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Strong optical anisotropy of the single-domain 5×2-Au reconstruction on vicinal Si(111)

J. R. Power and P. Weightman
IRC in Surface Science, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, United Kingdom

J. D. O'Mahony
School of Physics, Dublin Institute of Technology, Kevin Street, Dublin 8, Ireland

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Reflectance anisotropy spectroscopy is applied to metal overlayer growth on the silicon (111) surface. Submonolayer coverages of Au are applied to a stepped Si(111) surface. The evolution of the single-domain Au-induced 5×2 superstructure is seen to produce an optical anisotropy of considerable amplitude for saturation coverage. The optical anisotropy in the region of 2.7 eV is unambiguously assigned to the bonding orientation within the 5×2 unit cell. [S0163-1829(97)04431-7]

Gold overlayers on the (111) crystallographic surface of silicon in the submonolayer coverage regime have been extensively studied for decades with a variety of surface analysis techniques (see references in Ref. 1 for a comprehensive list). Yet despite the considerable body of information available, many questions still remain regarding the geometrical and electronic structure of Au-induced superstructures on Si(111). In an effort to simplify the problem, the use of vicinal or stepped Si(111) substrates for Au overlayer growth, rather than singular or flat surfaces, has recently become popular[1–5] since the presence of atomic steps can allow for control of superstructure growth by favoring nucleation along the step edges. Thus while the threefold symmetrical singular (111) surface would normally accommodate three equivalent superstructure domains by symmetry, slightly vicinal surfaces, if properly prepared, can limit the overlayer growth to a single domain only. Cross domain interference is thus avoided, considerably simplifying experimental analysis. The resulting difference in symmetry of the overlayer with respect to the underlying crystal can also be exploited experimentally, as we show in this work.

Using this approach to overlayer growth, Au coverages of the order of 0.5 monolayers on vicinal Si(111) cut 4° off the [111] direction towards $[11\bar{2}]$ have been shown by scanning tunneling microscopy (STM) to cause spectacular large scale reorganization of the Si(111) surface.[1] At saturation coverage, approximately 500-Å-wide terraces consisting of long chainlike Au-induced structures with a local 5×2 unit cell were observed with the chain length running exclusively along the $[\bar{1}10]$ (step edge) direction. No evidence of chain structures in the $[0\bar{1}1]$ or $[10\bar{1}]$ directions was found, the symmetrically equivalent directions on a singular Si(111) surface. The single-domain 5×2 terraces were seen to be separated by equally wide faceted regions exhibiting ordered step bunching with a facet normal direction of approximately [775], consistent with the offcut angle of the surface. At the saturation coverage for this structure, the surface order is extremely long range, with the 5×2 terraces and intermediate faceted regions creating a mesoscopic ''striping'' effect, with near defect-free chains on the terraces extending for micrometers across the surface (Fig. 7 of Ref. 1).

Besides showing an unusual physical structure, the single domain 5×2 surface also has an electronic structure with unexpected properties. The results of angle-resolved photoelectron spectroscopy show anisotropic electron density at the Fermi level for the system, indicating quasi-one-dimensional metallicity.[3] This is the first time, to our knowledge, that this has been seen in such a system. The linear optical technique of spectroscopic ellipsometry (SE) has also found unusual behavior for the single-domain system, with an extremely sharp change in the optical response being recorded at 2.7 eV for the saturated 5×2 surface.[5] That work also showed a clear difference in optical response between the three-domain and single-domain systems.

The strong anisotropy of the single-domain system makes it an ideal candidate for study with the technique of reflectance anisotropy spectroscopy (RAS). RAS, a powerful tool for observing surface-related optical anisotropy, was developed in its present form by Aspnes and Studna.[6] 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,[7,8] but it appears that a different calculation of the RAS response is required for each surface. Use of RAS has predominantly been confined to (100) or (110) crystallographic surfaces which have clear structural anisotropies — the (111) crystallographic surface has attracted little attention since it gives zero RAS by symmetry. This present study is, to our knowledge, the first to apply RAS to metal overlayer growth on a (111) surface. The RAS signal is nonzero here since the step-induced single-domain growth creates an overlayer with different symmetry to the underlying crystal.

The RAS experimental arrangement used in this work is similar to that described by Aspnes and co-workers.[9] The reflectance difference signal ΔR is normalized to the average reflectance R and is related to the surface and bulk dielectric function components by

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

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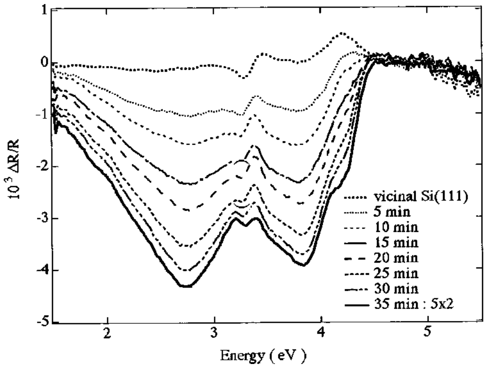

FIG. 1. RAS spectra at various stages of the growth of Au on the vicinal Si(111) surface from the clean 7×7 surface up to completion of the single-domain 5×2-Au superstructure. Spectra were taken at intervals corresponding to 5 min of Au deposition followed by annealing at 873 K. The curves progress downwards with increasing coverage.

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 direction [110] (parallel to the step edges), while the y crystallographic axis is $[11\bar{2}]$ (perpendicular to the step edges). It follows from Eq. (1) that when ϵ_b is predominantly real, a negative signal indicates preferential absorption in the y direction. Equation (1) is strictly valid only for $d \ll \lambda$.

The experiments were performed in an ultrahigh vacuum chamber with a system base pressure of 4×10^{-11} mbar. The vicinal Si(111) substrate was p type, lightly boron doped with a resistivity in the range $1-10$ Ω cm and was polished 4° off the [111] direction towards $[11\bar{2}]$. Thermal treatment of the surface to produce a clean regular array of ordered single-height steps followed the procedure detailed by O'Mahony *et al.*[10] with temperatures being monitored by optical pyrometry. Growth of Au on this clean surface was achieved using a stabilized Knudsen cell evaporator. Deposition proceeded in steps of 5 min, each step being followed by sample annealing at 873 K. Upon cooling after each anneal, low energy electron diffraction (LEED) patterns of the surface were observed and RAS spectra were recorded. No direct attempt was made to measure the actual coverage or deposition rate of the Au as the LEED images were sufficient to indicate the changing surface structure.

Figure 1 shows the series of RAS spectra recorded during the development of the 5×2 structure on the clean vicinal Si(111) surface. The top RAS spectrum corresponds to the clean vicinal Si(111) surface. A sharp 7×7 LEED pattern, with electron energy-dependent spot splitting due to the steps, was observed for this surface. This spectrum is consistent in amplitude and shape with those published for hydrogen-terminated Si(111) by Yasuda *et al.*[11] at various vicinalities. The principal spectral features near 3.4 eV and 4.2 eV for the clean surface are bulk related, corresponding to optical transitions across the direct silicon band gap. The anisotropy of the vicinal surface, due to the presence of steps, allows these bulk features to contribute to the total RAS signal [see Eq. (1)].

For an initial deposition of 5 min, estimated to correspond to less than 0.1 ML of Au, followed by annealing at 873 K, no noticeable change was observed in the LEED pattern. However, a significant change is already apparent in the RAS spectrum at all energies below 4.5 eV. Assigning changes in the spectra above 3.1 eV to surface optical transitions is complicated by the onset of bulk-related features, but any features present below this onset are unambiguously surface specific. For such Au coverages under similar growth conditions, STM images revealed wide-scale reorganization of the Si surface, converting the regular array of equally spaced steps on the clean surface into a series of wide terraces consisting of equal areas of the Au-induced 5×2 structure and the 7×7 structure, separated by compact stepped or faceted regions which display more regularity along the step edges than does the initial clean vicinal surface. The narrow terraces separating the steps within these stepped regions remain reconstructed in 7×7 units, with some local 5×5 ordering at the step edges (see Fig. 2 of Ref. 1).

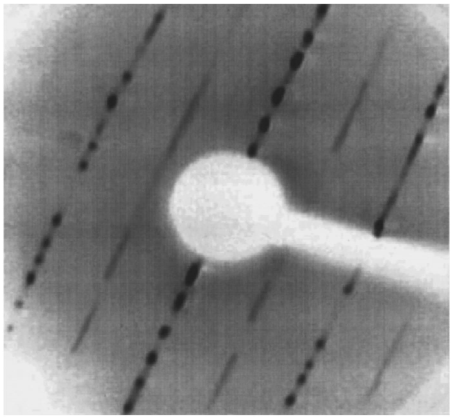

FIG. 2. A LEED pattern of the Au-induced single-domain 5×2 structure on vicinal Si(111) at saturation coverage taken with an electron beam energy of 73 eV. The streaking in the second order positions is due to random shifting in the registry of the row structure.

After 10 min of Au deposition, a surface feature develops near 2.7 eV in the RAS spectrum. Beyond this coverage, the LEED pattern begins to show evidence of the formation of a single-domain 5×2 structure, coexisting with the Si 7×7 structure. With further deposition of Au, the 2.7 eV peak dominates the RAS spectra, reaching a maximum amplitude after 35 min of Au deposition. This signal amplitude, 4.3×10^{-3}, is quite a significant anisotropy for a submonolayer metal-semiconductor system. At this point, the corresponding LEED pattern was fully single-domain 5×2, with sharp fifth order spots and streaking in the second order positions, consistent with the surface periodicities observed by STM for the saturated surface[1] (see Fig. 2). Concurrently with the evolution of the peak at 2.7 eV, a strong feature develops at 3.8 eV. Further smaller features are seen in the region of 3.3 eV and 4.2 eV. A sharp reduction of signal is observed beyond 4.2 eV, with no further anisotropy above 4.4 eV. Of note is that the RAS signal is *wholly negative* throughout the transition from the 7×7 to 5×2 structure. This indicates that the surface anisotropy responsible in this energy region is entirely in the $[11\bar{2}]$ direction, i.e., *perpendicular* to the apparent 5×2 chain length.

Continued deposition of Au on the 5×2 surface resulted in the eventual formation of the $\sqrt{3}\times\sqrt{3}$ structure after a

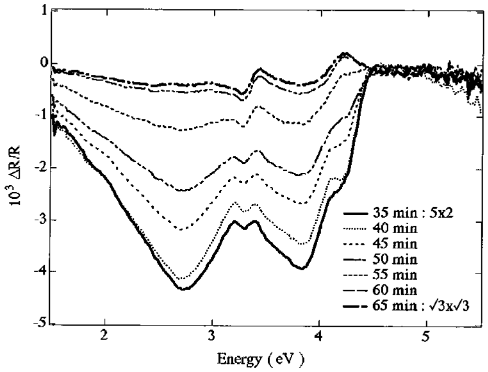

FIG. 3. RAS spectra at various stages of the growth of Au on the single-domain 5×2-Au superstructure up to completion of the $\sqrt{3}\times\sqrt{3}$-Au superstructure. Spectra were taken at intervals corresponding to 5 min of Au deposition followed by annealing at 873 K. The curves progress upwards with increasing coverage.

total of 65 min of deposition. LEED initially showed the presence of both 5×2 and $\sqrt{3}\times\sqrt{3}$ patterns until, at 65 min, the pattern was fully $\sqrt{3}\times\sqrt{3}$. Figure 3 shows the RAS spectra at regular intervals during this transition. Generally, the spectral features which maximized at the completion of the 5×2 structure decay with the gradual formation of the $\sqrt{3}\times\sqrt{3}$ with some interesting variation in the 3.3−3.4 eV and 4.2 eV energy regions (see Fig. 3). When the $\sqrt{3}\times\sqrt{3}$ superstructure is complete, the RAS spectrum again resembles that of the initial clean Si(111) surface, but with a number of residual anisotropic differences.

Significantly, SE (Ref. 5) has recently demonstrated a similar sharp optical transition for the single-domain 5×2 structure at 2.7 eV which disappears as the $\sqrt{3}\times\sqrt{3}$ structure is formed. No such transition was evident on the three-domain surface in that work. Disruption of the Au-induced chain structure due to cross-domain interference was considered the likely reason for the difference. The Au-induced chains within a threefold symmetrical 5×2 surface are inaccessible to RAS for symmetry reasons, but the SE results for the single-domain 5×2 structure at 2.7 eV are in agreement with the current data, though no surface directionality could be assigned to the optical anisotropy in that work because of the limitations of the experimental geometry used. The normal incidence work presented here resolves the directionality issues raised in the SE experiment.

Marks and Plass[4] have recently proposed a convincing and relatively simple geometric structure for the single-domain 5×2 surface. Using heavy-atom holography to locate the Au core positions, their model consists of staggered double rows of Au atoms extending in the [110] direction separated by bare silicon regions. The structure is consistent with much of the previously published data on this surface and on the three-domain surface and in particular may explain the high-resolution STM images of O'Mahony *et al.*[1] The maximum optical anisotropy shown in Fig. 1, at a saturation of the 5×2 structure, is in the $[11\bar{2}]$ direction, perpendicular to the length of the Au rows. The photoemission spectra from this surface[3] indicates that initial states are available near the Fermi level in the $[11\bar{2}]$ direction which could result in optical transitions of 2.7 eV to empty states above the Fermi level. In addition, both the filled and empty state images obtained by STM for this surface reveal a structure predominantly in the direction perpendicular to the apparent row structures (see Fig. 4 adapted from Ref. 1) consistent with bonding in the $[11\bar{2}]$ direction. Hence we associate the peak at 2.7 eV to preferential absorption along an Au-induced bonding direction within the 5×2 unit cell. This electronic structure information, coupled with the geometry of the Marks and Plass model,[4] should help finalize the structure of the 5×2 system since the optical response can be extracted from any detailed electronic structure calculations of the structure.

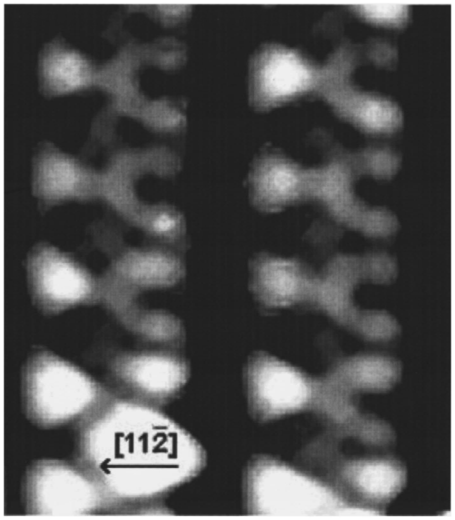

FIG. 4. A high-resolution 35 Å×40 Å scanning tunneling microscopy image of the filled states within the chains of the Au-induced 5×2 structure on Si(111). The brightest features are generally localized in the $y=[11\bar{2}]$ direction, perpendicular to the length of the chains (adapted from Ref. 1).

Apart from the Au-induced chain structures on the broad 5×2 terraces, the saturated 5×2 surface is known to contain three other principal features, namely, regular arrays of step edges within the [775]-oriented faceted regions, regular arrays of small terraces between the steps within the faceted regions, and random bright ''protrusion'' features which appear on top of the broad terraces of the 5×2 rows themselves.[1] The possibility of one or all of these features contributing totally or in part to the optical anisotropy must also be addressed.

The electronic structure of the faceted regions probed by STM (Refs. 1,2) indicates a density of states near the Fermi level confined principally to the step edges. Seehofer *et al.*[2] are ''tempted'' to assign these images to dangling bonds. Likewise, the bright protrusion features which appear on top of the 5×2 unit cell and within the facet terraces may be due to Si adatom dangling bonds, which does seem likely given the mass transport of Si on the surface during growth and annealing.[1] Dangling bond features are by their nature highly reactive — if they were to contribute to the RAS signal it is almost certain that both the amplitude and shape of the signal would change over time as the bonds become saturated with hydrogen, as shown by Yasuda *et al.* for dangling bonds on Si(001)-2×1.[12] In the present work no change was observed in the RAS spectrum for the saturated 5×2 system, even after a period of 72 h in ultrahigh vacuum. This effectively

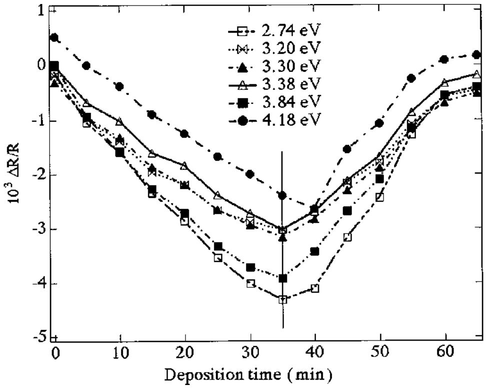

FIG. 5. Evolution of the RAS spectral features with deposition time. Note that the RA amplitude of the various spectral features displays a linear dependence with Au deposition time up to saturation of the 5×2-Au superstructure which is represented by a vertical line.

rules out the contribution of any Si dangling bonds to the RAS spectra for the 5×2 system and by implication rules out both step edges and protrusions.

Further evidence ruling out the contribution of the small terraces and the step edges in the faceted regions comes from the examination of Fig. 5. The RAS signal amplitude increases linearly in the $[11\overline{2}]$ direction with Au deposition time for all spectral features up to a saturation of the 5×2 structure. This indicates that any surface process or processes responsible for the RAS signal, such as the formation of the 5×2 rows or the formation of [775] facets, must scale *linearly* up to this saturation coverage. With reference to the detailed analysis of the STM data by O'Mahony *et al.*,[1] we note that for small Au coverages below saturation, all terrace features apart from the 5×2 structure on the compound terraces, namely, the 7×7 structure on the other half of the compound terraces and the 7×7 and local 5×5 structure on the narrow terraces within the stepped regions, are all optically isotropic and therefore cannot contribute to the RAS signal observed. Although there is increased ordering along step edges at low Au coverages, the steps on the clean vicinal Si(111)-7×7 surface display no significant anisotropy and the RAS signal is essentially zero below 3.1 eV. It is therefore unlikely that this step ordering could be responsible for the substantial initial increase in anisotropy. Hence, this increase must be related to the formation of the 5×2 structure itself. As the increase in RAS signal observed in this spectrum displays the same dependence on Au deposition time as subsequent spectra, up to a saturation of the 5×2 structure (see Fig. 5), it is reasonable to conclude that the 5×2 unit must be solely responsible for the observed anisotropy. Support for this view is provided by the work of Shibata *et al.*,[13] who established that the [775] facets have already formed after deposition of 0.3 ML of Au, that is, before saturation of the 5×2 structure. Since the RAS signal still increases in a linear fashion with Au deposition time even after the formation of the [775] facets, the formation of the [775] facets cannot be responsible for the RAS spectral features. One remaining alternative explanation for the origin of the RAS signal at 2.7 eV, that it arises from alternative structures on the terraces within the faceted regions, requires further consideration.

Near saturation coverage of the 5×2 structure, Au-induced features are observed on the narrow terraces of the [775] facets which may contribute to the strong anisotropy near 2.7 eV. Interestingly, these terraces are just large enough to accommodate a 5×2 unit cell, with the 5×direction oriented in the $[11\overline{2}]$ direction, indicating a close relationship between the two features.[1,2] Seehofer *et al.*[2] showed STM images of an Au-induced structure within the [775] facet terraces which in terms of the facet periodicity is labeled a 2×1 structure. This structure bears a striking resemblance to the 5×2 structure, the main difference appearing to be that the facet structure contains less ‘‘protrusion’’ features than the 5×2 superstructure. If this facet Au-induced 2×1 structure also contributes to the RAS signal near saturation, then the linear dependence we observe up to saturation of the 5×2 structure (see Fig. 5) is consistent with the facet terraces containing 5×2 structure also, in agreement with the interpretation of Seehofer *et al.*[2]

In conclusion, RAS has been applied to metal overlayer growth on the Si(111) surface. The structurally anisotropic single-domain Au-induced Si(111)-5×2 system shows strong optical anisotropy in the direction perpendicular to the apparent Au chain length. This optical anisotropy is unambiguously attributed to the effects of transverse bonding in the $[11\overline{2}]$ direction within the Au-induced chain structures on the 5×2 terraces.

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