Surface Science 621 (2014) 184–190

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Reconstructions and phase transition of clean Ge(110)

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ARTICLE INFO

Article history:
Received 13 September 2013
Accepted 30 October 2013
Available online 13 November 2013

Keywords:
Germanium
Surface reconstruction
Surface phase transition
Low energy electron diffraction (LEED)
Scanning tunneling microscopy (STM)
Low energy electron microscopy (LEEM)

ABSTRACT

The structure of the clean Ge(110) surface is characterized between room temperature and the Ge melting temperature using scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) and microscopy (LEEM). Rapid cooling from high temperature (~800 °C) to room temperature yielded a surface composed of the c(8 × 10) reconstruction, {17 15 1} facets, and a previously unreported (8 × 2) reconstruction. Heating from room temperature to above 430 °C extinguishes some, but not all, high-order LEED spots, indicating the presence of ordering up to at least 650 °C. LEED observations of the phase transition between the c(8 × 10) and a disordered phase differ from earlier work but are consistent with previously published STM data.

1. Introduction

Of the low index surfaces of germanium, Ge(110) has received relatively little attention in surface studies. The unreconstructed Ge(110) surface has rectangular symmetry with zigzag atomic rows running in the $[1\bar{1}0]$ direction. In the unrelaxed surface, each atomic layer is evenly spaced, and each surface atom has two nearest-neighbor tetrahedral bonds in the (110) plane, with one bond to the atomic layer above and one bond to the atomic layer below. Depending on annealing temperature, the surface reconstructs to a (16 × 2) structure (Fig. 1a), or a c(8 × 10) structure (Fig. 1b). Although there is not yet a consensus on the precise atomic positions within the (16 × 2) and c(8 × 10) reconstructions, the primary structural features of these surfaces have been determined with STM [1–5], diffraction [6,7], and theoretical [2,3,8–10] studies. The (16 × 2) and c(8 × 10) structures both feature rows of pentagonal clusters of adatoms, represented by red circles in Fig. 1. The spacing of rows of adatom clusters is similar in both the (16 × 2) and c(8 × 10) reconstructions, and their direction of propagation on the surface only differs by 5.8°. The (16 × 2) and c(8 × 10) reconstructed surfaces both feature {17 15 1} facets at step edges [3]. The projections of the surface normals of {17 15 1} facets onto the (110) plane, $<1\bar{1}1>$, are perpendicular to the direction of propagation of pentagonal adatom clusters in the (16 × 2) reconstruction, $<1\bar{1}2>$; i.e., {17 15 1} facets run in the same direction as rows of (16 × 2). One significant difference between the (16 × 2) and c(8 × 10) reconstructions is the missing top layer of (110) atoms that alternates across double-rows of adatoms in the (16 × 2) reconstruction. In the 16 × 2 reconstruction, each double-row of adatom clusters goes up, and then down, by one layer of Ge(110) atoms (Fig. 1a), whereas double-rows of c(8 × 10) are all in the same (110) plane (Fig. 1b).

Our work presented here is the first study which used both diffraction (LEED) and real space microscopies (STM, LEEM) to study details of the surface structure of Ge(110). We observed the c(8 × 10) structure, {17 15 1} facets, and an (8 × 2) structure, which had not previously been reported. Using LEED, we observed the phase transition between the c(8 × 10) structure and a disordered phase. Our data are consistent with the STM observations of this phase transition, which had not previously been observed with LEED.

2. Previous work on Ge(110) reconstructions

Germanium [6] and silicon [11] both form (16 × 2) reconstructions upon cooling from high-temperature disordered (1 × 1) states. The (16 × 2)-to-disorder transition occurs reversibly at 430 °C for germanium [6] and 760 °C for silicon [11]. The growth of (16 × 2) regions on the surface upon cooling past the transition temperature occurs more slowly for germanium than for silicon [3,12], and disordered regions generally remain on the germanium surface along with regions of (16 × 2) [3].

The unit cell in the so-named "(16 × 2)" reconstructions of germanium and silicon is in fact not precisely (16 × 2). The basis vectors for the reconstructed unit cells are not orthogonal, and the dimensions are only approximately (16 × 2). While structurally similar, the "(16 × 2)" reconstructions on silicon and germanium also differ from one another in the dimensions of their unit cells referenced to the dimensions of their respective (110) bulk unit cells. The Ge(110) (16 × 2) unit cell has dimensions $\sqrt{171} \times \sqrt{6}$ relative to the unit cell of the unreconstructed surface (Fig. 1a), and is properly referred to in Wood notation

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http://dx.doi.org/10.1016/j.susc.2013.10.023

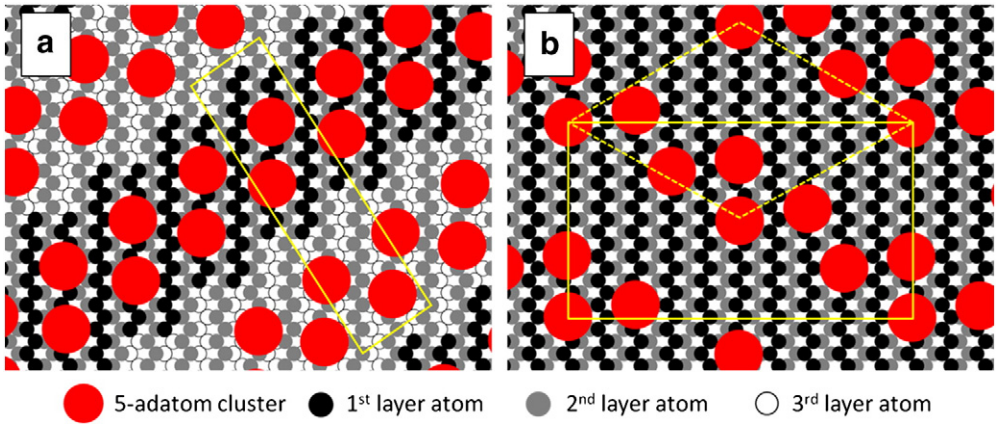

Fig. 1. (Color online) Models of Ge(110) (16 × 2) and c(8 × 10) reconstruction proposed by Ichikawa et al. [1–3]. Pentagonal five-adatom clusters are each diagrammed as a single red (dark gray) circle. Atoms in the top three layers are shown in their unrelaxed locations as if they were still in the bulk. (a) Ge(110) (16 × 2) reconstruction [1]. The (16 × 2) unit cell is outlined in solid yellow (white), with dimensions 52.3 Å × 13.9 Å. The so-called "(16 × 2)" unit cell in fact has dimensions √171 × √6 relative to the unit cell of the bulk Ge(110) surface, and its basis vectors are not quite orthogonal. (b) Ge(110) c(8 × 10) reconstruction [1–3]. Several different models have been proposed for the precise atomic positions within the pentagonal clusters and the relaxed surface layers [2–4]. The primitive unit cell drawn with a dotted line, and a rectangular c(8 × 10) unit cell is drawn with a solid yellow (white) line (32.0 Å × 56.6 Å).

as (√171 × √6)R(32.7°, 35.3°) or in matrix form: $\begin{pmatrix} 11 & 5 \\ -2 & 2 \end{pmatrix}$ [6,11]. The (16 × 2) unit cell for silicon is $\begin{pmatrix} -1 & 17 \\ -2 & 2 \end{pmatrix}$ [13]. For both silicon and germanium, the (16 × 2) reconstruction consists of alternating troughs of missing (110) surface atoms, one monolayer in depth, running in the [1 $\bar{1}$ 2] and [1 $\bar{1}$ $\bar{2}$] directions (perpendicular to [1 $\bar{1}$ $\bar{1}$] and[1 $\bar{1}$ 1], respectively). STM images of the (16 × 2) surfaces in germanium [1,3,9] and silicon [14,15] show alternating stripes of up and down (110) terraces, one layer in height difference and 5.2 nm in width, running in the [1 $\bar{1}$ 2] and [1 $\bar{1}$ $\bar{2}$] directions. In the Ge (16 × 2) reconstruction, zigzag chains of pentagonal five-adatom clusters run on top of both the up terraces and down terraces [14,15] (Fig. 1a). Although the Si (16 × 2) reconstruction shows a similar zigzagging of atomic clusters on top of both up- and down-terraces, the clusters are composed of six adatoms and are approximately hexagonal in shape [13].

The (16 × 2) reconstruction coexists with regions of {17 15 1} facets that run parallel to it in the [1 $\bar{1}$ 2] and [1 $\bar{1}$ $\bar{2}$] directions. There are four {17 15 1} facets: (17 15 1), (15 17 $\bar{1}$), (17 15 $\bar{1}$), and (15 17 1) with surface normal projections in the (110) plane: [1 $\bar{1}$ 1], [$\bar{1}$ 1 $\bar{1}$], [1 $\bar{1}$ $\bar{1}$], and [$\bar{1}$ 1 1], respectively. The angle of inclination of the (17 15 1) facet from (110) is 4.38°. On the Ge(110) surface, {17 15 1} faceting was first observed with LEED [7]. Whereas the (16 × 2) reconstruction consists of alternating rows of up and down (110) terraces, {17 15 1} facets consist of a series of rising or descending (110) terraces. High temperature STM studies of Ge(110) [3] and Si(110) [12] have shown that these facets first form from fluctuating step bunches as the temperature is lowered to the (16 × 2) transition temperature. As temperature is lowered, {17 15 1} facets form before (16 × 2) domains and serve as nucleation sites for (16 × 2) growth [3]. An 80 °C temperature difference between the onset of faceting and (16 × 2) growth has been observed in silicon [12]. A temperature differential in the onset of (16 × 2) growth and {17 15 1} formation was not found for germanium; rather, both were found to form at 430 °C with the {17 15 1} forming before (16 × 2) growth at that temperature [3]. Once formed, {17 15 1} facets are stationary and coexist with (16 × 2) as the sample is cooled [3,12].

Growth of (16 × 2) regions is slow and does not cover the entire surface [3]. STM images of disordered regions of the surface are blurry, indicating diffusing surface atoms, although occasional bright spots in the disordered region could be interpreted as five-membered clusters of adatoms, similar to those in the (16 × 2) structure, that exist in the otherwise disordered state [3]. LEED measurements of the high temperature disordered state on Si(110) reveal diffuse diffraction spots that could be interpreted as short range ordering [16], possibly clusters of Si atoms similar to the five-membered clusters found in Ge(110) c(8 × 10) and (16 × 2) structures [3]. The current study constitutes the first LEED study of Ge(110) above 430 °C since the initial work performed by Olshanetsky et al. [7].

As the sample temperature approaches 380 °C, the otherwise disordered surface begins to show local ordering: pentagonal clusters of adatoms (similar to those observed in the (16 × 2) structure) dominate the surface in a random configuration. At 380 °C, these five-membered clusters gradually become less densely packed and begin to align themselves in zigzag chains that run in the [2 $\bar{2}$ $\bar{5}$] directions. These zigzag chains constitute the c(8 × 10) reconstruction (Fig. 1b). Domain size in the c(8 × 10) surface is significantly affected by annealing time: a rapid quench from above 430 °C to 380 °C, followed by annealing at 380 °C, yields large domains of c(8 × 10) whereas a gradually decreasing temperature ramp from above 430 °C down to 380 °C yields small regions of c(8 × 10), as well as regions of disordered five-member clusters that do not show long range order [3].

The (16 × 2) regions formed by annealing between 430 °C and 380 °C do not change phase to c(8 × 10) upon cooling below 380 °C [1]. A reflection high-energy electron diffraction (RHEED) study, during which Ge(110) samples were annealed below 380 °C for multiple days, observed the transformation of the c(8 × 10) phase to the (16 × 2) phase [6,17], indicating that the c(8 × 10) structure is a metastable phase that forms due to the slow formation of the stable (16 × 2) phase [3,9].

3. Experiment

Measurements were carried out in an ultrahigh vacuum (UHV) system consisting of three connected chambers housing several commercial instruments, including a LEEM (Elmitec GmbH), STM (Oxford Instruments), and x-ray photoemission spectrometer (Vacuum Generators) [18]. Ge(110) samples were prepared from Sb-doped Ge(110) wafers (resistance between 0.1 and 1.0 Ω-cm) purchased from MTI Corporation. Wafers were two inches in diameter and 0.5 mm thick, with a reported miscut of less than 0.5° from (110). Approximately 1 cm^2 square samples were manually cut with a diamond scribe, rinsed in methanol, and placed in the STM–LEEM sample holder, before insertion into the UHV chamber.

Ge(110) wafers did not come with flats indicating the crystallographic orientation of the sample. The orientation of the sample within its holder was determined from STM images of the two domains of the