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)

C.H. Mullet, S. Chiang *

Department of Physics, University of California Davis, 1 Shields Avenue, Davis, CA 95616-8677, USA

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

* Corresponding author. Tel.: +1 530 402 711; fax: +1 530 752 4717.
E-mail address: chiang@physics.ucdavis.edu (S. Chiang).

0039-6028/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.susc.2013.10.023

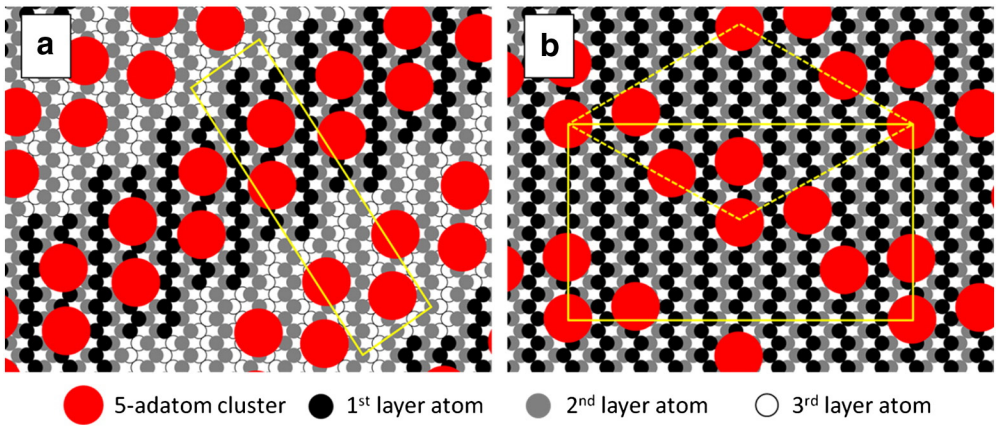

Fig. 1. (Color online) Models of Ge(110) (16 × 2) and c(8 × 10) reconstruction proposed by Ichikawa et al. [1–3]. Pentagonal five-adatom clusters are each diagrammed as a single red (dark gray) circle. Atoms in the top three layers are shown in their unrelaxed locations as if they were still in the bulk. (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

Ge(110) c(8 × 10) reconstruction. The orientation of the sample in the LEEM image, rotated by the LEEM's magnetic lenses, was determined by translating the LEEM sample stage while imaging in LEEM and observing in the LEEM image the resulting direction of motion of features on the sample surface.

Ge(110) samples were cleaned in UHV with repeated cycles of Ar^+ bombardment of the unheated sample for 15 min, followed by annealing the sample between 800 °C and 830 °C for 10 min (30 min for the last anneal before imaging in LEEM or STM). The energy of the Ar^+ beam was 0.25 keV. Sputtering and annealing cycles were performed in the analysis chamber (base pressure 2×10^{-10} Torr) before transferring the sample to the LEEM chamber (base pressure 1×10^{-10} Torr) or STM chamber (base pressure 4×10^{-10} Torr). Samples were sputtered and annealed until a clean c(8 × 10) LEED pattern was obtained.

The sample temperature was monitored with either a C-type or K-type thermocouple junction spot-welded to the sample-side of the molybdenum ring on which the sample rests. The thermocouple voltage and the sample filament current were each calibrated to the sample temperature with an infrared pyrometer, with emissivity set to 0.42 for germanium temperature readings in the LEEM chamber. The emissivity setting was calibrated at the melting temperature of germanium (937.4 °C), and at the same emission angle used for subsequent thermocouple calibrations, by intentionally melting a Ge(111) sample in the LEEM chamber while monitoring temperature with the pyrometer. The standard deviation of the temperature error for a quadratic best-fit calibration curve to sample filament current (used to set deposition temperatures) was 5 °C or less for each Ge(110) sample. The temperature ranges explored here were all between room temperature and 830 °C.

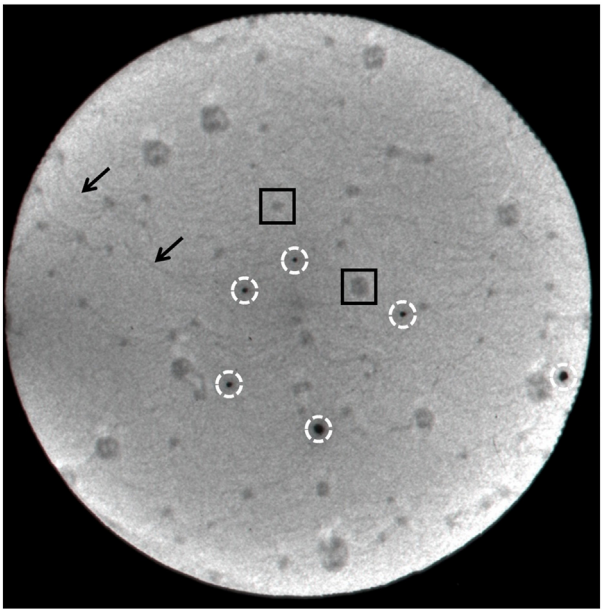

Fig. 3. LEEM image of Ge(110). 10 μm field-of-view, E = 3.9 eV. At this spatial scale, two types of surface features are apparent: defects and step bunches. Squares outline two of the many defects visible in this LEEM image. Arrows point to two of the numerous step bunches visible on the surface. White dotted circles outline six dark spots that are not surface features, but rather correspond to areas burned out in the LEEM's microchannel plate.

4. Results and discussion

4.1. Reconstructions of clean Ge(110) studied with STM and LEED

Fig. 2 shows room temperature STM images obtained after cleaning Ge(110) with the sputtering and annealing regime described above, and subsequently allowing the sample to cool to room temperature. The surface is composed of large regions of c(8 × 10) (Fig. 2), with some {17 15 1} facets found at step edges (Fig. 2a). Ge(110) has two rotational domains (diagrammed as an overlay on Fig. 2a). Domain sizes varied across the surface but were frequently less than 10 unit cells in area (Fig. 2b).

Bright field LEEM images of the clean Ge(110) surface yielded good step contrast at ≈4 eV. A LEEM image of the clean Ge(110) surface is presented in Fig. 3. Two types of surface features are prominent: local defects, presumably due to contaminants remaining after the surface cleaning procedure, and step edges. Defects are found throughout the surface and range in size up to 0.5 μm in diameter, with typically 1–2 defects per μm^2. The number of surface defects increases as the samples accumulated sputtering cycles in the cleaning process. Substrate steps and step bunches (multiple closely-spaced steps) are clearly visible in the LEEM images. Step bunches frequently terminate at defects.

Compared to our study of Ge(111) [19], Ge(110) had significantly lower bright field LEEM intensity at incident electron energies >2 eV, requiring greater incident beam intensity to produce a well-resolved image. The Ge(110) samples examined here also had a significantly larger surface step density and a greater number of surface defects than did the Ge(111) samples.

Fig. 4 shows the clean Ge(110) LEED pattern that resulted from allowing the sample to cool to room temperature after sputtering and annealing. The primary diffraction pattern is that attributed to the

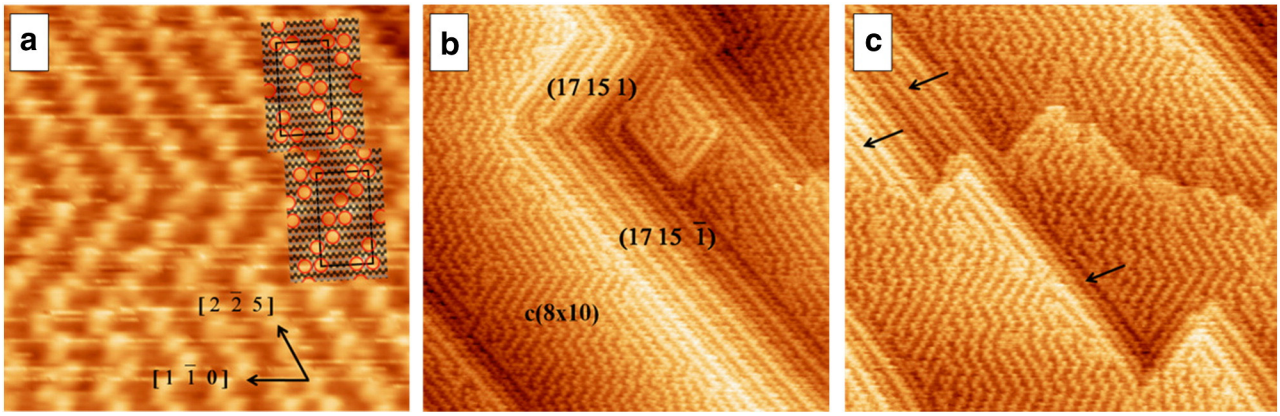

Fig. 2. (Color online) Constant current room temperature STM images of clean Ge(110). +2.0 V sample bias, 0.5 nA tunneling current. (a) Ge(110) c(8 × 10) reconstruction. Unit cell outlined in black for the two different domains, with red (dark gray) circles indicating positions of pentagonal five-adatom clusters from the model. 31.3 nm × 31.3 nm. (b) {17 15 1} faceting on the Ge(110) c(8 × 10) surface. Four {17 15 1} facets are present on the surface, with faces running along [1 $\bar{1}$ 2] and [1 $\bar{1}$ $\bar{2}$]. 100 nm × 100 nm. (c) Surface phase similar to Ge(110) (16 × 2), but with one half the (16 × 2) row periodicity, "(8 × 2)". Black arrows indicate rows of this new reconstruction near step edges. Terraces are primarily covered in domains of c(8 × 10). 99.4 nm × 93.6 nm.

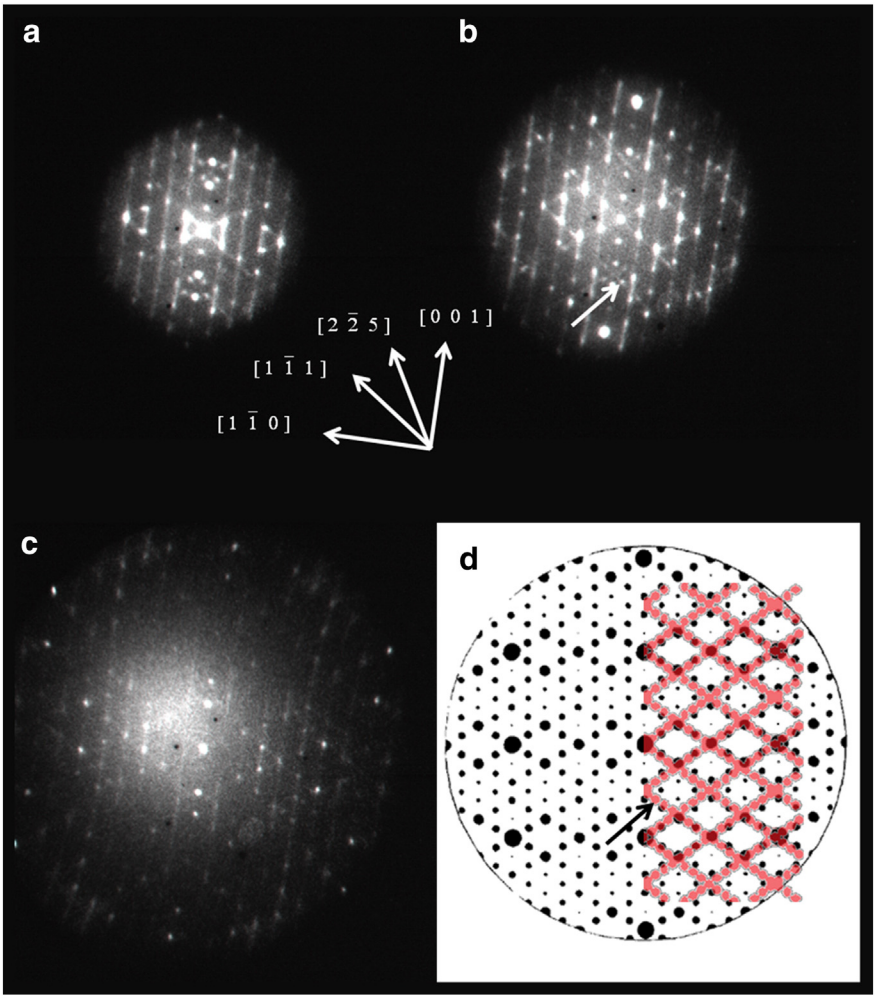

Fig. 4. (Color online) Clean Ge(110) c(8 × 10) + (16 × 2) LEED pattern. The surface was prepared by annealing to 800 °C, followed by a rapid quench to room temperature. (a) 3.8 eV; (b) 6.6 eV; (c) 13.7 eV; (d) One half of the (16 × 2) LEED pattern in overlaid in red (gray) on top of c(8 × 10) LEED pattern. For reference, the black arrow indicates the same fractional order (16 × 2) LEED spot identified by the white arrow in (b).

c(8 × 10) reconstruction (black spots in Fig. 4d) [7]. Taking the directions [$\bar{1}$ 1 0] and [0 0 1] as basis vectors, the c(8 × 10) diffraction pattern has integral and fractional order spots at (h/8, k/10), where h and k are integers that are either both odd or both even, with the exception of missing spots at: ($h = 4n + 2, k = 10\ m$), where n and m are integers [7]. While the primary diffraction pattern in Fig. 4 is c(8 × 10), weak (16 × 2) spots are also visible (Fig. 4b). The presence of (16 × 2) spots in the otherwise c(8 × 10) LEED pattern is interpreted below in conjunction with the STM data.

The only published LEED study of Ge(110) [7] reported that the c(8 × 10) structure formed after annealing at temperatures lower than 380 °C, as well as at temperatures greater than 430 °C. The LEED pattern obtained at intermediate temperatures (380–430 °C) (red (gray)) overlay in Fig. 4d) was attributed to {17 15 1} facets [7]. Subsequent RHEED and STM studies further clarified, and in some ways corrected, those initial findings. A RHEED study of Ge(110) annealed to temperatures between 380 °C and 430 °C [6] found that as the incident beam angle was varied, diffraction spots did not move in the directions required by a surface composed of {17 15 1} facets. The authors concluded that the surface reconstruction formed between 380 °C and 430 °C must not be faceted, and they proposed the currently accepted "(16 × 2)" model [6]. Subsequent high temperature STM studies found that the (16 × 2) reconstruction and {17 15 1} facets both form at 430 °C, with facets forming first from fluctuating step edges as the sample is cooled from high temperature to 430 °C, followed by (16 × 2) regions growing from the edges of facets [1,3].

The {17 15 1} facets and the (16 × 2) reconstruction share common structural features. Both consist of stripes of zigzag five-membered adatom rings running in the [1 $\bar{1}$ 2] and [1 $\bar{1}$ $\bar{2}$] directions [2,3]. In the (16 × 2) reconstruction, zigzag stripes are located on alternating (110) terraces (the stripe sequence is "up down up down…") (Fig. 1a), whereas {17 15 1} terraces are composed of successively rising or descending (110) terraces ("down down down…" or "up up up…") [2,3]. Distinguishing between 16 × 2 and {17 15 1} facets is accomplished with LEED through analysis of how diffraction spots move with energy [7,20], and with RHEED by how spots move with the angle of the incident beam [6]. The degree of sample miscut is one possible explanation for different conclusions from the earliest diffraction studies of Ge(110) as to whether the surface was composed of (16 × 2) or {17 15 1} facets. Surfaces with a greater miscut from (110) would show greater {17 15 1} — like spot movement compared to surfaces with a smaller miscut, as subsequent STM images have shown that steps on Ge(110) are frequently composed of {17 15 1} facets.

Our LEED results contrast with the only previous LEED study of clean Ge(110) in that we did not observe the reversible phase transition between the c(8 × 10) and (16 × 2) structures at 380 °C reported by Olshanetsky et al. [7]. The room temperature LEED results depicted in Fig. 4 are consistent with the most current STM studies of the ordering that occurs on the Ge(110) surface as temperature is lowered below

430 °C. An STM study found that growth of zigzag stripes that make up the (16 × 2) phase is slow, ranging widely from almost 0 Å/s to a maximum of 4 Å/s, with the growth occurring stripe-by-stripe from the edges of {17 15 1} terraces; these measurements were taken on samples heated beyond 430 °C, cooled down slowly to 430 °C, and then annealed at that temperature for some time [3]. The mostly c(8 × 10) LEED patterns shown in Fig. 4abc were obtained after a Ge(110) sample was cooled to approximately room temperature after a typical cleaning regimen. At the end of the 30-minute annealing period (800–830 °C) that culminates a series of cleaning cycles, sample heating was abruptly stopped, and the sample was quenched to room temperature. From a cooling curve constructed after abruptly ending sample heating, the sample spent less than 15 s in the 380–430 °C temperature range, where (16 × 2) growth occurs. From the slow growth of the (16 × 2) phase and the rapid sample cooling applied here, significant growth of (16 × 2) domains was not expected. From LEED analysis alone, the faint (16 × 2) spots in the room temperature LEED patterns shown in Fig. 4 could be attributed to small regions of (16 × 2) on the sample surface that form during sample cooling, and/or they could be attributed to {17 15 1} facets.

Our STM results on Ge(110) samples heated above 800 °C and then quenched to room temperature show that the (16 × 2) spots present in LEED are not due to (16 × 2) domains on the surface, but rather to {17 15 1} facets, as well as a previously unreported phase very similar to the (16 × 2) phase. Fig. 2b and c show STM images obtained after annealing the sample above 800 °C and then rapidly shutting off all heating, allowing the sample to cool to room temperature. Most of the sample surface is covered with alternating domains of the c(8 × 10) reconstruction running in the [2 $\bar{2}$ 5] and [2 $\bar{2}$ $\bar{5}$] directions, consistent with LEED observations. Step edges on the surface are primarily constituted of {17 15 1} facets with edges along [1 $\bar{1}$ 2] and [1 $\bar{1}$ $\bar{2}$].

Interestingly, we observed rows of a new reconstruction growing at the edges of {17 15 1} facets. The periodicity across these rows is 2.6 nm, exactly one half the periodicity across rows in the (16 × 2) reconstruction. The zigzag structure along the lengths of the rows of this new "(8 × 2)" reconstruction appears identical to the (16 × 2) reconstruction. The direction of the rows of this (8 × 2) reconstruction matches the orientation of rows in the (16 × 2) reconstruction. A likely explanation for this new reconstruction is that the rapid cooling conditions employed here allow time for pentagonal clusters of adatoms (likely already formed above 430 °C, see discussion below) to line up in zigzag rows as in the (16 × 2) reconstruction, but not enough time for formation of the up and down (110) terrace structure. Note that the domains of the new "(8 × 2)" reconstruction bear very close resemblance to the c(8 × 10) reconstruction. The (16 × 2) spots observed in LEED that would overlap with (8 × 2) spots are not obviously more intense, and a close quantitative analysis of LEED spot intensity was not performed. Distinguishing between the c(8 × 10) and (8 × 2) structures would approach the limits of the STM data presented here. Row periodicity across the c(8 × 10) unit cell is 2.79 nm (as calculated from the dimensions of the unit cell at 300 K), with rows aligned along [2 $\bar{2}$ 5]. The (16 × 2) row periodicity is 5.23 nm at 300 K, with rows aligned along [1 $\bar{1}$ 2]. Periodicity in the c(8 × 10) reconstruction differs by only 0.18 nm from half the periodicity across rows in the (16 × 2) reconstruction. The angle between [1 $\bar{1}$ 2] and [2 $\bar{2}$ 5] is 5.8°.

4.2. Order to disorder transition on Ge(110) above 430 °C

There is a lack of consensus in the literature as to the structure of the clean Ge(110) surface above 430 °C. A STM study reports that scans of the Ge(110) surface above 430 °C are primarily noisy and featureless, indicating a surface composed of rapidly diffusing adatoms [3]. However, individual bright spots with dimensions similar to the pentagons found in the (16 × 2) and c(8 × 10) reconstructions are occasionally distinguishable, although they do not show long-range ordering [3]. A LEED and LEEM study of the Si(110) transition from the (16 × 2) to disorder found that some diffuse fractional order LEED spots persist in the high temperature disordered phase [16]. There have not been any similar LEED studies of the high temperature Ge(110) disordered phase since the original study [7] that labeled the surface above 430 °C as c(8 × 10).

LEED results for several temperatures above the disorder transition at 430 °C, as well as for the 380–430 °C intermediate temperature range, are presented in Figs. 5 and 6. Before investigating the LEED pattern at elevated temperatures, a strong c(8 × 10) LEED pattern (Figs. 5a, 6a) was first established by annealing the sample well above 430 °C and then rapidly turning off sample heating and allowing the sample to

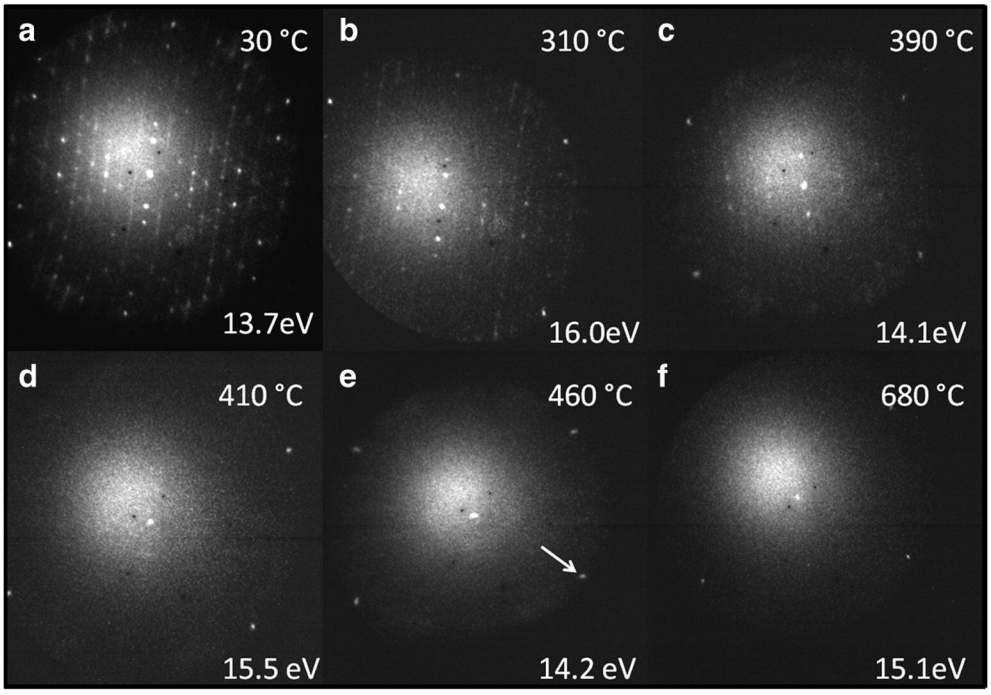

Fig. 5. (a)–(f) LEED of Ge(110) annealed 15–50 min at several temperatures above and below the disorder transition temperature, 430 °C. Energies were 13.7 to 16.0 eV. For reference, the arrow in (e) points to the (1, −1) LEED spot.

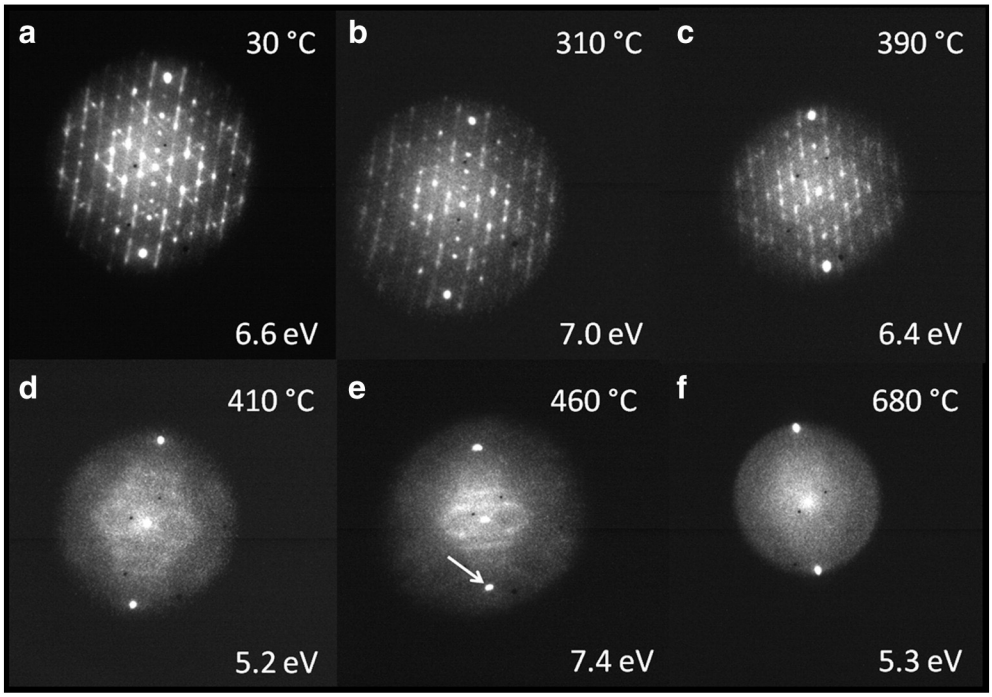

Fig. 6. (a)–(f). LEED of Ge(110) annealed 15–50 min at several temperatures above and below the disorder transition temperature, 430 °C. Energies were 6.4–7.4 eV. For reference, the arrow in (e) points to the (0, −1) LEED spot.

return to room temperature. After confirming the c(8 × 10) LEED pattern at room temperature, the sample was then annealed at an elevated temperature for 15–50 min. We found that upon annealing to 380–430 °C, the c(8 × 10) surface persists and does not transform to the (16 × 2) structure. The c(8 × 10) spots remained clearly distinguishable at 390 °C (Figs. 5c, 6c) and 410 °C (Figs. 5d, 6d), and there was no observed intensification of (16 × 2) spots. These new results remain consistent with a RHEED study [17] that showed that even annealing at temperatures below 380 °C was sufficient to convert the c(8 × 10) reconstruction to (16 × 2) for samples which were annealed much longer, up to two days. The lack of conversion of the c(8 × 10) phase to (16 × 2) over 15–50 min of annealing time is a further indication of the slow formation kinetics of the (16 × 2) phase.

We observed six strong (1 × 1) LEED spots above 430 °C: four at (±1, ±1) (Fig. 5e,f), and two with pronounced energy dependence at (0, ±1) (Fig. 6e,f). A LEEM/LEED study of the Si(110) high temperature disordered phase observed the same six spots, also with strong energy dependence for the (0, ±1) spots [16].

Annealing above 430 °C extinguishes the c(8 × 10) LEED pattern but does so slowly and incompletely. Note that our LEEM images of the Ge(110) surface did not change much during the phase transition. The phase change is indicated by most fractional order LEED spots extinguishing above 430 °C (Figs. 5ef, 6ef). However, 4 to 6 diffuse, but distinguishable, fractional order spots remain at temperatures above 430 °C (Fig. 7c). Viewed with LEED, the transformation from the c(8 × 10) phase to the disordered 1 × 1 phase appears gradual, rather than abrupt, for a temperature ramp of 1.5 °C/s (Fig. 7). These six spots most likely correlate to spots found in the c(8 × 10) diffraction pattern (Fig. 4d, black spots), though they are close to the six intersection points closest to (0, 0) of the rows of spots corresponding to the two rotational domains found in the (16 × 2) phase (Fig. 4d, red (gray) spots). The four brightest spots are at {1/4, 1/5} and the two weaker spots are at {0, 2/5}, taking the [$\bar{1}$ 1 0] and [0 0 1] directions on the surface as basis vectors.

The presence of fractional order LEED spots at high temperature indicates that some short-range ordering remains on the surface up to at least 680 °C. Ordering may be in the form of adatom clusters similar or identical to those that make up the c(8 × 10) and (16 × 2) reconstructions at lower temperatures. As mentioned above, one STM study observed protrusions in the high temperature disordered state with dimensions similar to the pentagonal rings found in the reconstructions below 430 °C [3]. A LEED/LEEM study of the (16 × 2)-to-disorder

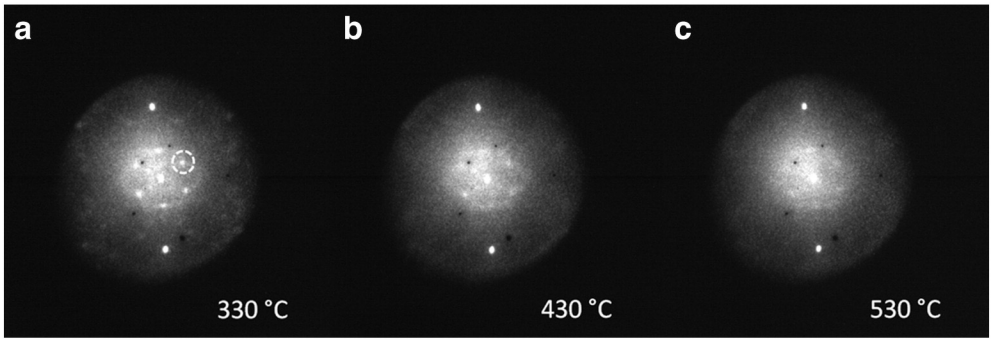

Fig. 7. LEED of Ge(110) c(8 × 10) at three points along a 1.5 °C/s temperature ramp. E = 8.5 eV. Transition to the high temperature disordered state is gradual at this temperature ramp. Six fractional order spots persist up to at least 655 °C (data not shown); one of these six spots is circled with a dotted line in (a).

transition in Si(110) found eight diffuse fractional order spots within the first diffraction zone above the disorder transition temperature [16], all of which are located at different positions than those found for the germanium case here. If adatom rings are the source for fractional order LEED spots in the disordered phase, we would expect different spots for Ge(110) than for Si(110), if for no other reason than that the Si(110) (16 × 2) structure that precedes the disordered phase is composed of six-membered rings [13], whereas the Ge(110) c(8 × 10) and (16 × 2) reconstructions are composed of five membered rings.

5. Conclusions

Our LEED results on clean Ge(110) confirmed the work of a prior RHEED study [6] which observed weak c(8 × 10) ordering at temperatures above 430 °C, indicating that some short-range ordering found in the c(8 × 10) reconstruction may persist at high temperatures, possibly in the form of pentagonal clusters that make up the reconstructions observed below 430 °C. The c(8 × 10) ordering disappeared as temperature was increased from 430 °C to 800 °C.

Rapidly quenching the surface temperature from 800 °C to room temperature produced surface features not previously observed on the Ge(110) or Si(110) surfaces. STM images of Ge(110) samples that were quenched rapidly to room temperature showed c(8 × 10) terraces, {17 15 1} facets, a new (8 × 2) phase, and no (16 × 2). The observed (8 × 2) reconstruction differs from the (16 × 2) reconstruction only in the absence of alternating rows of missing top layer atoms in the (16 × 2) that double the size of what would otherwise be an (8 × 2) unit cell. The rapid cooling we applied in the preparation of this surface may explain the absence of the alternating rows of missing top layer atoms required to form the (16 × 2) reconstruction.

The use of multiple surface characterization techniques, including both diffraction and microscopy, gives new insights into the complex surface structure of Ge(110). High resolution microscopy gives evidence for a new (8 × 2) reconstruction and an order-disorder transition. Future work will explore additional details on these topics.

Acknowledgments

The authors are pleased to acknowledge funding support from the National Science Foundation under Grant CHE-0719504.

References

[1] T. Ichikawa, T. Sueyosi, T. Sato, M. Iwatsuki, F. Udagawa, I. Sumita, Solid State Commun. 93 (1995) 541.
[2] T. Ichikawa, Surf. Sci. 560 (2004) 205.
[3] T. Ichikawa, Surf. Sci. 560 (2004) 213.
[4] Z. Gai, R.G. Zhao, W.S. Yang, Phys. Rev. B 57 (1998) R6795.
[5] H. Kim, A. Vailionis, D.G. Cahill, J.E. Greene, Surf. Sci. 457 (2000) 337.
[6] H. Noro, T. Ichikawa, Jpn. J. Appl. Phys. 1 24 (1985) 1288.
[7] B.Z. Olshanetsky, S.M. Repinsky, A.A. Shklyaev, Surf. Sci. 64 (1977) 224.
[8] A.A. Stekolnikov, J. Furthmüller, F. Bechstedt, Phys. Rev. B 70 (2004) 045305.
[9] T. Ichikawa, Surf. Sci. 544 (2003) 58.
[10] N. Takeuchi, Surf. Sci. 494 (2001) 21.
[11] Y. Yamamoto, S. Ino, T. Ichikawa, Jpn. J. Appl. Phys. 2 Lett. 25 (1986) L331.
[12] Y. Yamamoto, T. Sueyoshi, T. Sato, M. Iwatsuki, Surf. Sci. 466 (2000) 183.
[13] W.E. Packard, J.D. Dow, J. Appl. Phys. 81 (1997) 994.
[14] A. Santoni, L. Petaccia, V.R. Dhanak, S. Modesti, Surf. Sci. 444 (2000) 156.
[15] M. Yoshimura, T. An, K. Ueda, Jpn. J. Appl. Phys. Part 1 39 (2000) 4432(Regul. Pap. Short Notes Rev. Pap.).
[16] W. Swiech, T. Schwarz-Selinger, D.G. Cahill, Surf. Sci. 519 (2002) L599.
[17] T. Ichikawa, H. Fujii, A. Sugimato, in: N. Miura, T. Ando (Eds.), Proc. of the 25th Int, Conf. on the Physics of Semiconductors, Springer, Osaka, Japan, 2000, p. 296.
[18] C.L.H. Devlin, D.N. Futaba, A. Loui, J.D. Shine, S. Chiang, Mater. Sci. Eng. B-Solid State Mater. Adv. Technol. 96 (2002) 215.
[19] C. H. Mullet, Ph.D. Dissertation, University of California, Davis, 2012 (available as UMI AAT3540708).
[20] Tucker, J. Appl. Phys. 38 (1967) 1988.