlayer states responsible for the 2.5 eV structures show a substantial backbond character. The good agreement between theory and experiment in the region of 2.5 eV for

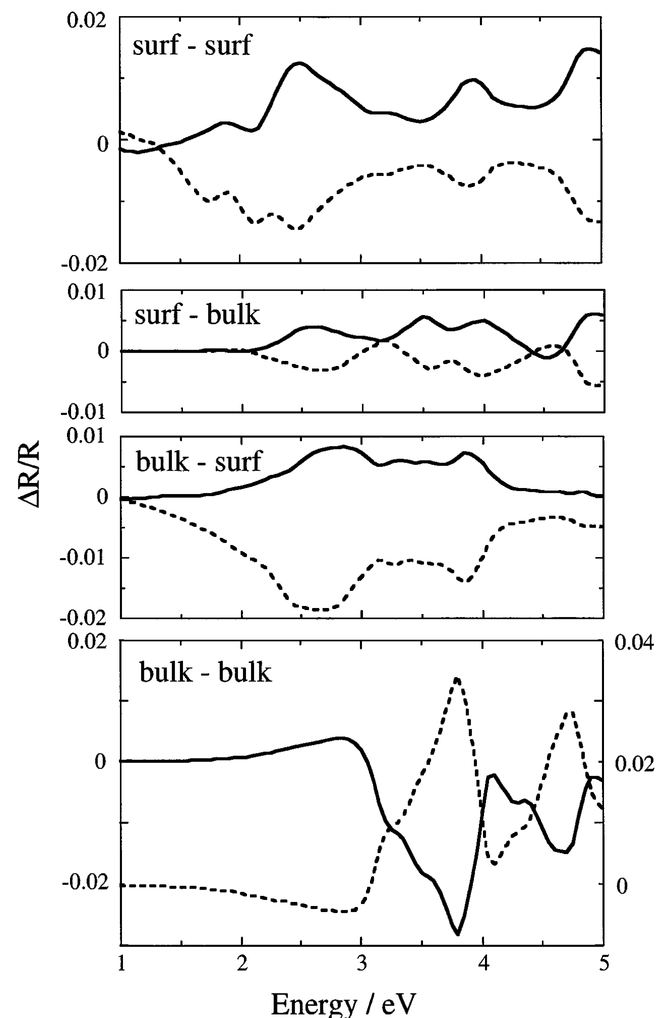

FIG. 2. The surface to surface, bulk to bulk, surface to bulk, and bulk to surface contributions to the total calculated RA spectrum shown in Fig. 1(b). The solid and dashed lines represent the 1 ML (2×1)-Ge and 2 ML (1×2)-Ge structures, respectively. For convenience, the amplitude of the optical anisotropy for the 2 ML bulk to bulk contribution is shown on the right-hand axis.

both coverages clearly illustrates that the correct optical transitions giving rise to the experimental RA spectra are dominated by transitions involving states localized at the Ge overlayer. In this way, the RAS sensitivity to dimer orientation is naturally explained.

Considering the higher energy feature at 3.6 eV, it can be seen from Fig. 2 that although this feature also contains some surface to surface and bulk to surface contributions, the stronger contribution here is a bulk to bulk term. Despite this, the sign of all contributions are dependent on the orientation of the surface Ge dimers, and so surface-perturbed bulk states are responsible for the higher energy features observed in the region of 3.7–4.0 eV. This situation is similar to that of GaAs(001), where the RA features appear to be from bulk to bulk transitions [28].

Previous structure calculations for clean Si(001) [25], Ge(001) [29], and Ge covered Si(001) [27] have shown that the stable structure formed at room temperature is a $c(4 \times 2)$ rather than a (2×1) reconstruction. Indeed, calculations of the RA response from both the clean Si(001) [27] and Ge(001) [29] surfaces, using $c(4 \times 2)$ structural input, displays better agreement with experimental RA data than previously obtained [30]. Although a $c(4 \times 2)$ local structure may be identified for monolayer Ge coverages on Si(001) from the STM images of Chen *et al.* [17], calculations of the RA response using $c(4 \times 2)$-Ge and $c(2 \times 4)$-Ge structures for the 1 and 2 ML Ge coverages, respectively, reveal inferior agreement with experiment than the (2×1) structures shown in Fig. 1(b). This may be explained by surface strain arguments, which generate large amounts of defects and dimer vacancies [17] causing loss of the wave functions long range $c(4 \times 2)$ correlation. Hence, only those processes describing basic surface dimerization, that is, the formation of the (2×1) structure, survive in the wave function behavior.

The presence of mixed Ge-Si dimers and the influence of steps in the growth of Ge on vicinal Si(001) must also be considered. During the initial growth of Ge on Si(001), it has been found that substitutional rather than ad-layer mixed Ge-Si dimers are formed on the surface [31], and some evidence that they may exist near 1 ML coverage has been presented [19,20]. The good agreement in RA intensity between the calculated and experimental RA intensities considering Ge-Ge ad-dimers alone for the 1 ML structure, especially in the region of 2.4–2.5 eV, shows that if substitutional Ge-Si dimers do exist at these monolayer coverages, then they must exist in small quantities. Although steps are known to contribute to the RA signal from clean vicinal Si(001), the effect has been found to be small for the overall RA spectrum [4]. In this study, any significant step contribution to the RA spectra for the (2×1)-Ge and (1×2)-Ge structures, especially in the region of the Ge dimer feature at 2.4–2.5 eV can again be ruled out by the excellent agreement between the experimental results and calculations, which ignores steps.

In conclusion, we have used RAS from the initial growth of Ge on vicinal Si(001) as a model system for determining the origin of the RA response. We have established that dimer related transitions are responsible for the RAS sensitivity to surface dimer orientation in this system.

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