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New evidence for the influence of step morphology on the formation of Au atomic chains on vicinal Si(111) surfaces

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Abstract – Gold atomic chain structures that grow on singular and vicinal Si(111) surfaces have attracted considerable interest as model systems for exploring quasi–one-dimensional metallic behaviour. The structure of the prototypical Si(111)-5×2-Au system remains controversial, however. Reflection anisotropy spectroscopy provides new, independent evidence supporting a recently proposed three-Au-chain structure. For stepped surfaces, the results provide good evidence that a single Au chain forms adjacent to $[\bar{1}\bar{1}2]$ steps and a double Au chain forms adjacent to $[11\bar{2}]$ steps. In both cases spectral lineshape and coverage data support a three-chain Si(111)-5×2-Au structure forming over the remainder of the terrace. For all the vicinal Si(111) surfaces, including Si(557) and Si(775), it is the step morphology, and not the terrace width, that determines whether single- or double-Au-chain structures are formed in the region of the steps.

The Si(111)-5×2-Au surface reconstruction has been intensively studied as a model system that shows quasi–one-dimensional behaviour associated with linear metallic chain structures [1–3]. However, despite the very large number of publications relating to this system, the structure of the 5×2-Au surface remains controversial. Recently, a new triple-chain structure was proposed, which provides better agreement with the experimental results from a range of techniques, in particular scanning tunnelling microscopy (STM) and angle-resolved photoemission spectroscopy (ARPES) studies [3].

This model is unusual because single-chain and double-chain models have dominated the discussions for sub-monolayer (sub-ML) coverages of Au on Si(111) and its small angle offcuts, although up to four-chain models have been considered [4]. For example, it is generally accepted that Au forms single chains on Si(557), the structure formed when Si(111) is offcut towards $[\bar{1}\bar{1}2]$ (fig. 1, top), while the current model for Si(775), formed when Si(111) is offcut in the opposite, $[11\bar{2}]$ direction, consists of double Au chains (fig. 1, middle) [5], although this may now be open to question in light of the triple-chain model (fig. 1, bottom) [3]. A key driver for the triple-chain model was a

new coverage determination of 0.6 ML Au for the Si(111)-5×2-Au reconstruction [6]. These careful measurements used as a reference the simpler single-Au-chain structure of Si(557)-Au, which is generally agreed to have a Au coverage of 0.18 ML relative to the Si(111) surface (fig. 1, top).

New reflection anisotropy spectroscopy (RAS) results are presented for sub-ML Au chain formation on Si(557) (offcut $+9.5°$ towards $[\bar{1}\bar{1}2]$ from [111]), Si(775) (offcut $-8.5°$ towards $[11\bar{2}]$), vicinal Si(111) offcut $+3°$ towards $[\bar{1}\bar{1}2]$, and vicinal Si(111) offcut $-4°$ towards $[11\bar{2}]$, where opposite offcut angles are given opposing signs, for clarity. Figure 1 shows that opposite offcuts have quite different step structures, but it is currently an open question whether the different chain structures of the [557] and [775] are determined by the local step structure or by the different terrace widths [5]. The singular Si(111)-5×2-Au structure, under normal preparation conditions, forms three domains of equal weight and is macroscopically optically isotropic, with no RAS response.

It has been shown previously, for the anisotropic systems, that the RAS response is very sensitive to the Au chain structure [7]. In addition, it is well known that the structure of the Si(557) and Si(775) surfaces change significantly, by faceting, both above and below the
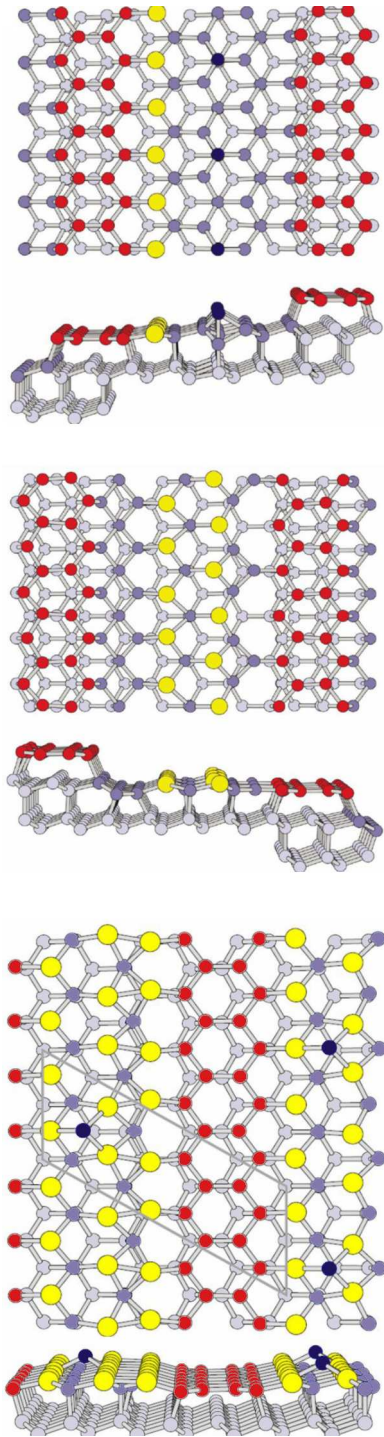
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Fig. 1: (Colour on-line) Schematics of some current structural models. Top: Si(557)-Au (after [5]). Middle: Si(775)-Au (after [5]). Bottom: Si(111)-5 × 2-Au (after [3]). The large yellow atoms are Au, the red atoms are the Si honeycomb chain, the dark blue atoms are Si adatoms and the grey atoms are the underlying Si.

Au coverage associated with each surface structure and provides independent confirmation of a triple-Au-chain structure for Si(111)-)-5 × 2-Au [6]. It also provides strong evidence that the steps determine the local Au chain structure in their neighbourhood, over a distance comparable to the terrace length of single-step-height (557) and (775) structures, before the triple-chain structure develops in areas away from the step region.

Commercially available n-type, P-doped vicinal offcuts of Si(111), of resistivity in the 1–10 ohm cm range, were used as substrates. The estimated error in offcut angle was 0.25°. Samples are cleaned by degassing at 600 °C for several hours in the ultra-high vacuum (UHV) system until the pressure is in the low 10^{-11} mbar range, and then by flash heating a number of times to 1200 °C, while maintaining the pressure below 2×10^{-10} mbar [9,10]. With care, this procedure produced single-domain structures for all the substrates. The samples were heated resistively, with the current flowing parallel to the steps on the Si(111) surface in order to avoid electromigration of the steps and possible step bunching [11–13]. A high temperature effusion cell (HTEZ-40) from MBE-Komponenten, designed for clean UHV operation up to 1600 °C, was used for the evaporation of Au. Deposition rates from the MBE cell were stable over long periods of time, as confirmed by a quartz crystal oscillator. A slow deposition rate was used, with 1 ML being deposited in about 450 s, allowing reasonably accurate coverage estimation in the sub-ML regime. At low coverages the deposition rates were cross-calibrated with the quartz crystal oscillator by using Auger electron spectroscopy and low-energy electron diffraction. For the completed Si(557)-Au structure a value of 0.19(3) ML Au coverage was obtained, where the estimated error is given in parenthesis. This is consistent with the accepted value of 0.18 ML.

The RAS spectrometer follows the design of Aspnes [14], but with the spectral range extended further into the infra-red region. Two magnesium fluoride polarizers, a calcium fluoride photoelectric modulator, a triple grating monochromator, and a combination of Si, InGaAs and liquid-nitrogen–cooled InAs detectors give a spectral range from 0.45 to 5.0 eV. *In situ* measurements are made using a strain relieved fused silica window. RAS measures the difference in reflectance, at near normal incidence, of light polarized in two orthogonal directions in the surface plane of a material [14,15]. The real part of the anisotropy in the reflection coefficients normalized to the average reflection coefficient, Re[$\Delta r/r$], was measured and is related to the surface and bulk dielectric function components by

$$\mathrm{Re}\left[\frac{\Delta r}{r}\right] = \frac{4\pi d}{\lambda}\mathrm{Im}\left[\frac{\epsilon_{\langle 110\rangle} - \epsilon_{\langle 112\rangle}}{\epsilon_b - 1}\right], \qquad (1)$$

where d is the overlayer thickness, λ is the wavelength of the light, $\epsilon_{\langle 110\rangle}$ and $\epsilon_{\langle 112\rangle}$ are the surface dielectric function components parallel and perpendicular to the steps, respectively, and ϵ_b is the bulk dielectric function.

coverage of the completed Au chain structures [6,8]. As the Au coverage increases at a substrate temperature of 600 °C, a well-defined minimum in the RAS signal is observed in real time. This can be used to determine the
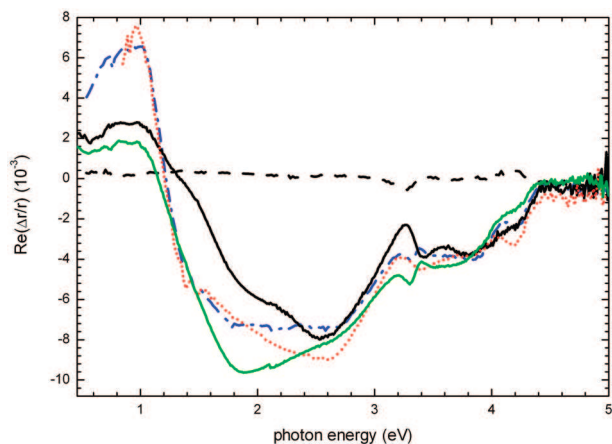
Fig. 2: (Colour on-line) The RAS response of the various structures at room temperature. Black dashes (- - -): Si(111), offcut by −4°. Blue dash-dotted line (⋅—⋅—): Si(111)-5 × 2-Au offcut by −4°. Red dots (⋅⋅⋅): Si(111)-5 × 2-Au offcut by +3°. Black line (——): Si(557)-Au, offcut by +9.5°. Green line (——): Si(775)-Au, offcut by −8.5°.

Fig. 3: (Colour on-line) Comparison between the Si(111)-5 × 2-Au offcut by +3°, with the Si(557) contribution removed and the terrace contribution rescaled (red line, ——), and Si(111)-5 × 2-Au offcut by −4°, with the Si(775) contribution removed and the terrace contribution rescaled (blue dash-dotted line, ⋅—⋅—).

RAS is surface and interface sensitive when the substrate is isotropic.

The room temperature RAS response of the four samples is shown in fig. 2. The response of clean Si(111), offcut by −4° is shown for comparison. There are small peaks in the 3.2–4.4 eV region that arise from step-modified bulk optical transitions across the direct Si band gap [16,17]. The peaks invert when the direction of offcut is reversed. All the samples show a positive peak in the region of 1 eV, but with varying amplitudes. A positive peak corresponds to a dominant optical polarization along the chain direction. The Si(557)-Au sample, offcut by +9.5°, has a minimum at 2.6 eV, while the minimum of the Si(775)-Au sample, offcut by −8.5° is at 1.9 eV. The Si(111)-5 × 2-Au sample, offcut by +3°, resembles Si(557)-Au, while the −4° offcut sample shows a broad, flat minimum. The difference in response between the +3° and −4° offcuts is clear evidence of the influence of the steps on the local Au chain structure. The terrace widths of the two opposite offcuts are closely similar, and a common RAS spectral profile would be expected if the Au chain structure depended principally on the terrace width.

If the influence of the steps extends to the same extent for all the offcuts, with the steps of the positive [$\bar{1}\bar{1}2$] offcut producing, locally, a single-Au-chain structure, like Si(557)-Au (fig. 1, top), and the steps of the negative [$11\bar{2}$] offcut producing, locally, a double Au chain structure, like Si(775)-Au, (fig. 1, middle), then the contributions of the step-induced structure to the overall response can be determined from the offcut angle of the various substrates and the spectra of fig. 2. The single-chain Si(557)-Au structure would occupy 32% of the +3° offcut surface, the remaining 68% being the triple-chain structure. Similarly, the double-chain Si(775)-Au structure would occupy 47%

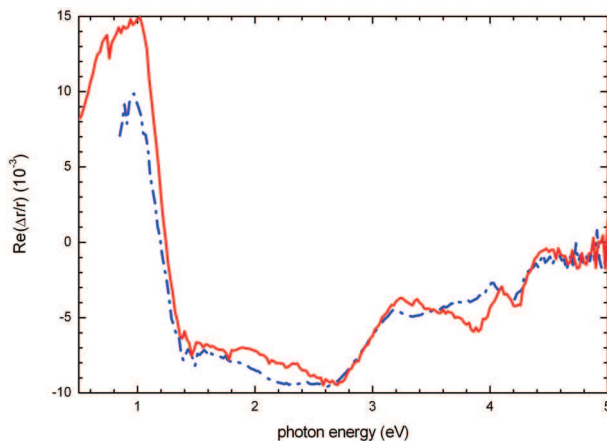of the −4° offcut surface, the remaining 53% being the triple-chain structure. Figure 3 shows the result of subtracting 32% of the Si(557)-Au spectrum from the +3° spectrum and dividing by 0.68 to produce the full triple-chain response. This is compared to the result of subtracting 47% of the Si(775)-Au spectrum from the −4° spectrum and dividing by 0.53, which should also produce the full triple-chain response. Figure 3 shows that very similar spectra are produced by this procedure in the region of the broad minima, supporting the simple hypothesis. This subtraction and scaling will not remove the different step-modified bulk optical transitions in the 3.2–4.4 eV region, nor does it account for the different amplitudes observed for the positive peak at ∼1 eV. This latter response, arising from a dominant polarizability along the chains, may be sensitive to the chain length, which on average would be expected to be longer for shallower offcuts, if a uniform kink density is assumed.

Further evidence supporting the simple model of a linear combination of step- and terrace-related features can be obtained from coverage measurements. The RAS response of Si(557)-Au is compared at room temperature and at the Au deposition temperature of 600 °C in fig. 4. Although the high temperature spectrum is broadened and reduced in amplitude, the figure shows that real time measurements of the optical response at, for example, 2.5 eV, should be possible during Au deposition. The results are shown in fig. 5, where the shutter was opened after 40 s and closed at times indicated by the arrows. The inset shows the Si(557) response as Au deposition is continued. The well-defined minimum observed on completion of the Si(557)-Au chain structure is typical and allows good estimates to be made of the Au chain coverages associated with the completed sub-ML structures of the four samples.
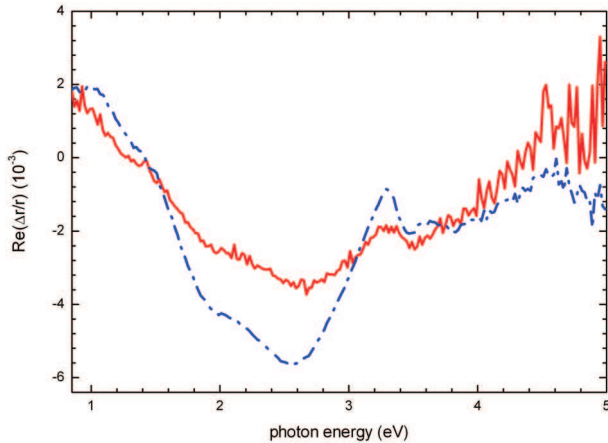
Fig. 4: (Colour on-line) The RAS response of Si(557)-Au. Blue dash-dotted line (−·−·−): room temperature. Red line (——): at the Au deposition temperature of 600 °C.
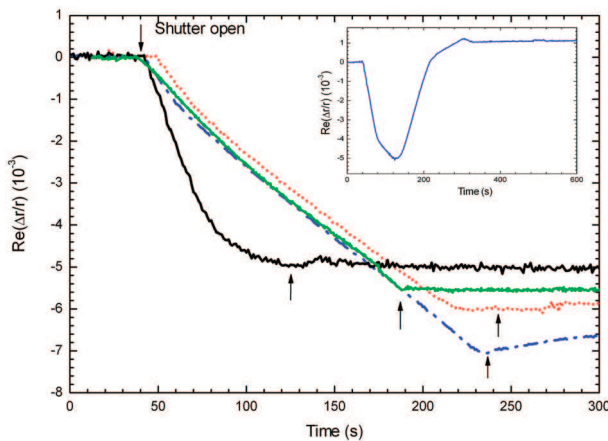

Fig. 5: (Colour on-line) The 2.5 eV transient during Au deposition on vicinal Si(111). Blue dash-dotted line (−·−·−): Si(111)-5 × 2-Au offcut by −4°. Red dots (···): Si(111)-5 × 2-Au offcut by +3°. Black line (——): Si(557)-Au, offcut by +9.5°. Green line (——): Si(775)-Au, offcut by −8.5°. The shutter was opened after 40 s and closed at points marked with arrows. The inset shows Si(557)-Au during continuing Au deposition, where the well-defined minimum associated with completion of the Si(557)-Au chain structure is clearly seen.

Table 1: Gold coverage data in monolayers. Estimated errors in the last figure are given in parenthesis.

Surface	Coverage	Si(111)-5 × 2-Au estimate	Au chain structure
Si(557)-Au	0.18(1)		single
Si(775)-Au	0.32(2)		double
Si(111)-Au (+3°)	0.44(4)	0.56(6)	triple
Si(111)-Au (−4°)	0.46(4)	0.58(6)	triple

Table 1 lists coverages based on the 0.176 ML Au coverage of Si(557)-Au [6]. Multiple measurements of the position of the RAS minimum for this structure reduced the measurement error to 0.01 ML Au. The singular Si(111)-5 × 2-Au coverages are extracted using the same procedure as above and, within error, provide independent confirmation of the single-, double- and new triple-chain structures of sub-ML Au coverages on the Si(557), Si(775) and Si(111) substrates, respectively. The coverage estimate for Si(775)-Au agrees, within error, with previous work [8], provided the new Si(111)-5 × 2-Au coverage of 0.6 ML [6] is used to rescale the previous results.

These results have resolved the key question of the origin of the single-Au-chain structure of Si(557)-Au and the double-chain structure of Si(775)-Au. The two possibilities are, firstly, that the double-chain structure is the preferred structure on (111) terraces and that this has sufficient space to form on the wider Si(775) terrace, but not on the narrower Si(557) terrace [5]. This was a plausible explanation because experimental evidence from singular Si(111)-5 × 2-Au was thought to support a two-chain structure and *ab initio* calculations indicated that these were the lowest-energy structures that formed on (111) terraces [18,19]. The second possibility is that the step morphology controls the Au chain structure in the region of the steps and this drives the formation of the single chain in the positive offcut direction and the double chain in the negative offcut direction. These new results show that the chain structures of Si(557) and Si(775) are determined by the step morphology. In addition, the results support the new triple-chain model for (111) terraces and, for vicinal offcuts, a simple model in which the proportion of single to triple chains for positive offcuts in the $[\bar{1}\bar{1}2]$ direction depends on the offcut angle, and similarly for the double- to triple-chain proportion for the negative $[11\bar{2}]$ direction offcut. The possibilities of band gap engineering on these surfaces appears not to be limited to odd Miller index plane offcuts [5].

In conclusion, RAS has been shown to provide detailed information on the chain structures that form at sub-ML coverages of Au on singular and vicinal Si(111). Evidence has been presented that supports the new triple-chain structure of Si(111)-5 × 2-Au [3]. Both spectral lineshape and coverage measurements provide new evidence that, for vicinal offcuts of Si(111), including Si(557) and Si(775), step morphology controls the local Au chain structure, with single Au chains forming in the region of $[\bar{1}\bar{1}2]$ offcut steps, and double chains forming in the region of $[11\bar{2}]$ offcut steps. For anisotropic chain structures grown on (111) terraces, RAS has been shown previously to provide important complementary information to conventional surface characterisation techniques such as STM and ARPES [20]. This work shows that new information about the influence of step morphology on the formation of these important chain structures is also available.

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