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Discussion

Comment on: "(2 × 1)-(1 × 1) phase transition on Ge(0 0 1): quasi-chemical approximation and Monte Carlo simulations" [Surface Science 563 (2004) 99–109][☆]

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It is well known that the Ge(0 0 1) surface reconstructs to form dimers, allowing a reduction of the dangling bonds by 50% compared to the bulk terminated case. At moderate temperatures the dimers appear symmetric giving rise to a (2 × 1) structure. At lower temperature the dimers are buckled in an alternating fashion, leading to a further reduction of the symmetry forming a c(4 × 2)-reconstructed surface. Around room temperature both phases coexist in an extended temperature range. In all published (and all our unpublished) STM images the dimers have been observed to align in dimer-rows without exception. Broad agreement has been obtained on the details of these low and intermediate temperature surface

structures. In contrast, the nature of the reversible phase transition (2 × 1)-(1 × 1) occurring close to the melting temperature is still heavily disputed. It is consistently reported to take place around 900–1100 K. However, persistent disagreement prevails on the extent of the dimer stability throughout the phase transition. Some authors believe that the dimer concentration is essentially maintained [1–5] and make domain wall proliferation responsible for the phase transition, while others claim that the phase transition is the direct result of massive dimer break-up [6,7]. The results of Cvetko et al. [8] are consistent with this latter view. The first conclusion is indirect and essentially based on, and follows, the early photo-emission observation of a finite density of states near the Fermi-level throughout the transition, which has been attributed to the presence of symmetric dimers [1]. Indeed, in agreement with calculations [9], the first spatially resolved spectroscopy (STS)

data show the presence of a metallic state on the (2×1)-domains, which is absent on the $c(4 \times 2)$-domains [10]. It should, however, be realized that also monomers must be expected to show metallic properties and no decision on dimer persistence or break-up can be made on the basis of photo-emission data alone. The dimer break-up model is based on a quantitative evaluation of low energy electron diffraction data [7] and agrees nicely with an earlier X-ray diffraction study by Johnson et al. [6]. We have, not estimated [11] but rather, determined the dimer formation energy for the first time to $|\varepsilon_D| = 1.2 \pm 0.3$ eV, in close agreement with calculations [12,13]. We arrived at our conclusion by realizing that the *integrated* intensity of the half-order spots is a *direct measure* of the dimer concentration.

In an attempt to further clarify the situation, Asada and Miura [11] recently discussed this phase transition. They discarded our analysis as "erroneous" and disregarded Johnson et al.'s earlier work [8]. Their argument leans on the fact that "(2×1) domains with opposite phases cancel the (2×1) diffraction intensity even though the surface is fully covered by dimers". This statement is basically correct, however, the real situation is subtler and must be considered with more caution. The cancellation is true only when looking exactly at the intensity at precisely the point in reciprocal space corresponding to the $(1/2, 0)$-order peak position with an ideal instrument (δ-function resolution). This implies, as the authors correctly state, that the diffraction intensity at this position would then relate to "the degree of long range order of dimers in the (2×1) translational symmetry". This fact is highly academic since any realistic instrument function does not permit straightforwardly that pure assignment. On top of that, the very fact that we deliberately have used the *integrated* peak intensity, as we stressed repeatedly in our paper, makes our data even completely *independent from long range order*, in contrast with Asada and Miura's conjecture! It is well known and widely accepted for more than 20 years in diffraction physics [14–16], that the summed intensity close to the (2×1) peak position is a *direct* measure of the dimer intensity. Just for further illustration, the solid curve in Fig. 1 shows the calculated diffraction
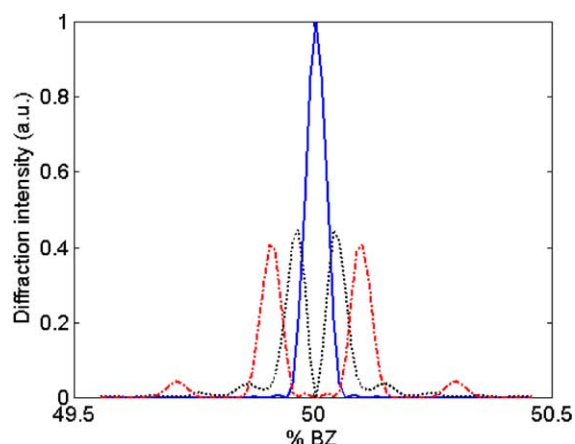

Fig. 1. Calculated profile for the 1/2 order diffraction peak for a 1D chain of 1024 dimers (—) and idem for a 1D chain of dimers in two (···), respectively four equivalent out-of-phase domains (-·-·-·).

peak profile around the 1/2-order spot for a linear domain of 1024 dimers with complete long range order, i.e. positioned on, e.g., even sites of the underlying lattice. As an example, the other curves in Fig. 1 refer to calculated peak profiles for the same situation, but with half of the dimers on odd sites, distributed in two (dotted line), respectively four (dash-dotted line) equally large domains. The integrated intensities are obviously equal, as they should for reasons of particle conservation and *directly relate to the number of dimers, irrespective of their lateral distribution!* Unfortunately, Asada and Miura appear to have missed this crucial point in our manuscript. Their model is definitely *inconsistent* with the quantitatively known data on the Ge(001) dimer concentration as a function of temperature. As illustrated in Fig. 1 the peak profile contains the information on the lateral distribution of the dimers. We note, in additional support of our data interpretation [7] that appreciable broadening of the half order spots only occurs around about 1050 K, corresponding to a dimer concentration of 0.3 and the probability for finding only surrounding monomers becomes substantial. This finding cannot be reconciled with the results of Ref. [11].

The model proposed by Asada and Miura [11] assumes some important energy terms whose val-

ues are physically unreasonable in our opinion. Assuming a dimer formation energy of 1.4 eV leads to an incredibly low dimer–dimer interaction energy $|\varepsilon_i|$ of "about 0.1 meV". This value is off by not less than about three orders of magnitude! The correct value obtained from early calculations by Ihm et al. [12], amounts to roughly 100 meV. The dimer–dimer interaction can also be determined roughly from the energy required for creating a kink in an A-step, running parallel to the dimer rows, which also amounts about 100 meV [17]. We note that in these estimates the long-range repulsive stress fields related to out-of-registry neighboring dimers has not yet been accounted for. Asada and Miura themselves do realize that 0.1 meV for $|\varepsilon_i|$ "seems to be too small to be physically reasonable". Without any justification and completely disregarding the consistent experimental and theoretical values for the dimer formation energy $|\varepsilon_D|$, they erratically decided to halve that value to arrive at what they again erroneously refer to as a "not unreasonable in physics" value for $|\varepsilon_i|$ of 10 meV. In reality, this value is definitely unphysical too. We have acquired several hundreds of STM-images of Ge(001) examples of which have been published in Refs. [18,19]. One of such images is reproduced
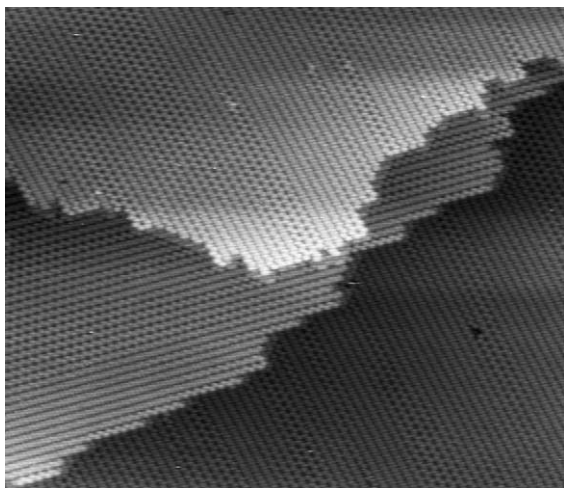

Fig. 2. STM image of Ge(001), obtained at room temperature and taken from Ref. [19]. Tunnel voltage: −1.6 V, tunnel current: 0.5 nA, size: 50×55 nm^2.

in Fig. 2 for the purpose of allowing a judgment of the actual dimer alignment. It contains ca. 10^4 dimer sites, which are all invariably situated in registry within the dimer rows, irrespective of whether they are buckled or not. We can now make an estimate of the number of out-of-registry dimers to be expected on the basis of the Asada–Miura (AM) model and compare that with the real situation on the Ge(001) surface. The elementary excitation in an extended dimer field requires the breaking of two adjacent dimers and the re-establishment of one dimer on an out-of-registry site. The latter involves the breaking of 4 dimer–dimer interactions and the effective breaking of one dimer bond at a total cost of $|\varepsilon_D| + 4|\varepsilon_i|$. Adopting AM's numbers and assuming a freeze-in temperature of 900 K (note that the phase transition sets in above 900 K) leads to an expectation frequency of these elementary excitations of $\sim 10^{-4}$. We should expect about one out of registry dimer per frame with the size in Fig. 2. It should be pointed out that the expectation frequency increases drastically if one considers a larger out-of-phase domain embedded into an in-phase domain. In reality an out-of-phase dimer (or out-of-phase domain) was never observed, not even after careful inspection of several dozens of images. So, one must and can safely conclude that the AM-conjecture does not apply. We also note, that our model [7] would predict an expectation frequency for the elementary excitation described above of about 10^{-9}, completely consistent with the data.

At this stage it should be sufficiently clear that in our opinion the rather mathematical model for the Ge(001) (2×1)-(1×1) phase transition, as proposed by Asada and Miura and supported by N. Azuma, lacks physical reality. Most importantly, they overlooked the fact that *the integrated intensity* $(1/2, 0)$-order diffraction peak and the dimer intensity is not just another interpretation, but instead contains hard factual structural information. This can actually be illustrated most clearly by calculating the full two-dimensional diffraction pattern from the image published on the right hand side of AM's Fig. 5 [11], even when we strongly feel that this image is unphysical. The diffraction

pattern has been obtained using the kinematic approximation:

$$I(\Delta k_\parallel) = \left[\sum_{\text{dimers}} \exp(i(\Delta k_{\parallel x} \cdot x_n + \Delta k_{\parallel y} \cdot y_n)) \right]^2 \Big/ N$$

in which $\Delta k_{\parallel x}$ and $\Delta k_{\parallel y}$ are the components of the wave vector change, parallel to the surface, along the axes parallel and perpendicular to the dimers, respectively, x_n and y_n the dimers' position coordinates and N is the number of dimers, being 1250 in this particular case, in an ideal single domain. The resulting profile of the $(1/2, 0)$-order peak is illustrated in Fig. 3. First we note that the fully integrated intensity of the profile shown in Fig. 3
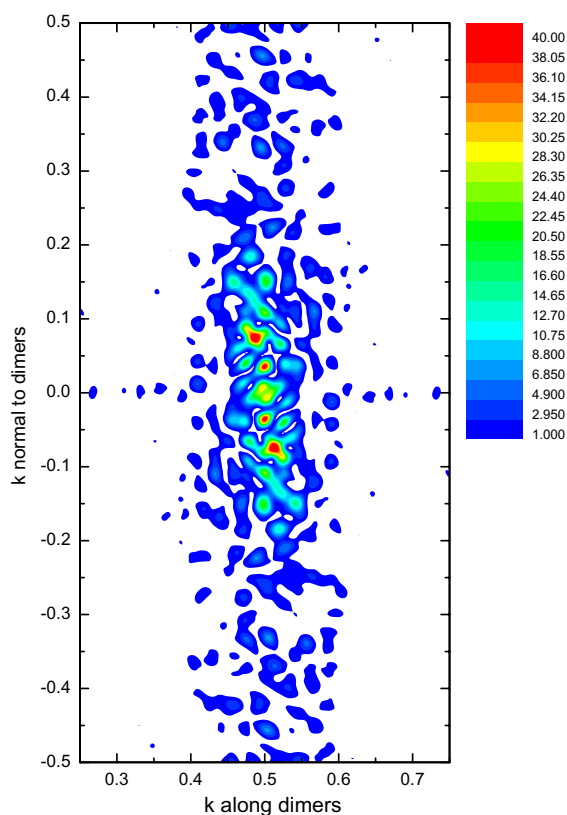

Fig. 3. Contour plot of the $(1/2, 0)$-order diffraction peak, calculated for the right hand side image of Fig. 5 in Ref. [11]. The wave vector changes parallel to the surface are given in units of π/λ.

adds up to 94%, i.e., very close to the dimer concentration of 91% in the real space, right hand side image of Fig. 5 of Ref. [11]. The extremely small mismatch is actually due to numerical integration errors related to the sharp diffraction features. We explicitly mention here that for diffraction from an ideal periodic array of dimers the intensity of the peak, integrated from $\pi/2$ to $3\pi/2$ along the dimers and from $-\pi$ to π perpendicular to the dimers, respectively, nicely adds up to exactly one as it should. Thus, also in this simulation example we obtain convincing evidence for the plain fact that the integrated peak intensity of the $(1/2, 0)$-order peak is directly related to the dimer concentration. It nicely demonstrates the power of diffraction approaches to obtain *quantitative* information on surface structure and composition.

At least as dramatic for the failure of AM's evaluation of the (2×1)-(1×1) phase transition is the obtained substantial and asymmetric broadening of the $(1/2, 0)$-order diffraction peak in the direction perpendicular to the dimers, i.e. along the dimer rows. For the given image the intensity at the exact Bragg position is even outnumbered heavily by more intense out-of-plane diffraction features. This type of asymmetric broadening has never been observed experimentally [7], neither qualitatively or quantitatively. We note in passing that a quantitative experimental evaluation of the dimer concentration can become cumbersome for very small dimer concentrations because of required background corrections. However, this only leads to small *absolute* errors in our data evaluation in Ref. [7].

We conclude that the model for the (2×1)-(1×1) phase transition proposed by Asada and Miura [11] lacks physical reality. It is inconsistent with literature-available quantitative data on the dimer concentration as a function of temperature. It does not clarify the physical nature of this high temperature phase transition. Their guessed numbers for both the dimer bond formation energy and the dimer–dimer interaction energy lack credibility and are at variance with the main body of existing literature. And, last but not least, any pertinent explanation of the nature of the (2×1)-(1×1) phase transition *must* incorporate very substantial dimer break up.

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