Dynamic changes in reflectance anisotropy from the Si(001) surface during gas-source molecular-beam epitaxy

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Comparisons of simultaneous reflection anisotropy (RA) and reflection high-energy electron diffraction (RHEED) measurements during gas-source molecular-beam epitaxy of Si on Si (001) surfaces have been used to establish a model for the dynamic changes in RA. The oscillatory behavior of RA is firmly linked to the periodic variations in domain coverage of the $(2 \times 1) + (1 \times 2)$ reconstructed surface during growth under the monolayer by monolayer growth mode. The absence of changes in domain coverage during growth interruption at 600 °C has also been demonstrated, which substantiates the prediction of Monte Carlo simulations. By comparison of RA and RHEED response at high and low growth temperatures, it has been shown that above 650 °C the absence of RA oscillations is linked to the change in growth mode from two-dimensional nucleation to step flow, whereas their absence at temperatures below 550 °C is due to a change in the joint density of states caused by a change in the electronic configuration. The lack of oscillatory RA response during growth on misoriented surfaces is discussed in terms of the averaging process in obtaining macroscopically observable RA from anisotropic local polarizability.

I. INTRODUCTION

Burgeoning interest in optical diagnostics for semiconductor growth has resulted from a need to obtain real time *in situ* information for control, optimization, and understanding the processes involved. It is of particular importance for growth techniques such as metal-organic vapor phase epitaxy operating at or near atmospheric pressure, for which electron-beam-based surface diagnostic methods are not applicable. Several linear and nonlinear optical diagnostic methods have been developed,^{1,2} of which the most widely used are ellipsometry (spectroscopic³ or otherwise), reflection difference/reflectance anisotropy spectroscopy (RDS/ RAS) and surface photoabsorption. They all involve the interaction of polarized light with the surface (and bulk) electric dipole moments.

Interest in the application of RAS was stimulated by Aspnes and co-workers^{4,5} and had until recently been concerned primarily with III-V compound semiconductors, principally GaAs,^{6–9} but it has now been extended to group-IV systems.^{10–12} With this method, the difference in reflectance between two orthogonal polarization states of light falling at near normal incidence on the semiconductor surface is measured. When applied to the surface of an isotropic bulk crystal, surface sensitivity is obtained by the cancellation of the bulk contribution in the reflectance difference signal due to a reduction in the surface symmetry with respect to that of the bulk caused by surface reconstruction or relaxation.

In this paper we seek to further the understanding of RAS and its application to the study of semiconductor growth processes. We present a detailed study of the changes in reflectance anisotropy (RA), or reflectance difference (RD), during epitaxial growth of Si on Si(001) substrates by gas-source molecular-beam epitaxy (GSMBE). This is augmented by simultaneous reflection high-energy electron diffraction (RHEED) measurements, which enables a correlation to be made between dynamic changes in RA and morphological changes on the surface due to growth. We consider the origin of the RA signal in this system, its changes during epitaxial growth, and the role of vicinal surfaces, together with the effect of surface temperature and surface hydrogen adatom concentration (from the pyrolysis of Si₂H₆) on the RA response.

II. EXPERIMENT

The RA studies were carried out in a modified GSMBE system equipped with *in situ* RHEED, which has been described previously.¹³ Disilane (Si₂H₆) was used as the Si precursor and the nominally singular Si(001) wafers used were boron doped ($\rho < 0.1 \Omega$ cm). They were prepared by wet chemical etching, which results in the formation of a surface oxide layer. This was removed thermally prior to growth by radiative heating to 900 °C to reveal the (2×1) + (1×2) double domain reconstructed surface. An electronbeam energy of 15 keV was used in all RHEED experiments and other diffraction conditions are indicated where appropriate in the text. The intensities of diffraction features were measured using a CCD camera linked to a frame-grabbing system.

In the purpose built dynamic RA instrument used, polarization of the incident light is modulated, in contrast to the method employed by the groups of Aspnes¹⁴ and Richter,¹⁵ where modulation is applied to the reflected light. The HeNe or air-cooled Argon-ion laser light sources (operating at 1.96 eV and 2.54 eV, respectively) were electro-optically modu-

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lated by two Pockels cells in series, each having a highquality polarizer attached to its entrance. The Pockels cells modulate the polarized incident light between two orthogonal linear polarization states when appropriate square wave voltages are applied. The output of the first cell, modulated at 4 MHz, falls onto the entrance polarizer of the second, thus providing on/off modulation of light that enters the second cell, enabling the average reflectance to be measured. The second Pockels cell modulates the linearly polarized incident light between two orthogonal polarization states at 6.5 MHz, which allows measurement of the reflectance difference between the two states. In effect, the near normal incident light arriving at the Si surface has its electric-field vectors modulated between the orthogonal $\langle 110 \rangle$ directions in the surface and its intensity modulated on/off. The reflected beam is focused on, and detected by, a Si photodiode. The resultant signals are measured using lock-in techniques and acquired digitally. The ratio of reflectance difference and average reflectance is calculated to give the RA response in real time. The overall gain of the system was calibrated using the difference in transmission of s and p polarized light through a thick parallel glass plate as a function of incident angle. The rotation axis of the glass plate is in the plane of incidence. Using the modulation method described above, the observed anisotropy is approximately given by $[1 - \cos^4(\theta_i - \theta_i)]/2$, where θ_i and θ_t are, respectively, angle of incidence and angle of refraction inside the glass plate. RHEED intensity oscillations and dynamic RA traces were recorded simultaneously during growth.

III. ORIGIN OF REFLECTANCE ANISOTROPY FROM THE Si(001) SURFACE

The basic model of reflectance difference, based on threephase classical electromagnetic (EM) theory,16 was established almost 25 years ago.¹⁷ For near normal incidence, the polarization of the EM wave is parallel to the surface and Fresnel theory provides an adequate description of reflection.¹⁸ In the work described here, the experimentally measured quantity is the difference in power reflectance between light of orthogonal polarization states where the electric vectors of each are along orthogonal $\langle 110 \rangle$ directions. This measured difference is divided by the measured average reflectance to give the RA response. If the influence of the surface on the average reflectance is small (<0.1%), the average reflectance can be substituted by the reflectance due to the bulk dielectric constants. Using the three-phase model developed by McIntyre and Aspnes¹⁷ and assuming that the incident wave is described by $e^{i(kr-\omega t)}$, we obtain, for the RA response,

$$\frac{\Delta R}{\bar{R}} = \frac{R_{[\bar{1}10]} - R_{[110]}}{(R_{[\bar{1}10]} + R_{[110]})/2} \approx \frac{R_{[\bar{1}10]} - R_{[110]}}{R_0}$$
$$\approx \frac{8\pi}{\lambda} \operatorname{Im} \left\{ \frac{(\tilde{\epsilon}_{[\bar{1}10]} - \tilde{\epsilon}_{[110]})d}{\tilde{\epsilon}_s - 1} \right\}, \tag{1}$$

where $R_{[\bar{1}10]}$ and $R_{[110]}$ are the power reflectances of light polarized along [$\bar{1}10$] and [110], respectively, \bar{R} is their average, R_0 is the power reflectance due to the bulk alone, *d* is the thickness of the anisotropic surface layer having complex dielectric functions $\tilde{\epsilon}_{[\bar{1}10]}$ and $\tilde{\epsilon}_{[110]}$ for the given polarization, and $\tilde{\epsilon}_s$ is the bulk dielectric function. At the photon energies we have used (1.96 eV and 2.54 eV), the bulk dielectric constant is mainly real,¹⁹ so the power reflectance anisotropy is proportional to the term Im{($\tilde{\epsilon}_{[\bar{1}10]} - \tilde{\epsilon}_{[110]})d$ }, which is often referred to as the surface-induced optical anisotropy (SIOA).

In comparing experimental results with the three-phase model, it is the anisotropy in complex reflectance that is frequently used and this is approximately related¹⁴ to the anisotropy in power reflectance by $\Delta R/\bar{R} = 2 \text{Re} \{\Delta \tilde{r}/\tilde{r}\}$. The anisotropy in complex reflectance can also be derived from the three-phase model and its real component is given by

$$\operatorname{Re}\left\{\frac{\Delta \tilde{r}}{\tilde{r}}\right\} = \operatorname{Re}\left\{-\frac{4\pi i}{\lambda}\left[\frac{(\tilde{\epsilon}_{[110]} - \tilde{\epsilon}_{[110]})d}{\tilde{\epsilon}_{s} - 1}\right]\right\}$$
$$= \frac{4\pi}{\lambda}\operatorname{Im}\left\{\frac{(\tilde{\epsilon}_{[\overline{1}10]} - \tilde{\epsilon}_{[110]})d}{\tilde{\epsilon}_{s} - 1}\right\}.$$
(2)

The sign of both expressions depends on the choice of the description of plane wave and hence the sign of the imaginary part of the dielectric function. In the convention used here, the imaginary part of the dielectric constant is positive.

There are two aspects of the surface structure that influence the SIOA. These are (i) the microscopic structure of the surface unit cell, which provides the anisotropic "atomic" polarizability, and (ii) any domain structure on the surface over which the macroscopically observable anisotropy is obtained. The unit cell of the Si(001) surface has $p(2 \times 1)$ symmetry since the surface atoms form dimers^{20,21} and the total energy is further lowered by their asymmetry.²² Wijers et al.²³ have calculated the local polarizability of the surface unit cell using a cluster model and demonstrated its anisotropy, which is one of the necessary conditions for the existences of SIOA, as shown in the classical treatment outlined above. From a molecular point of view, we shall see (Sec. IV D) that a dangling-bond surface state must be involved as either the initial or final state of the excitation process, but because of the sign¹¹ of SIOA and the width of the features in the RA spectrum compared to the limited dispersion of the surface states, it is unlikely to be a pure surface-to-surface transition.

The Si(001) surface is also known to have a domain structure whose boundaries are steps. If these steps are of monolayer height $(a_0/4)$, then the dimers in the adjacent terraces separated by them are oriented in the orthogonal $\langle 110 \rangle$ directions. For the anisotropic local polarizability to manifest itself as a macroscopically observable RA, an average of the polarizability over the sum of domain structures within the area illuminated by the incident beam must be nonzero. This implies that to observe a net optical reflectance anisotropy (or nonzero SIOA) from the Si(001) surface, there must be a difference in coverage of the two domains.

The averaging processes involve two effects. The first is quantum mechanical, since the lateral coherence area of the photon wave packet is much larger than an individual dimer. If the area of a domain is much greater than the size of the wave packet (coherence area), all the transition dipole moments (or dimers) are likely to be oriented along the same direction with respect to an individual photon, but when these two dimensions become comparable, the total transition probability has to be considered; this is the average derived from an individual photon. The second averaging takes place between all photons arriving on the surface within the illuminated area. When the electronic transitions in the surface layer involve localized (nondispersing) surface states, the RA sums the contribution from all dimers in each domain within the illuminated area. Hence the reflectance difference obtained should be proportional to the difference in coverage of the two different types of domain. There is no interference effect from terraces at different heights since the wavelength of the incident light is much greater than the step height.

Spectroscopic RA data for a single domain surface produced by misorientation have been obtained for Si(001) (Ref. 11) and Ge(001) (Refs. 11 and 10). There appears to be a discrepancy in the sign of experimental results, however, which has strong implications for the possible electronic transitions involved. The sign of the anisotropy is not important for the results described here, but it will be discussed in Sec. IV D.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

In this section, dynamic changes in the RA response during homoepitaxy of Si on Si(001) surfaces using GSMBE are considered. We will address the nature of the observed RA oscillations and provide supporting evidence for a model based on the origin of RA response outlined above. Evidence is also provided to demonstrate that there is no net exchange of adatoms between the two different domains during growth interruption at a temperature of 600 °C. With an assumption based on adatom-step interaction, this implies that there is little or no hopping between terraces during growth interruption at this temperature. The role of surface hydrogen, which is a product of the disilane pyrolysis, is discussed in relation to its influence on dangling bond states and their involvement in the RA response. Finally, the issue of misorientation and its influence on the RA response is discussed. With the exception of Sec. IV E, all results have been obtained on samples oriented very close to the (001) low index plane.

A. Growth on singular surfaces: the model

We have previously reported a RA and RHEED invesigation of Si homoepitaxy on the Si(001) surface using hydride precursors.¹² The simultaneously observed RA and RHEED responses both exhibit oscillatory behavior (see Fig. 1 in Ref. 12), but there are two major differences between them. First, the frequency of the RA oscillations is exactly half that of the RHEED intensity oscillations and second, when growth is stopped or interrupted there is little or no change in the RA signal whereas the RHEED intensity undergoes rapid recovery towards its pregrowth value. This effect is most clearly demonstrated at point B in Fig. 1 of Ref. 12, where the RA response is furthest from its initial value. The rapid recovery of the RHEED intensity after suspension of growth indicates a significant reduction in surface step density by coalescence of two-dimensional (2D) islands. The lack of change in the RA response during the same period suggests that it is insensitive to this variation in surface step density. In Ref. 12, we attributed the oscillatory RA response to the domain coverage changes during growth. This is easily explained in terms of the following model.

We will first consider the frequency difference between RA and RHEED oscillations and the origin of oscillatory RA response with the aid of Fig. 1, which is analogous to the illustration used by Neave et al.²⁴ to explain the RHEED intensity oscillations during III-V MBE growth. The lefthand column depicts the state of the Si(001) surface in real space during Si deposition, with the two types of domain clearly distinguished. The starting surface is assumed to be dominated by one type of domain labeled α and growth is assumed to be monolayer by monolayer occurring by 2D nucleation, 2D island growth, and step annihilation via coalescence of 2D islands. The middle column shows the familiar response of the RHEED specular beam intensity to a layer-by-layer growth process, while the right-hand column illustrates the changes in domain coverage difference, $\Delta \theta = \theta_{\alpha} - \theta_{\beta}$, where θ_{α} and θ_{β} are the coverages of domains α and β . Surface step density and domain coverage change as a result of Si deposition or adatom migration. Given that the surface is always completely covered by the two types of domain, θ_{α} and θ_{β} are under the constraints of $\theta_{\alpha} + \theta_{\beta} = 1, \ 0 \le \theta_{\alpha,\beta} \le 1$. As a consequence, growth (increase) of one domain coverage is always at the expense of the other. Between (a-d), one monolayer of Si is deposited. The surface step density changes from a minimum through a maximum and back to a minimum again. Since the RHEED specular beam intensity is very sensitive to the step density,²⁵ its intensity changes from a maximum through a minimum and returns to a maximum, thus completing one oscillation for the deposition of a monolayer. During the same period, the domain coverage changes from dominance by type α to dominance by type β . The domain coverage difference $\Delta \theta$ therefore changes from a maximum to a minimum. Deposition of a further monolayer of Si (e-i) leads to another complete oscillation of the RHEED specular beam intensity and returns the surface to one being dominated by the type- α domain. During the deposition of two monolayers of Si (ai), the RHEED specular beam intensity completes two oscillations while the difference in domain coverage only completes one cycle. As the RA response is proportional to the difference in domain coverage (Sec. III), it would oscillate at the frequency of domain coverage difference, exactly half that of RHEED specular beam intensity oscillations.

For simplicity, we have assumed a starting surface dominated by one domain type in the above model, but it is not a necessity. If the growth mode is monolayer by monolayer, the constraints given above ensure that the growth of one domain is at the expense of the other and the domain coverage difference will oscillate as a result of growth. Even if the surface starts with an equal distribution of the two domains, a layer-by-layer growth mechanism necessarily breaks the symmetry that exists between the two domains and an oscillatory RA response will be obtained.

The validity of this model depends on the existence of anisotropy in local polarizability between the two polarization states of light. This can be removed if the RA response between two orthogonal $\langle 010 \rangle$ directions is considered, which can be achieved by rotating the sample through 45°. As the surface unit cell is symmetric between these direc-



FIG. 1. Schematic representation of the surface during growth, the expected RHEED specular beam intensity, and differences in domain coverage.

tions, irrespective of the domain coverage, there should be no SIOA. In practice, we observed no oscillatory RA response between these directions, using identical growth conditions to those used for the $\langle 110 \rangle$ alignment.

B. Comparison with simultaneous RHEED measurements

Variations of domain coverage during MBE growth have been shown to exist using RHEED (Refs. 26 and 27) and more recently by photoemission measurements²⁸ and scanning tunnel microscopy (STM).²⁹ In the case of RHEED, this is achieved by measuring the intensities of half-order diffraction features associated with the two-fold periodicity in the orthogonal $\langle 110 \rangle$ directions, which is assumed to be an indication of the coverage of the corresponding domain. Intensities of both half-order diffraction features can be measured concurrently in RHEED by considering them in the halforder Laue zone with the electron beam incident along the [010] direction. These measurements were performed simultaneously with measurements of the intensity of the RHEED specular beam and the RA response and are shown in Fig. 2. The growth conditions were similar to those described in



FIG. 2. RA response and RHEED intensity oscillations of the specular beam and half-order features in the half-order Laue zone obtained with an [010] electron beam incident azimuth and angle of incidence (a) $\approx 2^{\circ}$ and (b) $\approx 0.5^{\circ}$.

relation to Fig. 1 of Ref. 12. The Ar⁺ laser operating at 488 nm was used to monitor the RA response between the orthogonal $\langle 110 \rangle$ directions. The electron-beam incidence angles used for Figs. 2(a) and (b) were 2° and 0.5°, respectively. In both cases, the frequency of the RHEED specular beam intensity oscillations was twice that of the RA response. The temporal behavior of the intensities of the halforder diffraction features was, however, strongly dependent on the choice of angle of incidence. The results obtained at the two different angles of incidence are considered separately.

At 2° [as shown in Fig. 2(a)], the frequency of intensity variation in each half-order diffraction feature was the same as the RA response, i.e., half that of the specular beam, but there is a 180° phase difference between the two half-order traces. The RA response appears to be in phase with one of the fractional-order features. This is consistent with the results of Sakamoto²⁶ where the intensity oscillation of the half-order diffraction features is assumed to indicate domain coverage oscillations. We can conclude from these findings that the period of the RHEED specular beam intensity oscillation corresponds to monolayer growth time, i.e., the layerby-layer growth mode is occurring on the monolayer level as opposed to the bilayer level; and the frequency of RA oscillations corresponds exactly to the frequency of domain coverage variations. Hence, the assertion of a linear relationship between dynamic changes in RA response and that of variations in domain coverage difference is consistent with the current understanding of growth from other surface diagnostic techniques.

In the case of Fig. 2(b), where RHEED measurements were obtained with a lower angle of incidence, the initial temporal behavior of fractional-order features is more akin to that of the specular beam intensity, with monolayer periodicity, in contrast to results at the higher incidence angle. There is, however, a gradual evolution into the expected bilayer periodicity. It is therefore evident that it is too simplistic to assume absolute domain coverage can be derived directly from the intensity of the respective half-order diffraction features. The difficulty arises because with this assumption, the effects of long-range order,³⁰ steps, and multiple scattering are effectively ignored. In particular, for low angles of incidence, the specular beam intensity (reflectivity) is relatively high and any change in reflectivity influences the transmission of electrons into the surface. As a consequence, the monolayer periodicity of the specular reflectivity can influence other diffraction features, such as half-order beams, to produce a temporal variation at a monolayer frequency superimposed on the bilayer response.

With no difference in the RA arrangement, the RA results in Figs. 2(a) and (b) are essentially the same and reflect changes in the domain coverage. RA is in fact a more direct and absolute measure of the difference in domain coverage on Si(001) surfaces because the electronic transition probably involves a mostly localized state.

The mechanism proposed here for the dynamic changes in RA response during growth on Si(001) is quite different from that for III-V growth on surfaces such as GaAs(001). With an elemental semiconductor such as Si, there is no change in the structure of the reconstructed surface unit cell other than the switching of dimer direction in alternate layers. The dynamic changes in RA response are solely due to this phenomenon. Surface stoichiometry changes such as those proposed for III-V growth⁵ are not possible. Although the step density may affect the RA response, 31,32 if this were the major factor one would expect the frequency of the RA oscillations to be the same as the step density variation given by the RHEED specular beam intensity and also for there to be a significant change in RA response on interruption of growth. This is clearly not the case for growth on Si(001) and domain coverage variation must be the largest factor determining the changes in RA response.

C. Growth interruption

As shown in Fig. 1 of Ref. 12, the response of RA to an interruption of growth is considerably different from that of RHEED. In contrast to the relatively fast recovery of

Reflectance Anisotropy

0

600

500



FIG. 3. RA response during growth interruption at 600 °C.

100

400

Time (seconds)

RHEED intensity, the RA response shows little or no recovery towards its original state. This is demonstrated more clearly in Fig. 3, which shows the RA response at 488 nm obtained by a growth interruption of $\approx 4 \text{ min}$ duration between two growth periods, with the temperature maintained throughout at 600 °C. Growth was stopped at point B and restarted at point C and it is apparent that the RA oscillations recommence with the identical phase angle. This clearly implies that there is virtually no domain coverage variation during the period of interruption but the RHEED recovery indicates a reduction of surface step density, which can only be caused by surface migration of atoms or islands. This effect has been predicted by Monte Carlo simulations,³³ but this is the first experimental evidence, to our knowledge, to show the absence of domain coverage variation during growth interruption.

When there is no growth and negligible evaporation (as in this case), changes in domain coverage can only occur by the exchange of atoms between neighboring terraces, which requires atoms to hop over steps. It is evident from the recovery of the RHEED specular beam intensity that atoms are migrating within terraces to reduce the step density. This migration is known to be anisotropic between the orthogonal $\langle 110 \rangle$ directions³⁴ and to involve preferential sticking³⁵ at different steps with respect to the dimer direction in the upper terrace next to the step. Any migration over the step could, however, lead to a relative change in the domain coverage, which would eventually lead to bilayer steps as one type of domain became dominant. This is clearly contrary to the RA results, and, in addition, ex situ atomic force microscopy (AFM) examination of the sample surface showed only monolayer steps.36

There can be several possible reasons for the observed behavior; (i) a kinetic barrier to hopping at the step edge, (ii) exchange between domains which is statistically zero, and (iii) effective absence of an adatom population. The Monte Carlo simulation³³ that predicted this outcome did not have any barrier to step hopping built into the model though more recent results³⁷ show such a barrier may be present in some materials. Preferential capture by different types of steps makes statistically zero exchange between domains unlikely. Our results appear to be consistent with the third reason above but cannot rule out the others.



FIG. 4. RA response during growth at different substrate temperatures showing the disappearence of oscillatory behavior at high temperatures.

D. Effect of substrate temperature

The growth mode of Si on Si(001) during GSMBE is strongly influenced by parameters such as substrate temperature. Experimentally, RA oscillations are lost as the growth temperature is raised beyond 650 °C or lowered below 550 °C. These two extremes are of interest in evaluating the influence of the growth mode and other surface phenomena on the RA response.

Figure 4 shows the RA response at 1.96 eV as a function of substrate temperature with a constant incident disilane flux. With increasing substrate temperature, the oscillation amplitude decreases but the initial change (i.e., the difference between the value before growth and the average value during growth) increases. No RA oscillations were observed at temperatures $\geq 650 \,^{\circ}$ C nor were any RHEED specular beam intensity oscillations detected above this temperature (not shown in the figure). The concurrent disappearance of RA and RHEED oscillations suggests a change in the growth mode. The disappearance of RHEED intensity oscillations with increasing temperature on a vicinal surface has been attributed to growth by step propagation without 2D nucleation and hence with no change in average surface step density.³⁸ The steps were defined by the misorientation of the substrate. If the growth mode is by step propagation and the surface remains flat, then the step propagation velocities must be the same for all the steps. In the case of a Si(001)surface, this would not lead to any change in domain coverage or surface step density. While the surface examined is very close to the (001) low index plane, there is nevertheless



FIG. 5. RHEED specular beam intensity and RA response during growth of Si on the Si(001) surface at (a) 600 °C and (b) 500 °C.

a small difference between the physical surface and the (001) low index plane and the disappearance of both RA and RHEED oscillations can be explained in terms of a growth mode transition even for a surface with a small misorientation. It would, of course, necessitate a reasonably long adatom migration length.

The increase in the initial change, as defined above, reflects an increase in the difference between domain coverages of the starting surface and the average during growth. While the starting surface has been obtained consistently by annealing at high temperatures, the increase in this difference implies that the steady state domain coverage during growth is changing as a function of the substrate temperature. Given the anisotropy in adatom diffusion³⁴ and the differential sticking at the two different steps,³⁵ the surface would change towards one dominated by a single domain, if the migration length exceeded the terrace width defined by the misorientation. The results observed suggest this effect may become more important as the substrate temperature is increased. An absolute confirmation of this can be found in the STM observation by Voigtländer²⁹ obtained from a vicinal Si(001) surface at a temperature of 562 °C, where the oscillation in the coverage of one domain is centered at a value in excess of 50%.

The situation in the low-temperature regime is quite different and in Fig. 5 we show RA measurements obtained at 2.54 eV together with RHEED specular beam intensity traces taken concomitantly, at temperatures of 600 °C and 500 °C with a disilane flux similar to that used previously. At temperatures much below 550 °C, there is no oscillatory RA response, but the RHEED specular beam intensity still shows oscillations, confirming monolayer-by-monolayer growth. The loss of RA oscillations cannot therefore be attributed to a change of growth mode.

Other studies of Si growth from hydrides^{39,40} indicate that the surface becomes increasingly covered by hydrogen (a reaction product) as the substrate temperature is reduced below 550 °C. While the resulting monohydride surface has the same symmetry, the electronic configuration of the surface unit cell is changed as the dangling bonds are taken up by chemisorbed hydrogen. With such a change in the configuration, the electronic transition that gives rise to the SIOA may be affected directly and cause a reduction in RA response. Spectroscopic study confirms that the RA response below 3 eV is drastically reduced by the adsorption of disilane or atomic hydrogen.⁴¹ Hence the disappearance of RA can be attributed to the removal of the dangling orbitals and implies that the dangling orbital (which is a surface state) must be involved either as an initial or final state in the electronic transitions that give rise to the anisotropic local polarizability.

Theoretical calculations²² have shown that the absorption features due to transition between the filled and empty dangling bond orbitals cannot be more than 1 eV. Even if one allows for the likely error in the estimation of band gap using the local-density-functional approximation, the absorption feature would still be at an energy significantly lower than the 2.7-eV peak of RAS spectra from the vicinal Si(001) surface at elevated temperatures⁴¹ and the energies used in this work. If the transition involves only localized states (no dispersion), then the features observed in RA spectra should have similar width. The work of Yasuda et al.¹¹ has shown that the features are broad and the sign of RD is incompatible with a surface states only contribution. Given that the dangling orbitals are involved as initial (final) states, then the final (initial) states must come from the bulk to provide the necessary dispersion to cause the broad features observed.

E. Growth on vicinal Si(001) surfaces

In Sec. IV D, we indicated one of the effects of a residual misorientation on the dynamic changes of RA response. We therefore made careful measurements of the extent of misorientation of each substrate using back reflection Laue and AFM techniques. Where RA oscillations were observed the residual misorientation was measured to be $< 0.1^{\circ}$, but a large number of substrates showed no oscillatory RA response under growth conditions identical to those used to obtain the results shown in Fig. 2, even though the RHEED specular beam intensity exhibited oscillations similar to those observed on nominally singular surfaces. For these substrates, the misorientation was generally greater than



0.5 Monolayer deposited

FIG. 6. Schematic representation of a vicinal surface with (a) zero- and (b) 0.5-monolayer coverage in relation to the area illuminated by the incident optical beam.

 0.1° as judged by RHEED measurements³⁸ and in one case was found to be 0.3° using *ex situ* techniques.

The presence of RHEED intensity oscillations indicates unequivocally that a process of 2D nucleation and layer-bylayer growth is occurring on all the substrates irrespective of the extent of misorientation, so the lack of an oscillatory RA response cannot be explained in terms of a step propagation growth mode. Figure 6 is a schematic representation of a misoriented (vicinal) surface at zero- and half-monolayer coverage, with no preferential attachment at the steps. The islands nucleated on adjacent terraces differ in height by $a_0/4$ and are of different domain types. The area illuminated by the incident optical beam, shown by the ellipses, is sufficiently large to encompass a large number of terraces of each type; i.e., in general, for moderate amounts of misorientation $(\geq 0.1^{\circ})$ the terrace width $(\leq 770 \text{ Å})$ is much smaller than the dimension of the optical beam spot. Under these conditions, the asymmetry in domain coverage generated by nucleated islands on adjacent terraces will cancel and the domain coverage difference averaged over the area probed optically will not change. Hence there will be no oscillatory

RA response. The RHEED intensity responds largely to surface step density changes and so it is not affected by this self-cancelling process and oscillations will consequently be observed.

We have not attempted to determine an absolute value of the extent or direction of misorientation that would prevent the observation of RA oscillations. The values quoted here are for our specific experiments, although we would not expect them to be significantly different for other conditions.

V. SUMMARY

We have performed simultaneous RA and RHEED measurements on Si(001) surfaces during GSMBE and demonstrated oscillatory changes in the RA response. The frequency of the RA oscillations was shown to be half that of the RHEED specular beam intensity oscillations. On the basis of diffraction measurements, dynamic changes in the RA response are attributed to the variation of domain coverages on the Si(001) surface during growth and the observed relationship between the frequency of RHEED and RA oscillations is a natural consequence of the model. Comparisons of the temporal behavior of the intensities of fractional-order features in RHEED further confirm this model and demonstrate that RA provides domain coverage information and that it is largely free from the influence of long-range order and interference effects. The lack of changes in RA during growth interruption at 600 °C demonstrate for the first time the lack of changes in domain coverage as predicted by Monte Carlo simulations. The disappearance of RA oscillations at high temperatures was shown to be consistent with a growth mode change. Their disappearance at low temperatures is attributed to changes in the electronic configuration of the unit cell due to chemisorbed hydrogen. This strongly implies that the electronic transitions that give rise to the RA involve the dangling bond orbitals of the Si dimer as initial or final states. The oscillatory RA response is shown to be diminished by substantial misorientation of the physical surface away from the (001) low index plane. This is likely to be caused by the cancellation of domain changes on adjacent terraces due to the averaging process under the illuminated area.

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- ¹D. E. Aspnes, Surf. Sci. **307**, 1017 (1994).
- ²M. E. Pemble, S. R. Armstrong, S. M. Curry, R. D. Hoare, G.

Logothetis, I. M. Povey, A. Stafford, and A. G. Taylor, Faraday Discuss. **95**, 199 (1993).

- ³C. Pickering, D. A. O. Hope, R. T. Carline, and D. J. Robbins, J. Vac. Sci. Technol. A **13**, 740 (1995).
- ⁴D. E. Aspnes, J. P. Harbison, A. A. Studna, and L. T. Florez, Phys. Rev. Lett. **59**, 1687 (1987).
- ⁵J. P. Harbison, D. E. Aspnes, A. A. Studna, L. T. Florez, and M.

K. Kelly, Appl. Phys. Lett. 52, 2046 (1988).

- ⁶K. Deppert, J. Jönsson, and L. Samuelson, Appl. Phys. Lett. **61**, 1558 (1992).
- ⁷F. Reinhardt, W. Richter, A. B. Müller, D. Gutsche, P. Kurpas, K. Ploska, K. C. Rose, and M. Zorn, J. Vac. Sci. Technol. B **11**, 1427 (1993).
- ⁸S. R. Armstrong, R. D. Hoare, M. E. Pemble, I. M. Povey, A. Stafford, A. G. Taylor, B. A. Joyce, J. H. Neave, D. Klug, and J. Zhang, Surf. Sci. **274**, 263 (1992).
- ⁹J. Rumberg, F. Reinhardt, W. Richter, T. Farrell, and J. Armstrong, J. Vac. Sci. Technol. B 13, 88 (1995).
- ¹⁰H. Wormeester, D. J. Wentink, P. L. de Boeij, C. M. J. Wijers, and A. van Silfhout, Phys. Rev. B 47, 12 663 (1993).
- ¹¹T. Yasuda, L. Mantese, U. Rossow, and D. E. Aspnes, Phys. Rev. Lett. **74**, 3431 (1995).
- ¹²A. R. Turner, M. E. Pemble, J. M. Fernández, B. A. Joyce, J. Zhang, and A. G. Taylor, Phys. Rev. Lett. **74**, 3213 (1995).
- ¹³J. Zhang, A. Marinopoulou, J. Hartung, E. C. Lightowlers, N. Anwar, G. Parry, M. H. Xie, S. M. Mokler, X. D. Wu, and B. A. Joyce, J. Vac. Sci. Technol. A **12**, 1139 (1994).
- ¹⁴D. E. Aspnes, J. P. Harbison, A. A. Studna, and L. T. Florez, J. Vac. Sci. Technol. A 6, 1327 (1988).
- ¹⁵S. M. Scholz, A. B. Müller, W. Richter, D. R. T. Zhan, D. I. Westwood, D. A. Woolf, and R. H. Williams, J. Vac. Sci. Technol. B **10**, 1710 (1992).
- ¹⁶L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon Press Limited, Oxford, 1960), p. 278.
- ¹⁷J. D. E. McIntyre and D. E. Aspnes, Surf. Sci. 24, 417 (1971).
- ¹⁸A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, England, 1988), p. 165.
- ¹⁹D. E. Aspnes and A. A. Studna, Phys. Rev. B 27, 985 (1983).
- ²⁰R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. B 34, 5343 (1986).
- ²¹A. W. Munz, C. Zielger, and W. Göpel, Phys. Rev. Lett. **74**, 2244 (1995).
- ²²P. Krüger and J. Pollmann, Phys. Rev. Lett. 74, 1155 (1995).
- ²³C. M. J. Wijers, G. P. M. Poppe, P. L. de Boeij, H. G. Bekker, and

D. J. Wentink, Thin Solid Films 233, 28 (1993).

- ²⁴J. H. Neave, B. A. Joyce, P. J. Dobson, and N. Norton, Appl. Phys. A **31**, 1 (1983).
- ²⁵J. Zhang, J. H. Neave, B. A. Joyce, P. J. Dobson, and P. N. Fawcett, Surf. Sci. 231, 379 (1990).
- ²⁶T. Sakamoto, T. Kawamura, and G. Hashiguchi, Appl. Phys. Lett. 48, 1612 (1986).
- ²⁷N. Ohtani, S. M. Mokler, J. Zhang, and B. A. Joyce, Appl. Phys. Lett. **61**, 1399 (1992).
- ²⁸Y. Takakuwa, T. Yamaguchi, and N. Miyamoto, Surf. Sci. **328**, 136 (1994).
- ²⁹B. Voigtländer (unpublished).
- ³⁰J. Wollschläger, J. Falta, and M. Henzler, Appl. Phys. A 50, 57 (1990).
- ³¹T. Yasuda, D. E. Aspnes, D. R. Lee, C. H. Bjorkman, and G. Lucovsky, J. Vac. Sci. Technol. A **12**, 1152 (1994).
- ³²J. Rumberg, J. T. Zettler, K. Stahrenberg, K. Ploska, L. Däweritz, P. Schützenübe, and M. Wassermeier, Surf. Sci. **337**, 103 (1995).
- ³³S. Clarke, M. R. Wilby, D. D. Vvedensky, and T. Kawamura, Phys. Rev. B 40, 1369 (1989).
- ³⁴ Y. W. Mo, J. Kleiner, M. B. Webb, and M. G. Lagally, Surf. Sci. 268, 275 (1992).
- ³⁵Y. W. Mo, B. S. Swartzentruber, R. Kariotis, M. B. Webb, and M. G. Lagally, Phys. Rev. Lett. **63**, 2393 (1989).
- ³⁶C. Pickering and A. Pidduct (private communication).
- ³⁷P. Smilauer and D. D. Vvedensky, Phys. Rev. B 48, 17 603 (1993).
- ³⁸J. H. Neave, P. J. Dobson, B. A. Joyce, and J. Zhang, Appl. Phys. Lett. 47, 100 (1985).
- ³⁹S. M. Gates, C. M. Greenlief, S. K. Kulkarni, and H. H. Sawin, J. Vac. Sci. Technol. A 8, 2965 (1990).
- ⁴⁰N. Ohtani, S. Mokler, M. H. Xie, J. Zhang, and B. A. Joyce, Jpn. J. Appl. Phys **33**, 2311 (1994).
- ⁴¹ J. Zhang, A. K. Lees, Z. Sobiesierski, D. I. Westwood, D. Raisbeck, M. H. Xie, A. G. Taylor, J. M. Fernández, and B. A. Joyce (unpublished).