

(2 × 1)-(1 × 1) Phase Transition on Ge(001): Dimer Breakup and Surface Roughening

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Using low energy electron microscopy, we have investigated the (2×1) - (1×1) phase transition occurring above 925 K on Ge(001). Dimer breakup has been identified as the physical origin of this transition. A quantitative description of the dimer concentration during the transition involves configuration entropy of random monomers within the dimer matrix. The dimer formation energy amounts to 1.2 ± 0.3 eV. Dimer breakup promotes *reversible* surface disorder by step proliferation and *irreversible* surface roughening above 1130 K.

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Although the technologically important group IV semiconductor surfaces Si(001) and Ge(001) have a relatively small surface unit cell, they manifest a wealth of fascinating and intriguing phenomena. The surfaces reconstruct to form rows of dimers yielding a (2×1) unit cell. The driving force for this reconstruction is a reduction of the number of dangling bonds per surface atom from two for the ideally bulk-truncated (1×1) surface to one for the (2×1) reconstructed surface. At a low temperature, the surface energy can be further reduced by dimer buckling, giving rise to higher order reconstructions such as $p(2 \times 2)$ and $c(4 \times 2)$ (e.g., [1]).

At a high temperature (~ 950 K), a transition from (2×1) to (1×1) has been reported by several authors (e.g., [2–4]), both for Si(001) and Ge(001). However, the identification of the physical origin of the phase transition is controversial or even contradictory. Johnson *et al.* [2] conclude from their x-ray diffraction study that the phase transition is caused by dimer breakup, accompanied by a "corresponding loss of height-height correlation across the surface." Le Lay *et al.* [3] concluded from a temperature dependent multiparameter fit of their angle resolved photoemission spectra of the Ge $3d$ levels that the number of dimers remains "essentially conserved during the phase transition." Cvetko *et al.* [4] concluded from their He atom scattering (TEAS) study that the transition is "characterized by step proliferation, thus indicating an order-disorder character." They observed an increase in the density of steps, "only partially involved in the disordering of the (2×1) phase." In their reflection high-energy electron diffraction (RHEED) study, Zeng and Elsayed-Ali [5] favor domain wall proliferation instead of dimer breakup. They observed also that "the surface starts to disorder at 127 ± 44 K above the onset temperature of 900 K for the phase transition."

We have used low-energy electron microscopy (LEEM) and diffraction (LEED) to investigate the high-temperature (2×1) - (1×1) phase transition, taking place between 950 and 1130 K. We have chosen Ge(001) rather than the technologically even more relevant Si(001) for several reasons: First, Ge(001) is easy to clean and can be prepared with substantially less defects than Si(001)

[6,7]. This is of interest since properties of the phase transition are known to depend strongly on defects. Second, the melting point of Ge is significantly lower than that of Si, which makes it more convenient to monitor the transition on Ge(001). Third, the vapor pressure at the melting point is for Ge about 3 orders of magnitude lower than the corresponding Si value. Evaporation is insignificant under all conditions discussed here. The observations for Ge(001) are highly significant for the closely related Si(001) surface.

As will be argued below, the phase transition is uniquely induced by dimer breakup. We can describe the dimer concentration during the (2×1) - (1×1) phase transition, irrespective of the (2×1) - (1×2) domain distribution. Its quantitative description demands the introduction of configuration entropy of dimers residing randomly on sites within the matrix defined by the low temperature dimer row mesh. Because of the decreasing dimer concentration, the effective interaction between dimers decreases. Therefore, also the step tension will decrease, providing a natural explanation for step proliferation accompanying (following) the phase transition. At very low dimer concentrations, the surface loses recollection of its starting reference plane [2] since with the disappearance of dimer bonds no in-plane bonding is available in the diamond-type lattice of Ge and Si. As a result, the (001) facet in a (1×1) configuration can roughen in an unbridled way. This has been recognized for Si(001) also by Métois and Heyraud [8]. We attribute the irreversible surface roughening after surpassing a temperature of 1130 K, observed also by Johnson *et al.* [2], to this feature. Within our model, we can satisfactorily merge the controversial interpretations referred to above. Moreover, we are able to experimentally determine for the first time the dimer formation energy to 1.2 ± 0.3 eV. When scaled by either the ratio of the melting points or that of the cohesive energies, this value is in perfect agreement with the calculated value of 1.9 eV for Si(001) [9].

The Ge(001) surface was prepared in ultrahigh vacuum by thoroughly outgassing at 800 K for about 20 h, followed by some cycles of 1700 eV Ar⁺-ion sputtering at

normal incidence for 30 min and annealing at 1050 K for 24 h. The thus prepared samples show sharp LEED patterns. The sample was heated from the rear by electron bombardment and the temperature was measured using a tungsten/rhenium thermocouple. Careful temperature calibration was performed using a pyrometer and by determining directly the melting temperature. We estimate the absolute accuracy of our temperature measurement to better than 25 K.

To obtain more information on the phase transition, it is important to have direct microscopic information with high lateral resolution during the phase transition. We have used LEEM to image the Ge(001) surface with a field of view of $4\ \mu\text{m}$ and a lateral resolution of about 7 nm. The electrons undergo conventional LEED. *In situ* LEEM dark field images are obtained by using one of the fractional orders of the LEED pattern taken at 4 eV. Figure 1 shows a sequence of LEEM images at various temperatures obtained for Ge(001) with a very low miscut angle. The left top image has been obtained at 723 K. The bright areas show, for example, (2×1) domains (even layers) and the dark ones refer then to equivalent (1×2) domains (odd layers). The grey areas show regions at the surfaces in which the (2×1) and (1×2) domains alternate within the resolution of the instrument. Similar images have been found by Tromp and Reuter for low miscut angle Si(001) [10]. For Ge(001), the lateral length scale is smaller than for Si(001), consistent with the lower step free energies of Ge(001) [11]. With increasing temperature, the grey regions grow at the expense of both black and white regions, until around 1040 K the contrast is lost completely. The loss of contrast is attributed mainly to a decreased size of the domains. Step proliferation sets in at roughly 950 K. The contrast can be restored at will by cooling the Ge(001) sample.

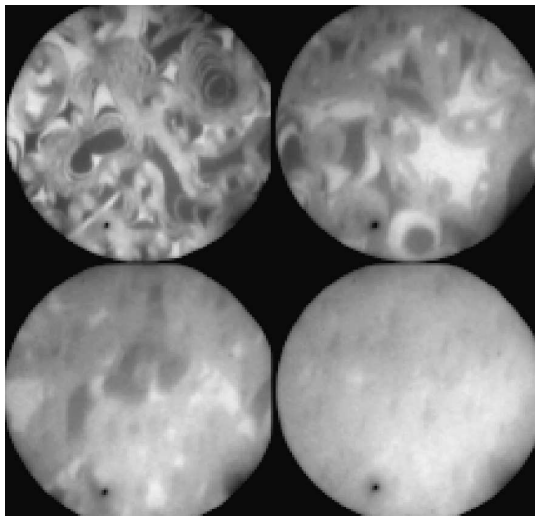


FIG. 1. Dark field LEEM images of Ge(001) with increasing temperature. The field of view is $4\ \mu\text{m}$. From right to left and from top to bottom: 723 K, 1009 K, 1033 K, 1054 K.

Using our instrument in LEED mode reveals that at 1050 K still very sharp half order LEED spots are present, indicative of a still (at least partly) dimerized surface. A further increase of the temperature leads to a reduction of the intensity of these spots. Figure 2 quantifies this feature. It shows the integrated peak intensity which is calculated by identifying the maximum of the peak and drawing circles around this position. The intensity of each spot is corrected by subtraction of a base plane, set by the circle. The integrated intensity is taken for circles with increasing diameter until it approaches a steady value. The intensity is then corrected for Debye-Waller effects and normalized. By virtue of the low energy of the electrons (4 eV) these corrections are only marginal, i.e., up to 15% in the temperature range shown here, in spite of the high surface temperature. We emphasize that the integrated intensity is a *direct measure of the dimer concentration*, irrespective of their lateral distribution. Above about 950 K, the dimer concentration decreases dramatically. However, we note that at 1050 K, where the LEEM contrast is fully lost, dimers are still present to a very significant concentration. This further supports the idea that the loss of contrast in the LEEM images is mainly due to a reduction of the lateral length scale of the domains to below the resolution limit. We emphasize that the observed complex behavior is completely reversible: The full data points have been obtained during increase of the temperature, while the open data points have been taken at decreasing temperature. Above 1130 K, an irreversible transition sets in in agreement with Ref. [2]. The results demonstrate that dimer breakup occurs in agreement with Ref. [2] and seemingly at variance with Refs. [3–5].

Following a well established approach in statistical physics, we attempt to relate the dimer concentration θ_d to that of broken dimers θ_m ($\theta_d + \theta_m = 1$) using a Boltzmann expression with the Helmholtz free energy:

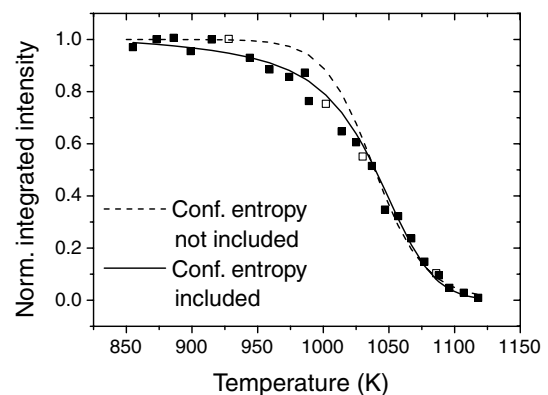


FIG. 2. Normalized integrated intensity of the half order spots corrected for Debye-Waller effects as a function of temperature. Full (open) data points taken with increasing (decreasing) temperature.

$$\frac{\theta_m}{\theta_d} = \exp\left(-\frac{u - Ts(T)}{k_B T}\right), \quad (1)$$

with u being the dimer formation energy and s the entropy, both on a per dimer basis. This equation can be rewritten as

$$\theta_d = \left[1 + \exp\left(-\frac{u - Ts(T)}{k_B T}\right)\right]^{-1}. \quad (2)$$

The dashed curve in Fig. 2 shows the result of a fit of this equation to the data points. It appears impossible to obtain a good fit in the entire temperature range. The dashed curve has been obtained with $u = 5$ eV and $s = 4 \times 10^{-3}$ eV/K. Not only the very poor fit is cumbersome, but also a dimer formation energy of 5 eV is clearly unphysical: Acceptable values should be well below the cohesive energy of 3.85 eV [12]. Scaling the calculated dimer formation energy of 1.9 eV for Si(001) [9] yields a dimer formation energy of only about 1.5 eV. We note that the obtained result for the entropy, s , is not physical either. At first sight, a solution is not straightforward since incorporation of terms accounting for vibration, translation, and vibration entropy contribute only 0.1 eV per degree of freedom to the total Helmholtz free energy. The only way out of this dilemma is the incorporation of configuration entropy. Note that this makes s dependent on θ_d , which in turn depends on temperature. As shown below, this provides direct insight into the physics of the (2×1) - (1×1) phase transition.

We consider now the following system: The broken-up dimers are randomly distributed within the field of dimer rows. Such an approach has been successfully pursued by Sparnaay for a thermodynamic description of the (2×1) - (7×7) phase transition on Si(111) [13]. This now permits us to write an analytical expression for the configuration entropy [14]:

$$s_{\text{conf}}(T) = -k \left[\frac{1 - \theta}{\theta} \ln(1 - \theta) + \ln \theta \right]. \quad (3)$$

Substituting this expression in Eq. (2) with $s = s_{\text{conf}} + s_{\text{rest}}$ yields the following equation:

$$\frac{k_B T}{\theta_d} \ln(1 - \theta_d) = -u + T s_{\text{rest}}. \quad (4)$$

This result satisfies the required boundary conditions: $\theta_d = 1$ and $\theta_d = 0$ at low and high temperature, respectively. The solid curve in Fig. 2 represents a fit of Eq. (4) to the data. The fit is very convincing in the entire temperature range. The resulting values are for the dimer formation energy, u , and for the remaining entropy term, s_{rest} , respectively, 1.2 ± 0.3 eV and 8×10^{-4} eV/K per dimer.

The obtained value of u is, to our knowledge, the first experimental determination of the dimer formation energy on a (001) surface of group IV semiconductors. No direct theoretical value is available for comparison. However, if one scales the value of 1.9 eV, calculated for Si(001) [9], with the ratio of the melting temperatures or

that of the cohesive energies of Si and Ge one obtains 1.35 and 1.55 eV, respectively. This provides strong retrospective support for our data analysis. Note that also the assumption of random dimers underlying Eq. (3) is quite well fulfilled: The dimer-dimer coupling is smaller than $k_B T$ at 1000 K [15]. We also note that the obtained value for s_{rest} of 8×10^{-4} eV/K is reasonable. At the temperatures considered here, this value is easily accounted for in terms of vibration and translation contributions to the entropy.

Resuming, we have obtained the following physical picture of the Ge(001) (2×1) - (1×1) phase transition, which should hold for Si(001) as well. The transition is caused by a breakup of dimers, randomly distributed over the lattice defined by the dimer row mesh. An important aspect of the dimerized group IV (001) surface is the relatively low in-plane interaction energy. Obviously, the dimer formation energy is by far the largest. The interaction energy between dimers is more than 1 order of magnitude smaller [7]. It is exactly the latter interaction energy that is responsible for the step tension and therefore for the meandering of domain walls (steps in this case). According to Refs. [7,16], some degree of step proliferation has to be expected already around 900 K. However, when some significant amount of the dimers gets broken up, the lateral interactions and therewith the step tension decrease even further. This promotes enhanced domain wall proliferation, physically following the breakup of dimers. This conjecture is fully in line with our own observation and with Ref. [5], which states that surface disorder follows the phase transition. In other words, strong step proliferation occurs after a strong reduction of the dimer concentration by thermally excited breakup of the dimers within the matrix.

The conflicting explanations in the literature for the physics of the high-temperature phase transition [2–5] are probably generated by the coincidence of dimer breakup and step proliferation for which we have provided above a robust link. The preference for one or the other is probably mainly related to the difficulty in quantitatively relating the intensities of the fractional order diffraction peaks to dimer intensities. Our results outlined above provide a powerful framework for reconciling all previous observations. The only exception probably is the conclusion reached in Ref. [3]. We note, however, that the fit of the Ge 3d photoemission peak shape requires extensive multiparameter curve fitting. This might even be more complicated by, e.g., inharmonic vibrations likely to occur near the melting temperature. We cannot see any conflict with either the RHEED results of Ref. [5] nor with the TEAS study [4]. Note that the dimer defects give rise to heavy incoherent scattering of thermal energy He atoms [17]. We agree largely with the results of Ref. [2]. However, we cannot support their conjecture, that dimer breakup goes along with “some kind of vertical movement.” We see no compulsory reason for this vertical movement since the

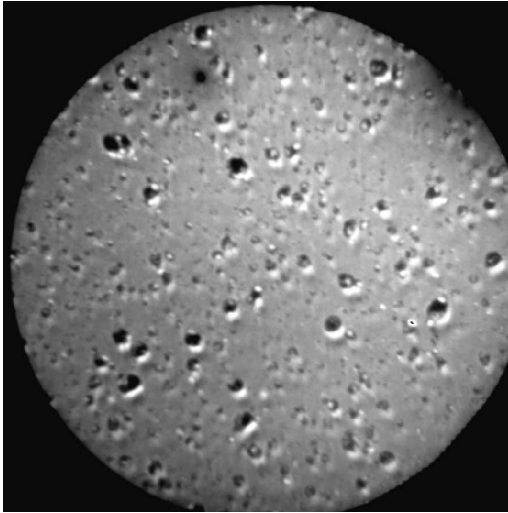


FIG. 3. PEEM image of the Ge(001) surface after the irreversible surface transition above 1130 K. The field of view is 100 μm .

inclusion of configuration entropy provides a quantitative description of the dimer concentration with temperature. We actually view the broken-up dimers as being in active thermal equilibrium with dimers within the matrix. We hold a sufficiently long lifetime of dimers responsible for maintaining the recollection of the original surface, keeping the (001) facets smooth. The lifetime and therefore the concentration of dimers within the matrix decrease with temperature. In addition, we mention that the simulation of Johnson [2], taking into account the vertical movement, leads to a dimer formation energy which is too low by a factor of 4, when compared to the scaled theoretical result for Si(001) [9].

As mentioned above, an irreversible (001)-surface roughening occurs upon surpassing a substrate temperature of 1130 K. A resulting photoelectron energy microscopy, PEEM, image taken at room temperature is shown in Fig. 3. Indeed Fig. 3 supports quite unbridled irreversible facet roughening, occurring just below the melting temperature, as proposed by Johnson *et al.* for Ge(001) [2] and by Métois and Heyraud for Si(001) [8]. Our model also provides a natural framework for the explanation of this phenomenon. Note that in the ideal bulk termination, suggested by the (1 \times 1) structure, there is no in-plane bonding. This implies that there is no energetic inhibition for a monomer to reside in a higher lattice layer as long as contact is made to the lattice. There is even a (translation) entropy or Helmholtz free energy drive for this roughening process explaining at the same time its irreversible nature. Obviously, this situation is reached best for a very low dimer concentration, which apparently has to be well below 1% (see Fig. 2 for 1130 K). In fact, also this result is perfectly in line with our model. The displacement of a monomer from an in-terrace to an on-terrace position involves a high activation barrier, E_a , probably estimated

well by the breaking of one bond, i.e., 50% of the cohesive energy at 1.9 eV. A simple-minded guess for the occurrence of irreversible roughening, assuming a unique frequency factor, leads then to the condition that the rate of atoms jumping onto the terrace should outweigh the adatoms-dimer recombination rate; or with the dimer formation energy, E_{df} , $\theta_d \leq \exp[-(E_a - E_{df})/k_B T] \sim 10^{-3}$, in fair agreement with the observation. Note also that the inclusion of configuration entropy allows explaining the 127 ± 44 K temperature difference between the onset of the phase transition and the irreversible surface roughening found by Zeng *et al.* [5]. In our case this difference amounts to about 180 K.

In summary, we have been able to quantitatively describe the dimer concentration during the (2 \times 1)-(1 \times 1) phase transition on Ge(001). Its physical origin is the thermally excited breakup of dimers, which promotes enhanced step proliferation. This result sets a nice framework for merging thus far conflicting literature studies and for understanding the irreversible facet roughening transition. Herewith we can describe the high-temperature behavior of the technologically important surfaces of Si(001) and Ge(001). Moreover, we suspect that the inclusion of configuration entropy is needed to quantitatively describe the high-temperature reconstruction-deconstruction phase transition on (several) other clean surfaces as well.

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