Temperature- and exposure-dependent study of the Ge(001)$c(8 \times 2)$-Au surface

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Using scanning tunneling microscopy (STM), Auger electron spectroscopy, and low-energy electron diffraction, we have determined the optimal gold exposure for the Ge(001) $c(8 \times 2)$-Au surface. We find deposition of submonolayer (ML) gold onto a Ge(001) surface held at temperatures between 570 and 870 K produces a $c(8 \times 2)$ surface reconstruction. The relative extent of $c(8 \times 2)$ domains increases with Au exposure, and at 0.75 ± 0.05 ML the surface is entirely covered by $c(8 \times 2)$ chains. The 0.75-ML exposure is equivalent to six gold atoms per unit cell. Beyond 0.75 ML, exposure to additional Au leaves the $c(8 \times 2)$ domains intact, and extra Au is accommodated at three-dimensional islands on the surface. STM images of the $c(8 \times 2)$ phase are dominated by bright chains running along the Ge{110} directions with an interchain spacing of 1.6 nm. At low coverage the domains are highly asymmetric, and extended along the chain direction. These atomically flat domains routinely span several germanium terraces and indicate that chain formation involves considerable mass transport of gold and germanium atoms.

Motivated in part by a desire to study the behavior of electrons confined to one dimension (1D), metallic chains formed on semiconductor surfaces continue to be an active area of research.[1–3] Many metals induce chain reconstructions on semiconductor surfaces at submonolayer coverage. Metal-induced chains on vicinal silicon have proven to be particularly versatile, exhibiting metallic states with a highly 1D character.[4] Unfortunately, on cooling, many of these structures undergo a Peierls distortion at temperatures above which the onset of exotic 1D behavior is expected to occur.[5] Recently it has been shown that chains on the Ge(001)$c(8 \times 2)$-Au surface exhibit extended Bloch states along the chain direction, with no evidence of a Peierls distortion at temperatures as low as 80 K.[6] These authors suggest that the Ge(001)$c(8 \times 2)$-Au surface is an ideal candidate to study unique 1D electron physics. Following this report, the $c(8 \times 2)$ surface has received considerable attention,[7–12] and controversy regarding the exact structural and electronic properties of this surface has developed. For example, the reported Au exposure responsible for the $c(8 \times 2)$ reconstruction ranges from 0.2 monolayers (ML)[7] to 1.5 ML.[13]

The formation of Au-induced chains on Ge(001) was first reported by Wang and co-workers.[13,14] These authors identified a surface exhibiting a (4×2) low-energy electron diffraction pattern and scanning tunneling microscopy (STM) images characterized by atomic chains running along the {110} directions of the Ge substrate at a Au coverage of 1.5 ML. In contrast, Schäfer *et al.*[6] identified a surface with $c(8 \times 2)$ symmetry at a Au coverage slightly above 0.5 ML, while van Houselt *et al.*[7] reported a missing row reconstruction with $c(8 \times 2)$ symmetry at 0.2–0.3 ML exposure. To address these differences and to determine the atomic structure of nanowires on the Au/Ge(001) surface, Sauer *et al.*[12] recently conducted total-energy and electronic-structure calculations on a number of candidate surface structures with Au coverages ranging between 0.25 and 1.00 ML. By calculating the formation energy, simulating STM images, and determining the band structure associated with these various structures, they concluded that no one model structure could explain all the experimental results reported.

Given the controversy regarding the exact nature of Au-induced nanowires on the Ge(001) surface and understanding the importance of the Au stoichiometry as input for any density functional calculations, we have investigated the gold-induced surface structure as a function of substrate temperature and Au exposure. The surfaces were investigated using room-temperature STM, low-energy electron diffraction (LEED), and Auger electron spectroscopy (AES). By carefully calibrating the Au flux against the Si(111) 5×2-Au surface[15] we have determined the optimal Au exposure to form the $c(8 \times 2)$ phase is 0.75 ± 0.05 ML, which corresponds to a stoichiometry of six gold atoms per unit cell.

All measurements were performed in a single ultrahigh vacuum (UHV) system with a base pressure of better than 2×10^{-10} Torr. Ge(001) wafers (p type, $\rho \sim 10$ cm) were prepared by repeated cycles of Ar sputtering (500 eV) and annealing (1070 K for 1 min followed by 1000 K for 10 min). Temperatures were measured using an infrared pyrometer. The efficacy of this sample preparation was verified using LEED, AES, and STM. The clean Ge(001) surface exhibits a two-domain (2×1) surface reconstruction.

Gold was deposited onto the Ge samples using a tungsten basket evaporator. Gold exposures up to 1.1 ML were studied. During deposition the sample was held at temperatures between room temperature and 900 K. Following deposition, the samples were annealed at the deposition temperature for 1 min. We did not directly measure the Au coverage on the Ge(001) surface, rather, the evaporator flux was calibrated using LEED and Au-induced Si(111) reconstructions. It is known that the silicon (5×2) reconstruction is optimized at a Au coverage of 0.62 ML (1 ML $\equiv 7.83 \times 10^{14}$ atoms/cm^2) and the $(\sqrt{3} \times \sqrt{3})$ reconstruction appears at 1 ML.[15] To define exposure on the Ge(001) surface, we corrected for the areal density of atoms on the unreconstructed Ge(001) surface (1 ML $\equiv 6.25 \times 10^{14}$ atoms/cm^2). The accuracy of this method is estimated to be ± 0.05 ML owing to the uncertainty in identifying the optimal (5×2) LEED pattern. This technique accurately determines the net Au flux. The actual Au coverage at the surface, particularly at higher substrate temperatures, may be affected by Au interdiffusion, or a reduction of the

Au sticking coefficient. As a second measure of Au exposure, we determined the AES ratio between the Ge (91 eV) and Au (74 eV) Auger transitions. To ensure the stability of Au flux over time, we always compared the AES ratio against the original calibration.

All LEED, AES, and STM measurements were performed at room temperature. LEED and AES measurements were performed immediately following annealing and prior to any STM experiments. While LEED measurements were performed on samples prepared over the entire range of temperatures (300–900 K), STM imaging was restricted to samples held at 800 K during Au exposure.

In agreement with Wang. Li, and Altman,[14] STM images reveal that initial Au deposition onto samples held at 800 K creates missing dimer defects on the Ge(001) (2×1) surface (Fig. 1). At 0.1-ML coverage, large $c(8 \times 2)$ domains are observed in STM. LEED images obtained at this coverage show no evidence of the $c(8 \times 2)$ phase, consistent with the fact that the domains are still widely dispersed. The $c(8 \times 2)$ reconstruction is characterized by parallel chains spaced 1.6 nm apart running along the $\{110\}$ directions of the Ge(001) surface. At low coverage the domains tend to be anisotropic and are extended along the chain direction, and often span several Ge(001) terraces (Fig. 1). These domains also exhibit extremely straight step edges parallel to the chain direction. Because the surface of the $c(8 \times 2)$ domains are atomically flat and at the same time span several underlying germanium terraces, domain formation must involve mass transport of both germanium and gold atoms. One effect of this mass transport is that the relative area of germanium S_B terraces (terraces terminated by a step edge perpendicular to the Ge dimer rows) decreases compared with S_A terraces (step edge parallel to dimer rows). Au exposure appears to preferentially etch S_B terraces. This is consistent with Wang. Li, and Altman,[14] who observed that $c(8 \times 2)$ surfaces exhibited an increased abundance of double height steps following Au exposure.

LEED measurements of samples held at 800 K during Au deposition show weak evidence of the $c(8 \times 2)$ phase at $\sim$0.2 ML exposure. The diffraction peaks associated with the reconstruction are more evident with increasing exposure, and the reconstruction is fully developed by 0.75 ML (Fig. 2). The $c(8 \times 2)$ pattern persists in LEED up to the highest exposures studied (1.1 ML), with no evidence of additional diffraction features.

The LEED observations are supported by STM measurements. With increasing Au exposure, the $c(8 \times 2)$ phase covers a larger fraction of the sample surface, and at 0.75 ML the surface is entirely covered by $c(8 \times 2)$ chains (Fig. 3). The domains are oriented in one of two perpendicular $\{110\}$ orientations consistent with the two possible orientations of the Ge(001) 2×1 reconstruction on the starting surface. Further Au deposition (up to 1.1 ML) has no effect on the chains, and excess Au is accommodated at 3D islands that form on top of the intact $c(8 \times 2)$ layer.

To determine the range of temperature over which the $c(8 \times 2)$ reconstruction is stable, we performed diffraction measurements on samples exposed to 0.75 ML equivalent Au as a function of substrate temperature. No evidence of Au chains is observed in LEED below 570 K. The additional diffraction spots associated with the $c(8 \times 2)$ reconstruction
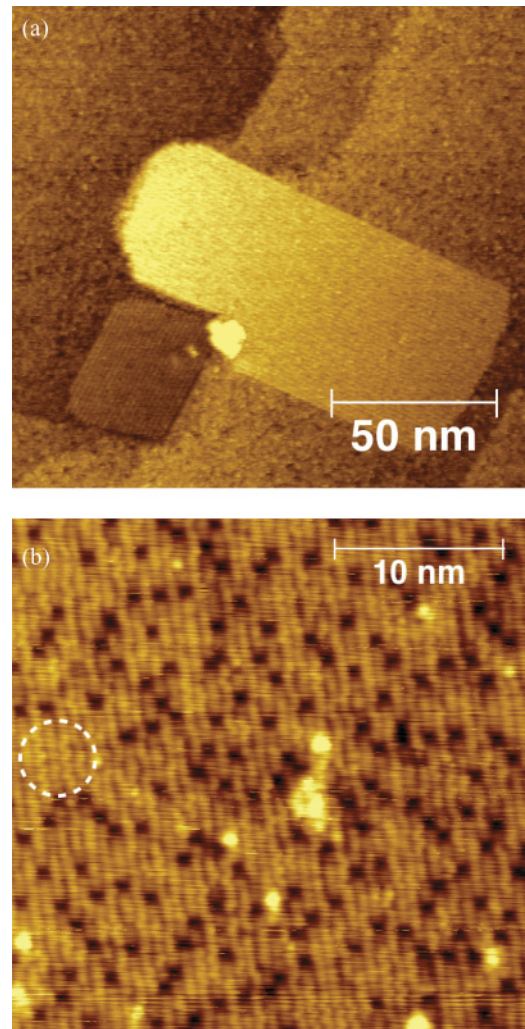

FIG. 1. (Color online) STM image of the Ge(001) surface obtained at 1.72 V sample bias and 0.5 nA current following 0.10 ± 0.05 ML equivalent exposure of Au onto a sample held at 800 K. (a) The surface exhibits widely dispersed $c(8 \times 2)$ domains, often extending over several Ge(001) terraces. (b) On the adjacent Ge(001) terrace, initial Au exposure results in many missing dimer defects (1.5 V bias, 1 nA tunnel current). The image also exhibits regions with buckled Ge dimers as outlined.

are first observed at 570 K. With increasing temperature, the relative intensity of the $c(8 \times 2)$ features strengthens until $\sim$630 K. Between 630 and 790 K the $c(8 \times 2)$ pattern remains largely unchanged. By 870 K the pattern fades and finally reverts back to the (2×1) pattern characteristic of the Ge(100) surface by 890 K. AES data obtained above 890 K show no evidence of Au at the surface. Combined with our STM measurements, these results indicate that the $c(8 \times 2)$ phase is optimized at a Au exposure of 0.75 ± 0.05 ML at substrate temperatures between 630 and 790 K. The results also indicate a single $c(8 \times 2)$ structure is present above 0.1 ML and for temperatures between 570 and 870 K.

As stated, the STM images of the $c(8 \times 2)$ domain are dominated by parallel chains spaced 1.6 nm apart. The STM images are largely independent of sample bias ($\pm$2 V) and stable imaging is obtained at voltages as low as $\pm$0.5 V.
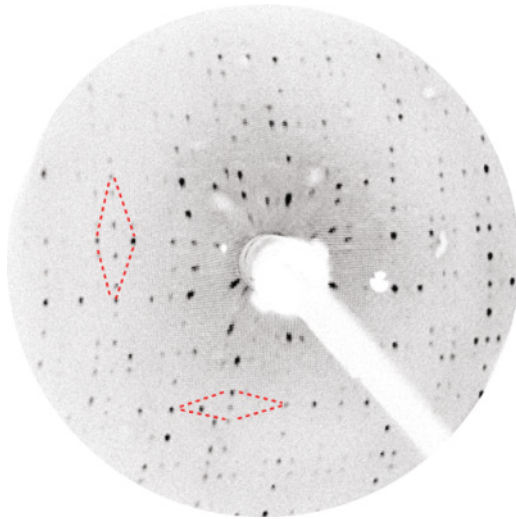
FIG. 2. (Color online) LEED image of Ge(001) surface following 0.75 ± 0.05 ML Au exposure onto a sample held at 800 K. The image was obtained at an electron energy of 63 eV and exhibits a two-domain $c(8 \times 2)$ pattern (see unit cells indicated).

Although LEED indicates $c(8 \times 2)$ symmetry, in most instances we are unable to resolve any periodic corrugation along the chains. In Fig. 3 we display the corrugation measured perpendicular to the chain direction at a sample bias of 1.0 V and a tunnel current of 0.3 nA. We measure a value $\Delta z \approx$ 0.09 nm, which is consistent with values reported by Wang, Li, and Altman[14] and Schäfer et al.[6] Although the measured corrugation is dependent on tip condition, for a given tip it is only weakly dependent on sample bias (0.5 V < $|V|$ < 2 V), as reported by others.[6,8,10] We do not observe the much larger corrugations (0.4–0.6 nm) reported by several groups[7–10] obtained under similar tunneling conditions. van Houselt et al.[7] observed a corrugation as large as 0.6 nm and proposed the $c(8 \times 2)$ phase is a missing row reconstruction and that the "chains" are actually two opposing (111) microfacets. Because the measured corrugation in STM is a convolution of both surface structure and tip geometry, the authors point out that a very sharp STM tip is required to measure the full depth of the troughs between the densely packed facets. They suggest that the lower corrugations measured by others is a result of a larger tip radius in those experiments. It may be that the tip radius in our experiments was also too large to measure the larger corrugation, however, as Fig. 1 demonstrates, the resolution was still sufficient to resolve buckled dimers and missing dimer defects on the adjacent Ge(001) terrace.

Given the debate over the structure of the $c(8 \times 2)$ surface, Sauer et al.[12] recently performed total energy calculations for 150 candidate structures. The candidate structures were grouped into four broad classes: (i) gold chain, (ii) dimer row, (iii) bridging dimer, and (iv) deep trench structures. The authors found that no one structure reproduced all the experimental details. For example, a dimer row model with a mixture of Au dimers and Ge-Au heterodimers and a stoichiometry of six Au atoms per unit cell was found to be energetically stable, however, the simulated STM images were problematic. Alternately, a deep trench model reproduced
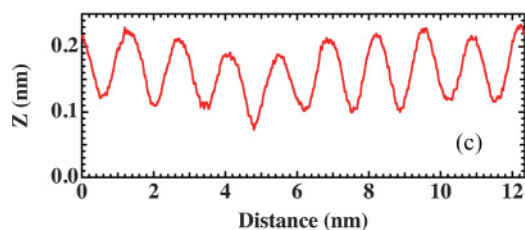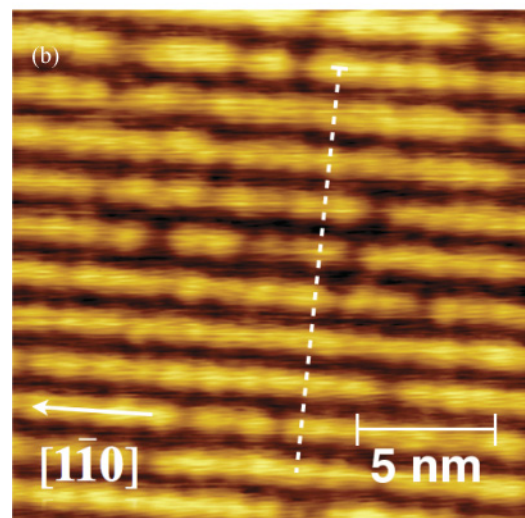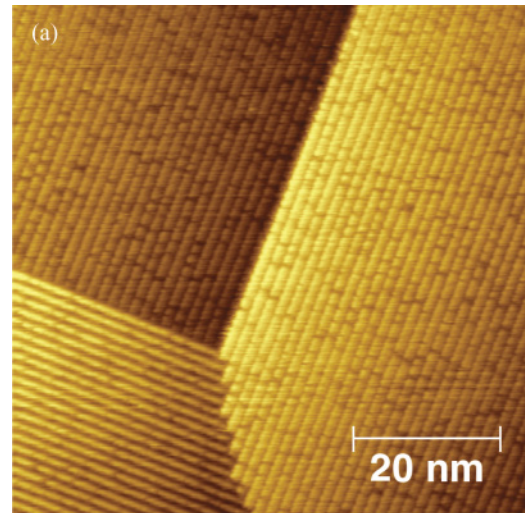

FIG. 3. (Color online) STM images following 0.75 ± 0.05 ML exposure onto a sample held at 800 K. (a) The surface is completely covered by $c(8 \times 2)$ domains in one of two possible perpendicular orientations (tunneling parameters: 0.9 V sample bias, and 0.3 nA current). (b) The reconstruction is dominated by parallel chains oriented along [1$\bar{1}$0] with an interchain spacing of 1.6 nm (1.0 V and 0.3 nA). (c) A linescan perpendicular to the chains yields $\Delta z \approx$ 0.09 nm.

the large corrugations observed in the STM images of van Houselt et al.,[7] but has a relatively high formation energy. It is interesting to note that in each structural category the lowest formation energy occurred at a Au stoichiometry of six Au atoms per unit cell, similar to the optimal 0.75-ML exposure we find in our experiments. In addition, our observations at low coverage indicate formation of $c(8 \times 2)$

domains involves considerable mass transport. While this does not necessarily rule out dimer or bridging dimer models, it would seem to be a necessary condition to form a deep trench structure.

In summary, we have measured the structure of Ge(001) $c(8 \times 2)$-Au surface as a function of Au exposure and substrate temperature. Based on STM and LEED observations, we have determined the surface is completely covered by $c(8 \times 2)$ domains following a 0.75 ± 0.05 ML equivalent Au exposure. This exposure is equivalent to a stoichiometry of six gold atoms per unit cell and agrees with the lowest-energy structures determined by Sauer *et al.*[12] STM measurement as a function

of exposure (0–1.1 ML) and LEED experiments as a function of temperature (300–900 K) suggest a single $c(8 \times 2)$ structure is observed for an exposure greater than 0.1 ML and for temperatures between 570 and 870 K. We also observe that Au exposure leads to etching of Ge S_B steps to form atomically flat $c(8 \times 2)$ domains often spanning several Ge terraces, and indicates domain formation involves considerable mass transport.

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