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Irreversible order-disorder transformation of Ge(0 0 1) probed by scanning tunnelling microscopy

L Persichetti[1], **A Sgarlata**[2], **M Fanfoni**[2] **and A Balzarotti**[2]

[1] Department of Materials, ETH Zurich, Hönggerbergring 64, Zürich 8093, Switzerland
[2] Dipartimento di Fisica, Università di Roma 'Tor Vergata', Via della Ricerca Scientifica 1, Rome 0133, Italy

E-mail: luca.persichetti@mat.ethz.ch

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Abstract

We investigate the surface structure of Ge(0 0 1) during the (2 × 1)–(1 × 1) phase transition occurring at $T > 1130$ K by high-resolution scanning tunnelling microscopy. We find a drastic size reduction of dimerized domains in line with substantial dimer breakup accompanied by surface roughening. Completing the picture provided by previous spectroscopic observations, probing with high spatial resolution reveals the nucleation of several nanodomains with distinct vicinal orientations and reconstructions. The structural transformation is irreversible and is not observed for other singular faces of Ge.

Keywords: semiconductor surfaces, melting, germanium

(Some figures may appear in colour only in the online journal)

Introduction

One of the main lessons learnt from the first thirty years of nanoscale science is that several phenomena, which appear to be trivial at the macroscale, represent a formidable challenge when looking at them from the bottom. There are a plenty of examples, such as friction [1], ice nucleation [2] or the mechanical behaviour of nanosprings [3]. Among them, melting is certainly one of the most debated [4, 5]. The equilibrium behaviour of solid surfaces and nanosystems close to the bulk melting point (T_m) comprises a rich variety of phenomena. There are certain systems in which a quasi-liquid film forms at the surface as the temperature approaches the bulk melting temperature (surface melting). Depending on the system, the thickness of the liquid film may or not diverge as $T \rightarrow T_m$ (complete and incomplete melting, respectively). Other surfaces instead remain solid and crystalline all the way up to T_m (surface nonmelting) [5]. It was also demonstrated that a vicinal surface with crystal orientation close to a non-melting face may spontaneously decompose into coexisting dry and melted facets as T_m is approached, leading to the so-called surface-melting-induced-faceting [6, 7]. This plethora of effects have been

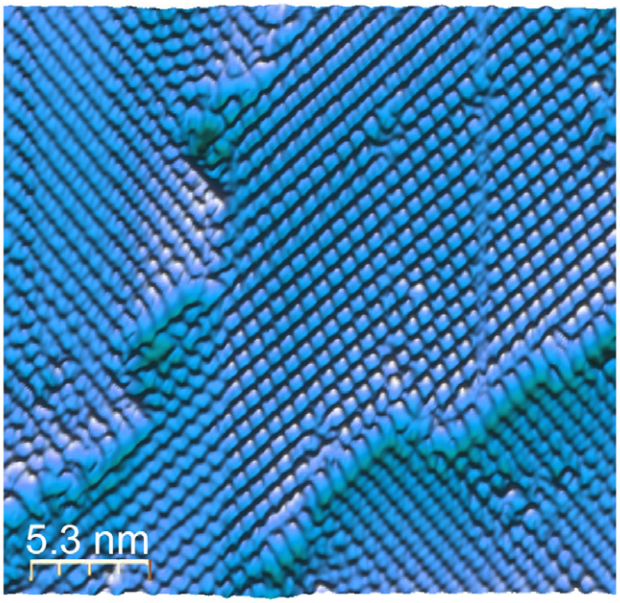

Figure 1. Filled-state STM image of the Ge(0 0 1) surface obtained after the cleaning procedure and showing alternated (2 × 1)–(1 × 2) terraces. The image has been acquired using a sample bias voltage $U_s = -1.1$ V and a tunnelling current $I = 1.1$ nA.

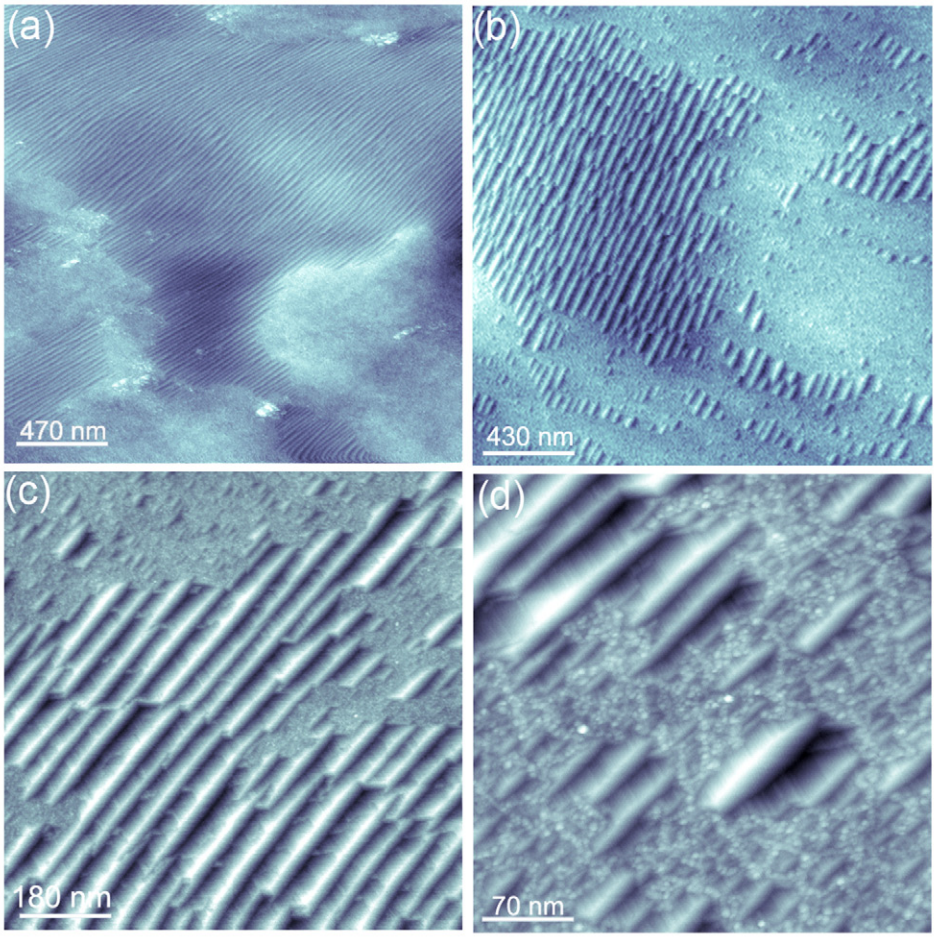

Figure 2. Large-scale STM images of the nominal Ge(0 0 1) surface after few seconds flash annealing to 1170 K.

mainly studied for metal surfaces, whereas little is known for semiconductors. Despite it is clear that for these materials the negative Hamaker constant, arising from the long-range attraction, hinders complete surface melting [5], a detailed understanding of the high-temperature behaviour is hampered by the complex surface reconstructions of semiconductors. Whereas it is known, for e.g., that Ge(1 1 1) exhibits incomplete melting [8], the case of Ge(0 0 1) is much more controversial and has been heavily disputed. It has been observed that the (2×1) structure is progressively lost between 1130 K and the melting point, but conflicting pictures of this phase transition have been depicted: Either dimer breakup [9, 10] or step/ domain walls proliferation [11, 12] have been indicated as the origin of the phase transition and the nanoscopic mechanisms of the transition are basically unknown due to the lack of atomic-resolution information.

Here, we present a scanning tunnelling microscopy (STM) investigation of the high-temperature structure of the Ge(0 0 1) surface. Atomic-scale resolution STM images reveal a rather complex scenario consisting in extended rearrangement of both the meso- and the nano-scale structure of the surface. The drastic reduction of (2×1) dimers is accompanied by the loss of the (0 0 1) reference plane which induces roughening and the appearance of nano-domains of diverse crystal orientations.

Experimental details

Experiments were carried out by using commercial epi-ready, prime-grade polished Ge(001) wafers (Sb-doped with resistivity of 7 to 9 Ω cm). The samples were prepared in ultra-high-vacuum (UHV) ($p < 5 \times 10^{-11}$ mbar) by thoroughly outgassing at 800 K, followed by several sputtering/annealing cycles of Ar^+ sputtering (830V, 20min) and annealing at 1103 K by direct current heating. At this stage, surface quality was checked by STM showing flat (0 0 1) terraces with alternated (2×1)–(1×2) reconstruction (figure 1). After cleaning, the samples were flashed to 1173 K for a few seconds. Careful temperature calibration was performed using optical pyrometer and by determining directly the melting temperature on a sacrificial sample. Absolute accuracy of the temperature measurements is estimated to be ±25 K. We remark that spectroscopic surface analysis data drawn from literature [13] rule out the possible segregation of bulk impurities at the surface within the temperature range of flashing. STM measurement are performed at room-temperature and in constant-current mode using W-etched tips.

Results and discussion

Figure 2 shows the surface morphology after one flash to 1173 K. STM images reveal a surface arrangement which

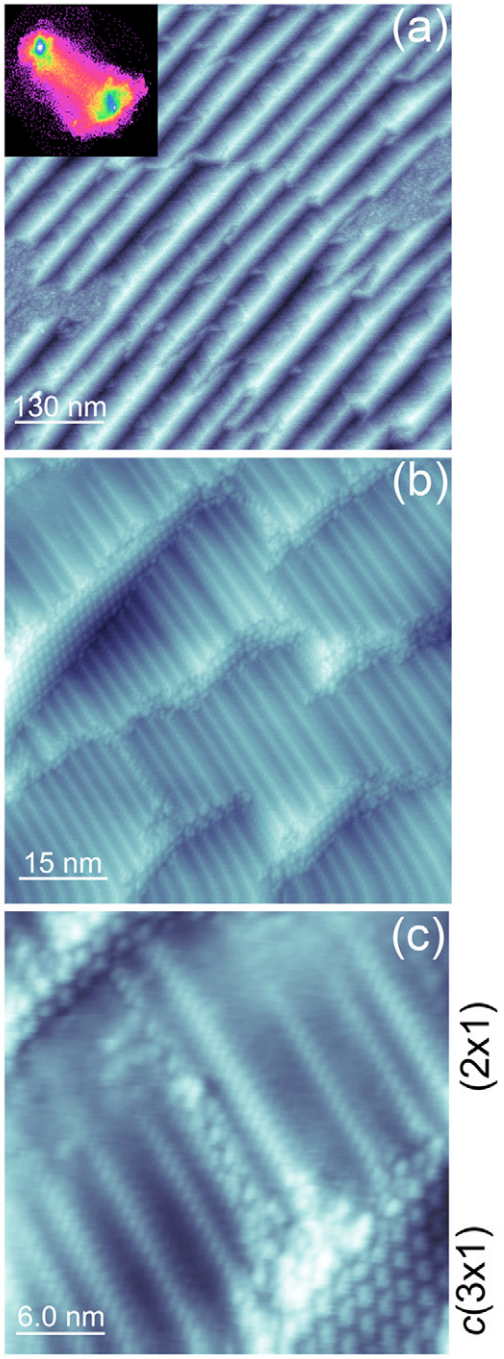

Figure 3. Filled-state STM images of a faceted domain showing the (2 × 1) and the *c*(3 × 1) reconstructions. In the inset of panel (a), the corresponding FP is reported. Images have been acquired using a sample bias voltage $U_s = -1.1$ V and a tunnelling current $I = 1.5$ nA.

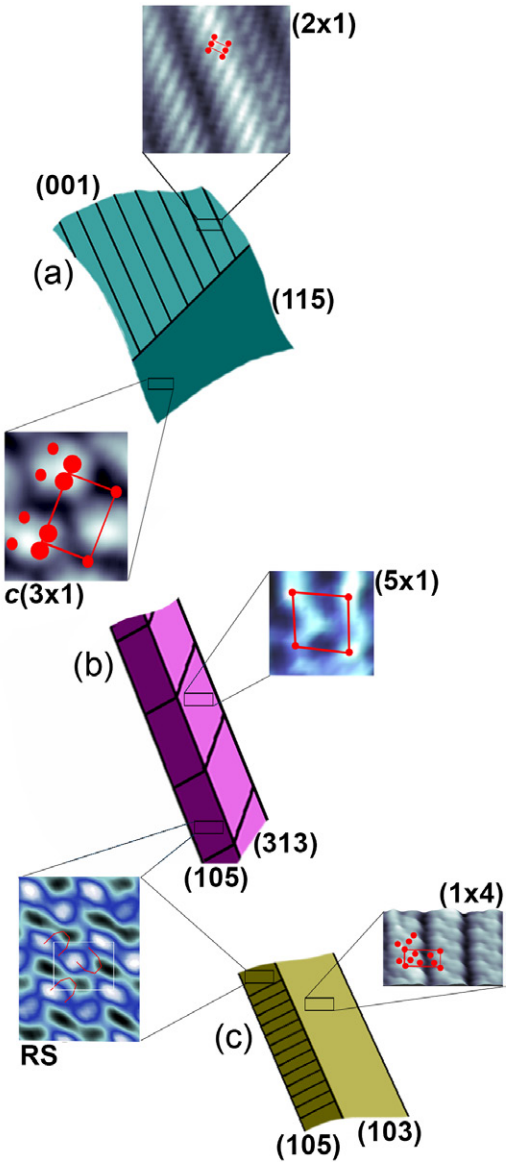

Figure 4. Schematic structural models of the observed faceting and surface reconstructions. The sizes of STM images are: (2 × 1) reconstruction (7.2 × 7.2) nm^2; *c*(3 × 1) reconstruction (1.2 × 2.4) nm^2; (5 × 1) reconstruction (3.2 × 3.2) nm^2; RS reconstruction (2.8 × 2.8) nm^2; (1 × 4) reconstruction (4.8 × 7.6) nm^2. Each reconstruction has been imaged with the same scanning parameters as in the other figures.

dramatically differs from the well-known alternated (2 × 1)/(1 × 2) domain structure (reported in figure 1) obtained for low temperature annealing to $T < 1100$ K. On the surface, disordered areas coexist with ordered faceted domains; from a statistical analysis, the relative abundance of the ordered areas is between 20 and 30% of the total surface. The disordered domains show a rough and unreconstructed morphology [figure 2(d)] which is consistent with the partial loss of order observed in spectroscopic investigations [10, 11]. As pointed out by van Vroonhoven *et al* [10], surface disorder can be satisfactorily explained by the absence of in-plane bonding for the (1 × 1) bulk termination of the diamond-type lattice of Ge. This means that the breakup of surface reconstruction is accompanied by the loss of height-height correlation and surface roughening. Compared to non-local techniques, high-resolution STM probing reveals, however, further details of the structural transformation occurring at high temperature. Studying carefully the structure of the ordered areas, one discovers a complex and rich scenario of diverse faceting and surface reconstructions. These different structures coexist on the surface and appear as domains of tens to hundreds of nanometres in size which randomly nucleate inside the large unreconstructed areas. The relatively small size of the domains together with their random distribution over the surface hinder

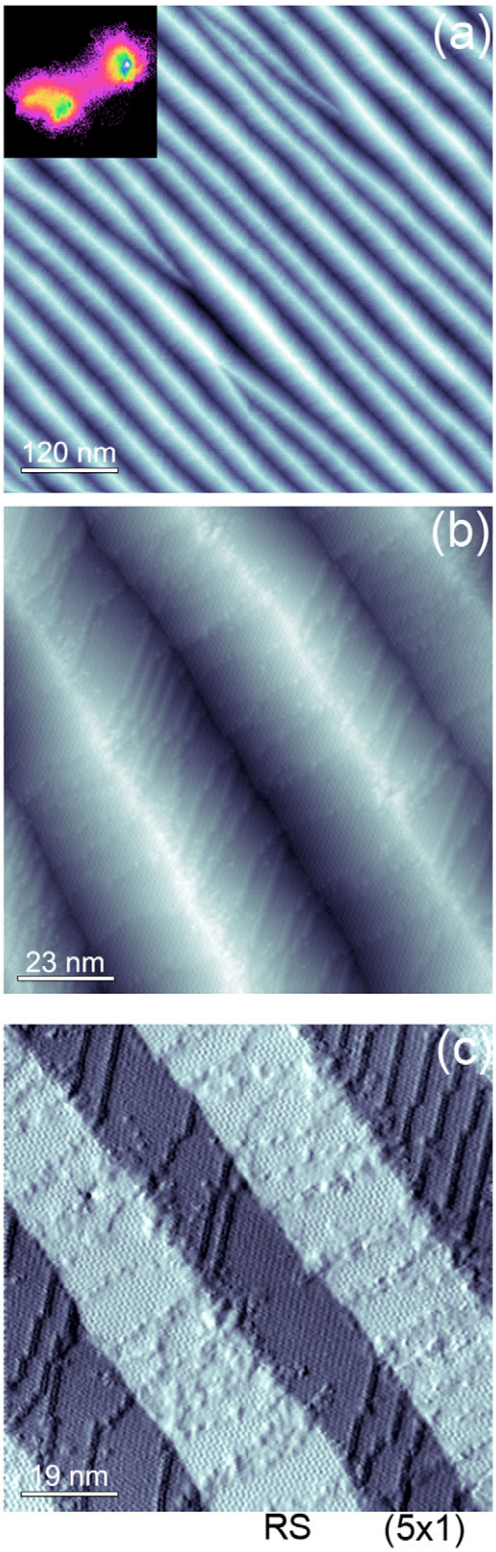

Figure 5. Filled-state STM images of a faceted domain showing the RS and the (5 × 1) reconstructions. In the inset of panel (a), the corresponding FP is reported. Images have been acquired using a sample bias voltage $U_s = -1.2$V and a tunnelling current $I = 1.25$ nA.

their observation by means of surface-averaged techniques. One example of these faceted domains is reported in figure 3. Quantitative information on faceting can be obtained by

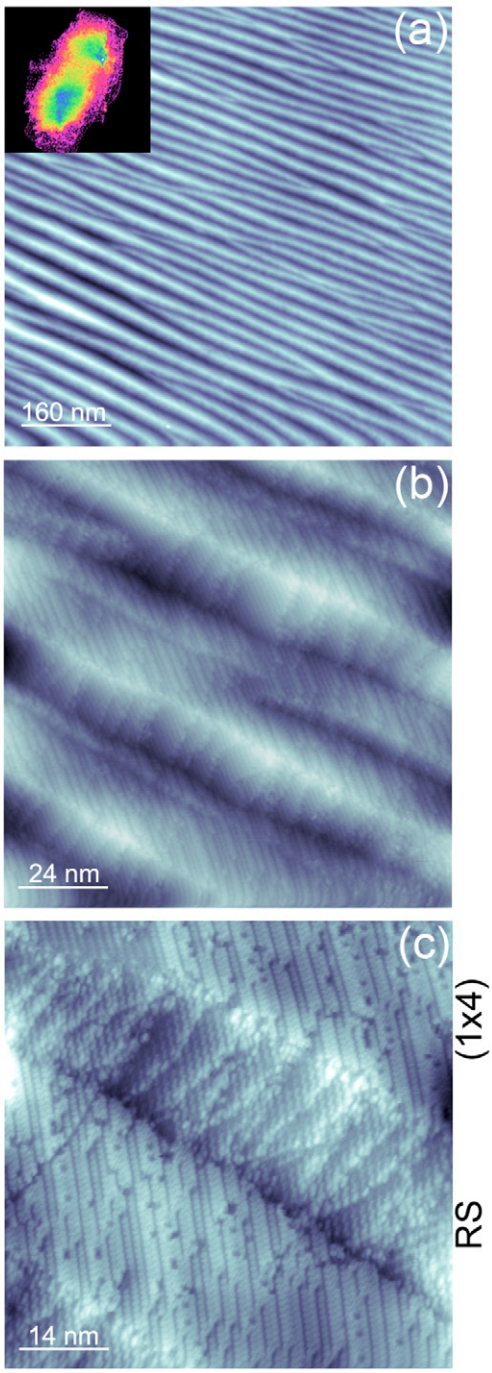

Figure 6. Empty-state STM images of a faceted domain showing the RS and the (1 × 4) reconstructions. In the inset of panel (a), the corresponding FP is reported. Images have been acquired using a sample bias voltage $U_s = 1.2$V and a tunnelling current $I = 90$ pA.

applying the so-called facet plot (FP) analysis [14]. It consists of a 2D diagram in which the position of each spot represents the local normal orientation relative to the centre, which corresponds to the (0 0 1) plane, while the intensity represents the relative amount of the surface with that orientation. The two distinct spots in the FP shown in the inset of figure 3(a) thus indicate that the surface breaks up into two crystallographic faces.

From atomic resolution images [figures 3(b) and (c)], one face is composed by a staircase of steps and narrow

(0 0 1) terraces with (2 × 1) dimers. The other face shows wide reconstructed facets with the $c(3 \times 1)$ reconstruction typical of (1 1 5) vicinal surfaces of Ge [15]. Figure 4(a) shows a schematic of the faceting together with a model of the observed surface reconstructions. Moving to other areas of the sample, we observe again faceting but showing other crystallographic orientations. A large reconstructed domain is displayed in figure 5 which shows almost perfect nanoripples. These are bounded by two facets oriented along two distinct orientations, as indicated again by the FP [figure 5(a)]. One facet shows the rebounded-step (RS) reconstruction of (1 0 5) surfaces [16], while the other has the (5 × 1) reconstruction of (3 1 3) terraces [17] [figures 5(b) and (c)]. The corresponding structural model of faceting and reconstructions is reported in figure 4(b). The regular alternation of the two facets is locally interrupted by defects, such as zig-zag edges or interrupted ripples [figure 5(a)]. The abundance of the faceted domains described in figures 3 and 5 is roughly 4/5 of the total reconstructed surface, the remaining part having a similar rippled structure [figures 6(a) and (b)]. Here, one facet is again the RS-(105) surface, but the other shows a different reconstruction which is identified as the (1 × 4) one of (1 0 3) faces [18] [figure 6(c) and schematics in figure 4(c)]. In the latter, many vacancies are evident, as expected from the high adatom mobility at the annealing temperature.

Our atomic scale observations perfectly match previous spectroscopic results [10]. STM images clearly show that most of the surface consists of disordered domains; the remaining (2 × 1) dimer concentration is very low- i.e. a few percent of the total surface- indicating that a significant dimer breakup has occurred. The consequent dramatic reduction of in-plane bonding explains surface roughening, as hinted in [10]. In addition, the high spatial resolution of STM shows that the loss of the (0 0 1) reference plane drives faceting along different neighbouring vicinal orientations. It is known, in fact, that even a small misorientation from the (0 0 1) plane stabilizes a plenty of diverse faces without unique dominant surface orientation [18, 19]. The coexistence of several faceted domains with the boundaries therein explains, on the other end, the proliferation of steps and walls observed in many previous observations [11, 12]. We remark that the surface roughening above 1130 K is fully irreversible and cannot be annealed out without additional sputtering cycles. We also note that this order-disorder transformation is inherent of the Ge(0 0 1) surface. The same annealing treatment on Ge(1 1 1) does not result in any remarkable structural change and the whole surface consists of flat $c(2 \times 8)$-reconstructed terraces, as in the case of low-temperature annealing.

Conclusions

The well-known dimerized structure of Ge(0 0 1) is dramatically altered by annealing at $T > 1130$ K. We investigate this irreversible structural change at the atomic-scale by STM, providing a framework for previous spectroscopic observations with lack of spatial resolution. We find that the transition is driven by the disappearance of (2 × 1) dimers which induces surface roughening and the nucleation of several nanodomains with different crystal orientations and reconstructions alternated by unreconstructed, disordered areas. The transformation is irreversible and is not observed on other singular faces of Ge.

Acknowledgments

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