Reply to "Comment on 'Monotonically decreasing size distributions for one-dimensional Ga rows on Si(100)' "

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In this Reply, we provide a detailed analysis of experimental data for the nucleation of metal rows or islands during deposition of Ga on Si(100) quantifying the influence of defects. Contrasting the proposal of Kocán *et al.* [Phys. Rev. B **74**, 037401 (2006)], we find that this process is not dominated by heterogeneous nucleation at *C* defects. We also argue that such heterogeneous nucleation could not in itself be responsible for the unusual monotonically decreasing island size distributions observed in this system. In addition, we offer possible explanations for why behavior observed by Kocán *et al.* for In deposition on Si(100) appears to differ from that for Ga deposition.

Kocán *et al.*[1] propose that the single-atom-wide metal rows or islands that form during deposition of Ga on Si(100) nucleate almost exclusively at *C* defects. However, we show through additional analysis of experimental data that this is not the dominant nucleation process, contrasting the claim in Ref. [1]. Furthermore, we explain why the presence of such a heterogeneous nucleation pathway should *not* play a decisive role in producing the unusual monotonically decreasing island size distribution observed for this system by scanning tunneling microscopy (STM).[2] Instead, we argue that this unusual distribution, which was the focus of our previous study,[2] derives from restricted aggregation. We do, however, agree that nucleation at *C* defects can be significant in the Ga on Si(100) system, and discuss its effect on the estimation of terrace diffusion barriers.

For room temperature deposition in a single continuous dose at 10^{-3} ML/s for 2.5 min, our previous study reported the slow increase in mean island size up to $\langle s \rangle \approx 15$ atoms with increasing Ga coverage up to $\theta \approx 0.15$ ML.[2] This implies an island density of $N_{isl} = \theta/\langle s \rangle = 0.01$/site. We have noted that the defect density was always less that 0.01/site, and typically around 0.003/site, which immediately reveals that most nucleation occurs away from defects.

However, it is appropriate to provide a more definitive assessment of the issue of defect-mediated nucleation in the Ga on Si(100) system. Thus, we present a more detailed analysis of data from one experiment in which a series of incremental evaporations were carried out over a period of about 6 h, together with *in situ* scanning to study the nucleation of Ga rows. A significant buildup of *C* defects could occur over this prolonged period[3] (in contrast to that for usual continuous dose experiments), so we are deliberately considering a "worst case" scenario. The illustration of Ga row nucleation reported in Ref. [4] is from this run. For this particular sample, the initial defect density was substantially larger than typical. Specifically, over a 50×50 nm^2 area (corresponding to an area of about 8500 Si dimers), there were 172 triple missing dimers, 22 single missing dimers, and 52 *C*-type defects.

After the first evaporation stage (data acquired within 1 h of imaging the initial clean surface), of 12 nucleation events, 5 were away from any defect, 4 were at *C*-type defects, and 3 were at non-*C*-type defects. Figure 1 shows three of the nucleation events, where event (a) occurs at a *C*-type defect, whereas events (b) and (c) do not, even in the presence of
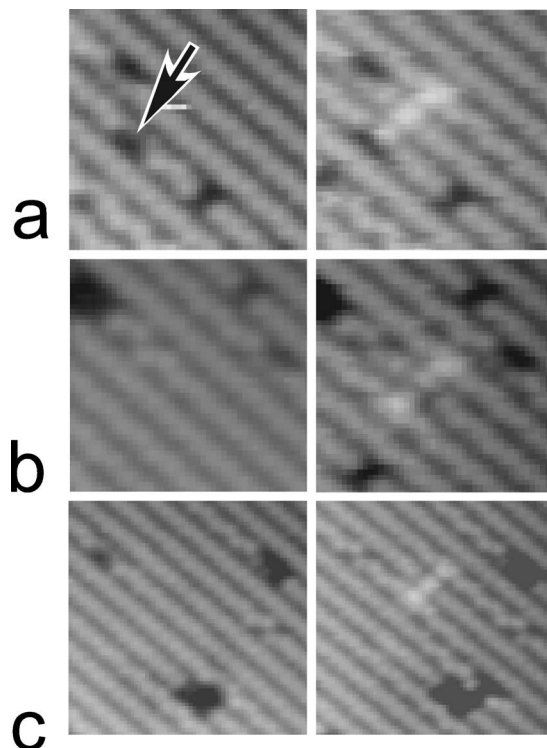

FIG. 1. Filled-state STM images of nucleation of Ga atomic rows on Si(001). These three pairs of images show the same area of the surface before (upper panels) and after (lower panels) the deposition of a small amount of Ga. Panels (a) show nucleation at a *C*-type defect, indicated by an arrow in the upper panel. Panels (b) and (c) show nucleation away from any surface defect. Panels (a) and (b) are 5×5 nm^2. Panels (c) are 8×8 nm^2.

C-type defects within a few nm of the nucleation site. For a total of 63 separate nucleation events tracked during the entire course of incremental evaporations, 21 occurred away from any defect, 26 occurred at *C*-type defects, and 16 occurred at non-type-*C* defects. This analysis reveals unequivocally that nucleation at *C* defects is significant, but not dominant, and also that nucleation at other defects can be significant.

We reiterate in the data reported in Ref. 2, five of six metal coverages were the results of single Ga depositions on bare Si(001), and only one coverage (0.09 ML) was a second evaporation. Therefore, the total density of *C*-type defects on the surface would be substantially less than the example given above.

It seems that behavior is different for the cited examples in Ref. 1 of In (and Ag or Pb) deposition on Si(100) where nucleation was observed to occur almost exclusively at *C* defects. Why? Two possibilities might be considered. First, it is difficult to rule out tip effects. For experiments with scanning during deposition, the tip might enhance adatom mobility, e.g., pushing homogeneously nucleated dimers to defect sites where binding is stronger, or causing their breakup (thus allowing reformation of islands at defects). In fact, in our own studies of In deposition on Si(100) with the scanning direction orthogonal to the metal rows (i.e., along the Si dimer rows), we find evidence suggesting that In adatoms can be pushed into "forbidden" positions in between two parallel metal rows separated by the minimum distance of $2a$ (a is the surface lattice constant).[5] To avoid these potential corrupting effects, we tried to avoid repeated scanning of the same sample area wherever possible in our Ga on Si(100) studies. Second, we claim that intrinsically different behavior occurs for In and Ga adatoms on Si(100). Specifically, we present evidence to indicate that Ga-Ga adatom binding is stronger than In-In binding. This would enhance the stability of homogeneously nucleated Ga islands relative to that of In islands. Certainly, if homogeneously nucleated islands can breakup, it becomes much more likely that islands are ultimately formed at the stronger defect binding sites.

Our evidence for the difference in binding for In and Ga comes from separate two-species deposition experiments in which we first deposit one element and then the other. When Ga is deposited first, the subsequently deposited In is found only at the end of Ga rows, as observed in earlier studies.[6] In contrast, when In is deposited first, the subsequently deposited Ga is found intermixed within the interior of the rows as well as at their ends. Both cases are shown in Fig. 2 to facilitate comparison. This comparison demonstrates that Ga is bound effectively irreversibly in Ga rows, whereas In can detach from In rows due to weaker adspecies binding. A similar asymmetry in binding is seen between In and Sn, where once again, In is less stable than Sn.[7] Finally, we remark that for Pb/Si(100), where nucleation is proposed to occur almost exclusively at *C* defects as for In/Si(100), detachment of Pb from the ends of atomic rows is also observed, indicative of weaker adatom binding.[8]

Next, we argue that the presence of heterogeneous nucleation in itself should not produce a monotonically decreasing island size distribution. For pure irreversible heterogeneous nucleation at defect sites, the island size distribution reflects
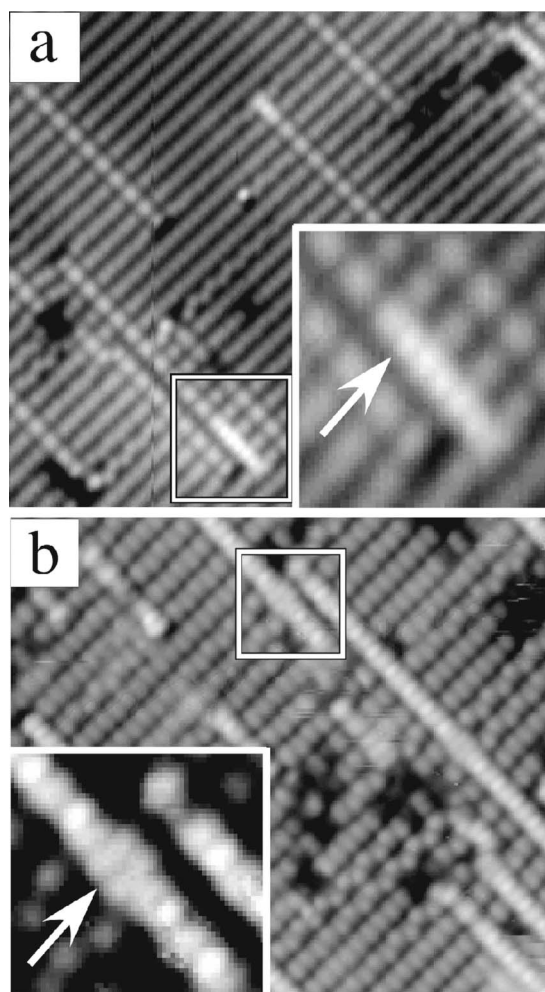

FIG. 2. Ga+In co-deposition studies comparing atomic row structure. (a) Deposition of In onto 0.09 ML Ga/Si(100): aggregation of In only at row ends. See Ref. 6. The image is 18.5 $\times 20$ nm^2 with a $\sim 4 \times 4$ nm^2 inset of the outlined small square region showing In at end of Ga row (indicated by arrow). (b) Deposition of Ga onto 0.07 ML In/Si(100): intermixed row structures. The image is 14.5 $\times 16$ nm^2 with a $\sim 3 \times 3$ nm^2 inset of the outlined small square region showing a Ga dimer within a In row (indicated by arrow).

the area distribution of "capture zones" for individual defects.[9,10] For typical "random" distributions of defects, such area distributions are monomodal, which should thus result in a peaked monomodal island size distribution. Consequently, consistent with the conclusions of Ref. 2, we maintain that restricted aggregation is the primary factor leading to this monomodal distribution. From this perspective, our previous simulations did incorporate the most essential features needed to generate this unusual distribution, the focus of our previous study.

Finally, we discuss the determination of surface diffusion barriers from modeling of STM data for island densities and distributions. Kocán *et al.*[1] correctly noted that incorporation of defect-mediated nucleation into the modeling would modify estimates of these barriers. In fact, previous DFT estimates[11] of diffusion barriers for Al on Si(100), and initial results from our *ab initio* quantum chemistry analysis (to-

gether with the assumption that barriers for Ga are no higher than for Al) suggest significantly lower values than our estimates in Ref. 2. If true, the apparent reduced effective rates for diffusion and aggregation (despite such low "bare" diffusion barriers) needed to produce the observed island density could result from a number of factors.

To explore this issue, we first considered a modification of the atomistic model in Ref. 2 introducing *C*-type defects with a density of 0.003/site. In the metal on Si(100) systems of interest here, once a metal atom attaches adjacent to a *C* defect, one of the two adjacent aggregation sites is blocked and the metal row grows away from the defect in only one direction. Simulations of a corresponding model produce a somewhat increased island density relative to the case with no defects, if one keeps the same diffusion barriers of 0.4 eV (and 0.8 eV) along (orthogonal to) metal rows as in Ref. 2. This is in part due to nucleation occurring at most defects. Also restricted aggregation with islands at *C* defects (since aggregation occurs only at one end) helps to maintain a high adatom density which facilitates homogeneous nucleation. As a result, somewhat lower values of diffusion barriers are required to match the experimental island density. However, decreasing the barriers to, e.g., 0.35 eV (and 0.7 eV) already produces a significantly lower island density than in experiment.

To further reduce effective diffusion and aggregation rates (and boost the island density) while maintaining low bare diffusion barriers, one could also consider the role of other defects. The presence of missing dimer type defects, which do not trap metal atoms as efficiently as *C* defects, likely blocks direct diffusion of Ga especially in the fast direction along the metal rows, and thus reduces the effective diffusivity again facilitating island nucleation. We have also included such "inert" defects in a simple way in our modeling, but found that they do not have much effect on the island density (for our prescription). Other refinements of the model should be explored to determine if experimental observations can be recovered with lower bare diffusion barriers. One could introduce reversible capture of adatoms at *C* defects, as this would reduce the fraction of such defects populated by islands (bringing model predictions more in line with experiment).

In summary, we show that *C* defects do not play a dominant role in nucleation of Ga rows or islands on Si(100), and that the presence of heterogeneous nucleation is not responsible for the unusual monotonically decreasing island size distribution. However, refined modeling incorporating defects is likely needed to obtain reliable estimates of diffusion barriers.

[1] P. Kocán, P. Sobotík, and I. Ošt'ádal, preceding Comment, Phys. Rev. B **74**, 037401 (2006).

[2] M. A. Albao, M. M. R. Evans, J. Nogami, D. Zorn, M. S. Gordon, and J. W. Evans, Phys. Rev. B **72**, 035426 (2005).

[3] M. Nishizawa, T. Yasuda, S. Yamasaki, K. Miki, M. Shinohara, N. Kamakura, Y. Kimura, and M. Niwano, Phys. Rev. B **65**, 161302(R) (2002).

[4] J. Nogami and M. M. R. Evans, Surf. Rev. Lett. **6**, 1067 (1999).

[5] See EPAPS Document No. E-PRBMDO-74-081628 for a video (QT format) of atomic motion of In and Ga on Si(001), including some tip induced effects. This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).

[6] M. M. R. Evans and J. Nogami, Phys. Rev. B **59**, 7644 (1999).

[7] J. Nogami, in *Atomic and Molecular Wires*, edited by C. Joachim and S. Roth (Kluwer, Dordrecht, 1997), pp. 11–21.

[8] L. Juré, L. Magaud, J.-M. Gómez-Rodríguez, P. Mallet, and J.-Y. Veuillen, Phys. Rev. B **61**, 16902 (2000).

[9] P. A. Mulheran and J. A. Blackman, Philos. Mag. Lett. **72**, 55 (1995).

[10] Capture zones (CZ) are constructed by a Voronoi-type tessellation of the surface with one zone or cell per defect. CZ shapes should reflect any anisotropy in surface diffusion. Strictly, the island size distribution is obtained by convoluting the CZ area distribution with a Poisson distribution to reflect fluctuations in the number of atoms deposited within each CZ, but this would preserve a monomodal shape.

[11] G. Brocks, P. J. Kelly, and R. Car, Phys. Rev. Lett. **70**, 2786 (1993).