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Reflectance difference spectroscopy of highly oriented (2×1) reconstructed Si(001) surfaces

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We report on reflectance difference spectroscopy (RDS) from highly oriented, single-domain (2×1) reconstructed Si(001) surfaces. It is much closer to the ''ideal'' surface than the vicinal one commonly used in RDS. It was prepared using electromigration technique which resulted in large terraces (5 μm). Certain features that are attributed to 2×1 and 2×2 structures are significantly changed in spectra obtained from vicinal surfaces. This indicates that the steps suppress formation of the 2×2 structures. The vicinal surfaces may have limited practical utility in RDS studies of the Si(001) surface. [S0163-1829(98)52312-0]

Reflectance difference spectroscopy (RDS), also known as reflectance anisotropic spectroscopy, measures changes in reflectivity as a function of the light polarization and is sensitive to optical anisotropy. When a material is optically isotropic in bulk, but has an anisotropic surface, RDS can be used as a surface-sensitive optical probe.[1] An important class of materials, semiconductors with a cubic lattice structure, is optically isotropic, and several semiconductor surfaces are optically anisotropic. As a surface-sensitive optical probe, RDS is unlike most other optical techniques which tend to be bulk sensitive, and unlike most surface-sensitive probes which are either based on incident electron beams or electron emission. As such it provides information that cannot be obtained with other techniques. In addition, RDS can be used in a variety of environments, unlike other techniques that require a vacuum. These factors make RDS a potentially useful technique. However, at present the use of RDS as a practical probe is still limited. This has been due in part to the difficulty of obtaining good data, and in part to a limited availability of theoretical results. Early RDS studies, for example, focused on (001) and (110) surfaces of III-V semiconductors.[2–4] These surfaces are relatively easy to study because they are inherently anisotropic. The interpretation of the resulting spectra has been limited, however.

In recent years several experimental[5–7] and theoretical[6,8,9] RDS studies have been performed on the Si(001) 2×1 reconstructed surface. This surface has received more attention, and theoretical RDS spectra are available for this surface.[6] The difficulty with the Si(001) surface lies in obtaining good RDS results. The anisotropy on this surface is due to the dimer associated with the reconstruction. On a typical surface equal amounts of 2×1 and 1×2 reconstructed domains are present. These domains differ only in the orientation of the dimers, which are oriented at 90° with respect to each other. As a result, the RDS signals of these two types of domains cancel each other. To obtain RDS spectra from the Si(001) surface, it is therefore necessary to create a surface that has an excess of one of the two dimer orientations. This is typically accomplished by using vicinal surfaces that have angles of miscut between 1° and 4°.[10–12] The relative coverage of the majority domain varies with angle of miscut. A potential drawback of this technique is that, based on the angle of miscut, the average terrace width varies from 40 to 160 Å, which is on the order of 10 to 40 dimers. As a result, a significant fraction of the dimers borders on a terrace edge and are affected by the step. To minimize the effect of terrace edges we performed RDS measurements on highly oriented surfaces. Using an electromigration technique a surface with large terraces covered with uniformly oriented dimers was prepared.[13–16]

The samples used in this study were 7×28 mm^2 rectangular pieces of n-type silicon with the long side of the sample oriented along the ⟨110⟩ direction. The samples were cut off from polished silicon wafers with a surface oriented to ⟨001⟩ to within 30′ in the ⟨110⟩ direction, and within 3″ along the ⟨110⟩ direction. Before a sample was introduced into vacuum it was cleaned in organic solvents such as trichloro-ethylene and acetone, etched with hydroflouric acid for 30 sec, and boiled in a 1:1 solution of H_2SO_4 and H_2O_2 for 10 min. Within 20–30 min after the chemical cleaning the sample was introduced through a load lock into the UHV system.

The UHV system consists of a heat-treatment and deposition chamber and a separate chamber for the optical measurements. The pressure in the UHV returned to its base pressure of 2×10^{-10} Torr within ten min after the introduction of the sample. After the pressure returned to normal, the sample was annealed by gradually heating it to 1000 °C by a dc that ran through the length of the sample. At 1000 °C the current through the sample reached 7.5 A at 12 V. The sample was kept at 1000 °C for 3 h. The temperature of the sample was measured with an optical pyrometer. At no time during sample heating did the chamber pressure exceed 5×10^{-10} Torr.

After the anneal the presence of a uniform 2×1 reconstruction was varied *in situ* by low-energy electron diffraction (LEED). If the reconstruction was not sufficiently uniform, a second anneal was performed. The LEED pattern of a sample prepared with the electromigration method described above is shown in Fig. 1(a). As can be seen in the figure, the (2×1) LEED pattern is clearly visible while the (1×2) pattern is very faint. This indicates that the surface is predominantly covered with 2×1 reconstructed domains. Note that the LEED pattern does not show the presence of the 2×2 structures that are discussed below. We attribute this to the limited size of the 2×2 domains. Scanning tunneling microscopy studies show, for example, that even at low temperatures the size of these domains is only on the order of ten dimers[17] and that around room temperature the phase defects between the small 2×2 domain rapidly migrate.[18] To measure the step distribution on the surface,

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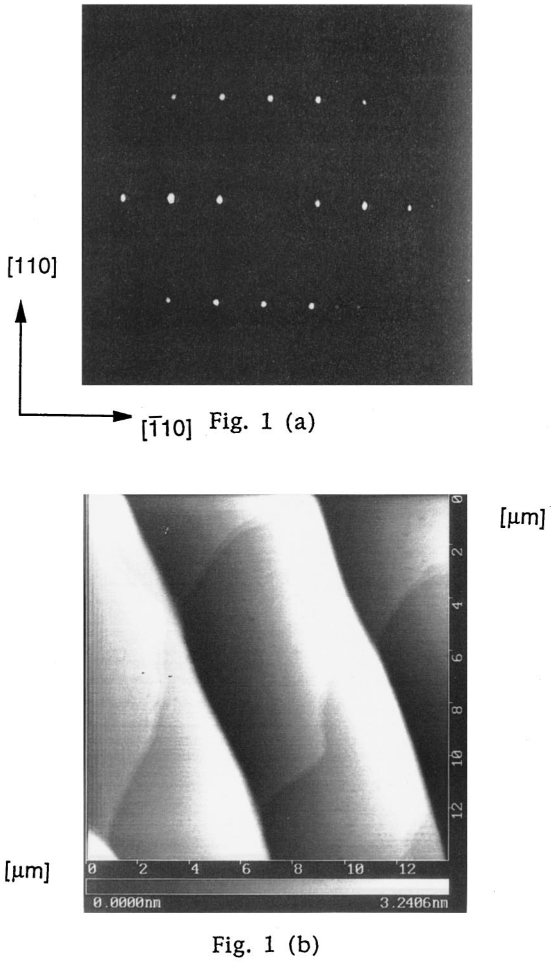

FIG. 1. (a) A LEED pattern obtained from a highly oriented Si(001) surface prepared with the electromigration technique described in the text. The beam energy is 60 eV. The figure shows a 2×1 reconstructed Si(001) surface with a uniform dimer orientation. (b) A 13×13 μm^2 AFM image of the same surface. The terraces shown in the figure are typically 5×5 μm^2, and are separated by bunched steps.

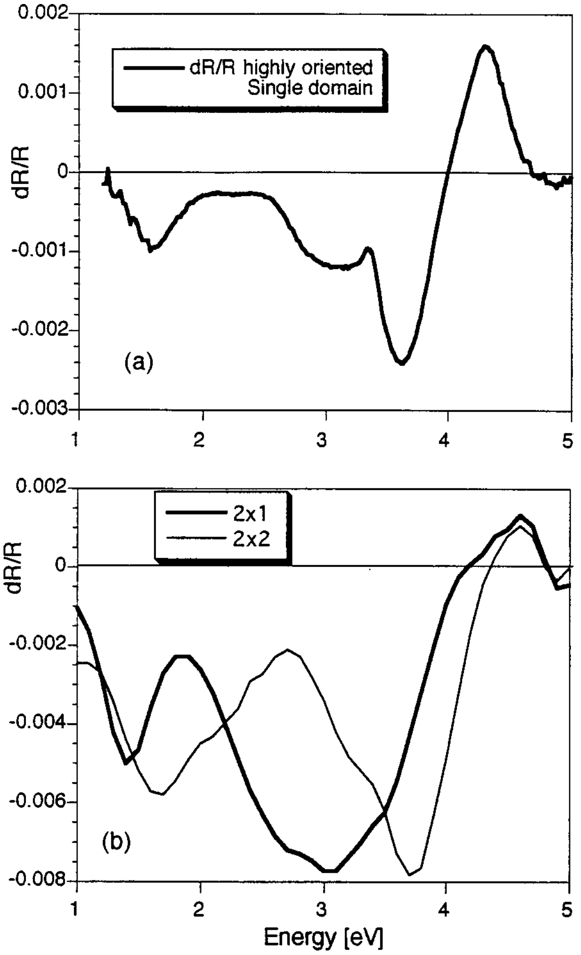

FIG. 2. (a) A RDS spectrum of a highly oriented single domain 2×1 Si(001) surface. (b) Theoretical spectra of 2×1 and 2×2 structures reported by Kipp *et al.* (Ref. 6). The figure shows that several features in the experimental spectrum, at 1.6, 3.1, and 3.7 eV agree very well with corresponding features in the theoretical spectra.

in-air atomic-force microscopy (AFM) measurements were performed on the reconstructed surfaces. A typical AFM image is shown in Fig. 1(b). The AFM image shows bunched steps approximately 5 μm apart in the $\langle 110\rangle$ direction and double-layer steps every 5 μm in the $\langle 110\rangle$ direction. The terraces between these steps are atomically flat. This terrace width is about 1000 times larger than that obtained with vicinal surfaces. For the RDS studies a number of 2×1 reconstructed surfaces were prepared as described above and transferred *in vacuo* to the chamber in which RDS measurements are performed. The RDS measurement system is similar to the one developed by Aspnes.[19]

A typical spectrum of a highly oriented 2×1 reconstructed surface is shown in Fig. 2(a). The RDS signal $dR/R=\text{Re}[2(r_{\bar{1}10}-r_{110})/(r_{\bar{1}10}+r_{110})]$, where r_{-110} and r_{110} are the complex reflectivities for light polarized, respectively, parallel and perpendicular to the dimer row of the majority domain. To interpret the various features in the RDS spectrum, we compare the experimental data with theoretical spectra reported by Kipp *et al.*[6] These spectra, shown in Fig. 2(b), were calculated for two structures that occur on the 2×1 reconstructed Si(001) surface; a 2×1 structure, in which all the dimers buckle in the same direction, and a 2×2 structure, in which the dimers buckle in alternating directions. The latter structure is found in the $p(2\times2)$ and $c(2\times4)$ reconstructions. Theoretical calculations show that the 2×2 based structures are about 90 meV lower in energy than the 2×1 structure.[20] At room temperature the surface is therefore expected to be mainly covered with 2×2 structures. When we compare the experimental spectrum with the theoretical spectrum for the 2×2 structure we find that the sharp features in the experimental spectrum at 3.7 and 1.6 eV agree very well with the spectrum calculated for the 2×2 structure. Similarly, the broader feature at 3.1 eV corresponds well with the spectrum calculated for the 2×1 structure. The peak at 4.3 eV, appearing in the experimental spectrum clearly, is very small in the theoretical spectrum.

Shown in Fig. 3 are spectra obtained from a highly oriented sample and various miscut samples. The spectra labeled 0, 1, 2, 3, and 4 were obtained from a highly oriented surface and vicinal surfaces at, respectively, 1°, 2°, 3°, and 4° off normal. These vicinal surfaces are prepared with the conventional method. This involves heating the sample for several hours to 400 °C for degas, followed by a quick

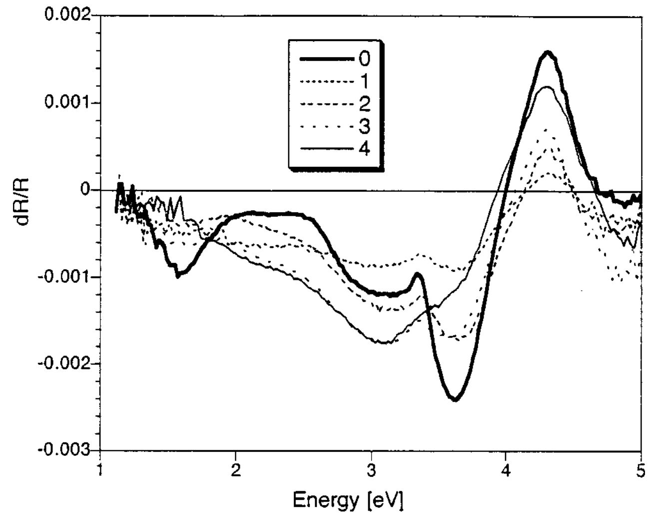

FIG. 3. Various RDS spectra obtained from single domain 2×1 Si(001) surfaces. The spectrum labeled 0° was obtained from a highly oriented surface prepared with the electromigration technique. The spectra labeled 1°, 2°, 3°, and 4° were obtained from vicinal surfaces at, respectively, 1°, 2°, 3°, and 4° off normal. These surfaces were prepared using the conventional method, which consist of annealing to 1000 °C for 1 min.

(1 min) anneal to 1000 °C. Based on LEED observations, the anisotropy, the ratio between the 2×1 and 1×2 reconstruction areas, vary with the miscut angle. The coverage of the majority domain of the 4° off sample is typically 90%. The majority domain coverage of the vicinal samples decreases monotonously with the decreasing miscut angle, to 60% for the 1° off sample, as has been shown in the STM observation and theoretical studies.[11,12]

When we compare the results from the highly oriented samples with RD spectra obtained from vicinal surfaces, we find that the angle of miscut has a significant effect on the RD spectrum. As can be seen in this figure, the spectrum of the 1° off sample shows the smaller features in all energy range because of the poor anisotropy of the surface. The peak intensity around 4.3 eV decrease monotonously with the decreasing anisotropy. It has also been pointed out in the RD change at high temperature.[7] The pronounced peak at 1.6 eV is reduced in the 2° and 3° miscut sample, and has completely disappeared in the 4° miscut sample. However the features around 2–4 eV show the complicated change with the miscut angle. These features around 3.1 and 3.7 eV are related to the 2×1 and the 2×2 structures, as was expected based on the theoretical spectra. Therefore the ratio of the peak intensities at 3.1 and 3.7 eV should be related to the ratio of the 2×1 and the 2×2 reconstruction. The reduction in the features associated with the 2×2 structure with the increase of miscut angle indicates that the area of 2×2 structures decrease and that of the 2×1 structures increases. Because the number of steps increases with the increase of miscut angle, we attribute this effect to the presence of steps on the surface. However, the complete interpretation of these peaks on RD spectra is difficult. On these surfaces, the anisotropy also changes with the miscut angle as discussed before. Furthermore, the 1.4-eV feature that is also present in the theoretical spectrum for the 2×1 structure is not present in our experimental spectra.

In summary, using various vicinal Si(001) samples, we were able to measure RDS peaks at 1.6, 3.1, 3.7, and 4.3 eV. With the change of miscut angle, these peaks changed, respectively. The peak intensity at 4.3 eV decreases monotonically with the decrease of the anisotropy. We attribute other features to the presence of 2×1 and 2×2 structures, based on calculations by Kipp *et al.*[6] With miscut angle increasing, the feature at 1.6 eV is significantly reduced and the ratio of the peak intensities at 3.1 eV to that at 3.7 eV decrease. We attribute these changes to the presence of step edges which affect the surface structure such as the 2×1 and 2×2 structures in which the buckled dimers change their ordering.

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