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Discussion

Comment on "Surface morphology and electronic structure of Ge/Si(1 1 1) 7×7 system" [A. Lobo et al., Appl. Surf. Sci. 173 (2001) 270]

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In a recent paper, Lobo et al. [1] reported on a study of Ge nanostructures grown on Si(1 1 1)7×7 and characterized by atomic force microscopy (AFM) and X-ray photoemission spectroscopy (XPS).

The purpose of the present comment is to question the core results presented in the article by Lobo et al. [1], in particular the results obtained by AFM. Indeed one of us (FR) has studied at length the same system and found results that are in sharp contrast with what is reported in [1].

Firstly, it may appear to the reader that the AFM imaging was performed on the same samples used previously for XPS measurements, ex situ, *after* the spectra were acquired: this aspect is not discussed clearly or even addressed in the text; in fact the description of the experimental procedure is a bit ambiguous concerning this point. It is well known in fact that, depending on the intensity of the incoming beam and the overall exposure, surface techniques such as electron spectroscopies or electron diffraction (XPS, electron energy loss spectroscopy (EELS), Auger electron spectroscopy (AES), low energy electron diffraction (LEED), etc.) may be very damaging for the substrates being studied [2,3], due to the strong beam–surface interaction (which often lasts a relatively long time because of the need for good statistical sampling).

Secondly, the formation of trenches around the islands is not at all apparent from the AFM images presented by Lobo et al., and besides, it was already shown for the same system with very clear scanning tunneling microscopy (STM) imaging performed in situ right after deposition by Boscherini et al. [4]. We would like to remark that in Fig. 4(a) presented in [1], perhaps a plot profile could have helped in assessing the depth and extension of the trench, which in our opinion is not very well visible from the image.

Furthermore, the phenomenon of Ge–Si intermixing in the growth of Ge on Si surfaces has by now been reported by several authors. Consequently, the issue to be addressed presently is not whether there is any intermixing, but its quantitative determination. This answer was answered partially by Boscherini et al. [5], who were able to determine the intermixing of the Ge–Si alloy for the whole interface, since the

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measurements were performed by X-ray absorption fine structure (XAFS) at the Ge K-edge. To our knowledge, it has not been possible so far to determine the composition of a single nanocrystal of Ge as deposited on Si(1 1 1). In the paper by Lobo et al., there is only some vague speculation about intermixing (namely on pages 275–276), but even a crude quantitative estimate of the effect is missing completely.

What is also lacking here is a comparison of AFM and XPS results, which could lead to a quantitative determination of Ge–Si intermixing. In fact, recently Capellini et al. [6] have shown that it is possible to obtain the relative composition of Ge islands grown on Si(0 0 1) by comparing AFM and XPS data. In principle, this type of analysis could also be applied to the data reported by Lobo et al., even though they only report results for two samples (besides the sample grown at room temperature which does not exhibit islanding); this could have led at least to a crude quantitative estimate of the alloying effect for their samples grown at 450 and 550 °C. In any case, we agree with Lobo et al. that spectromicroscopy of individual islands could help to solve the problem of determining the composition of single nanocrystals.

Further still, it is not at all clear to us what is meant in this context by columnar growth of Ge, or the authors' reference to a double-column structure (Fig. 2(c) in [1]). It is apparent that the islands being imaged in [1] have undergone a certain degree of ripening; perhaps also here a plot profile taken across the image could have been useful for the reader. This effect (ripening) has also been reported before [4,7] for Ge on Si(1 1 1) by using STM in situ, leading to the conclusion that the islands evolve into an atoll-like shape, with the formation of a central hole which can be 1.5 nm deep. Perhaps due to the oxidation of the samples or to possible damage caused by exposure to X-rays, we maintain that this effect is not clearly visible in the images reported in [1]. In order to clarify this point, in Fig. 1, we report two images of islands which have undergone ripening; in Fig. 1(a), the trench around the island is clearly visible, whereas in Fig. 1(b) also the central hole can be seen: the depth can be inferred from the line scans taken across the images. Besides, even though Lobo et al. claim to have used all due precautions in ascertaining that the imaging was not influenced by the tip, Fig. 2(b) from [1] seems to have been affected by a tip artifact: namely the image appears to have been created by a so-called "*double*" tip. This

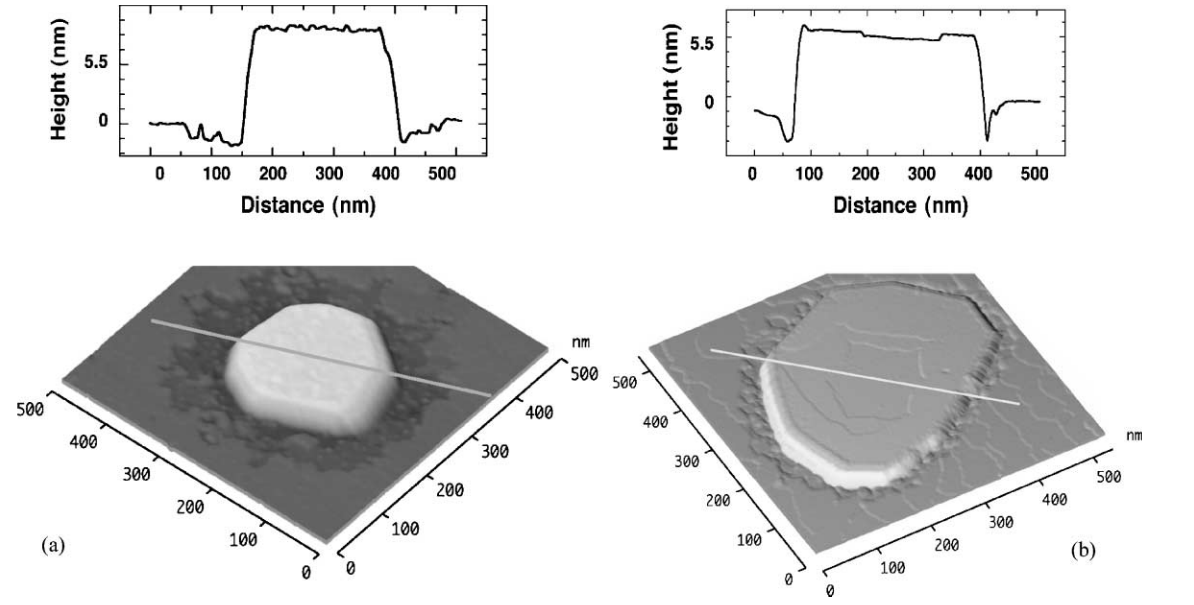


Fig. 1. Ge/Si(1 1 1): (a) $527 \times 527\,nm^2$ STM image of an island at the first stage of ripening (3.5 nm of Ge/Si(1 1 1) at $T = 500\,^{\circ}C$)—island height: 10 nm. (b) $527 \times 527\,nm^2$ AFM image in the gradient mode of an island transformed in atoll at the final stage (2 nm of Ge/Si(1 1 1) at $T = 500\,^{\circ}C$)—island height: 8 nm.

observation stems from the presence on the image of a very high density of ''*doubled*'' or ''*twin*'' features.

Finally, and most importantly, we would like to point out here that the statistical analysis reported in the paper by Lobo et al. is somewhat suspect, in particular because both the distributions they report (for island height and width) seem ''delta-like'', i.e. with hardly any ''statistical spread'' (to our knowledge their statistical spread is about ± 2 nm). This is very unlikely to occur in a process of self-assembled growth of nanostructures like the one we are dealing with here, which normally implies relatively poor controllability of dimensions (it would be perhaps normal for lithographic patterning)—if one is analyzing the data correctly.

Our experimental conditions [8,9], specified below, are very similar to those reported in Ref. [1]; all our experiments were performed using STM in situ, immediately after deposition; the XAFS measurements were taken successively, ex situ using synchrotron radiation. The details of our experimental procedure have been described elsewhere [4,5,7,8].

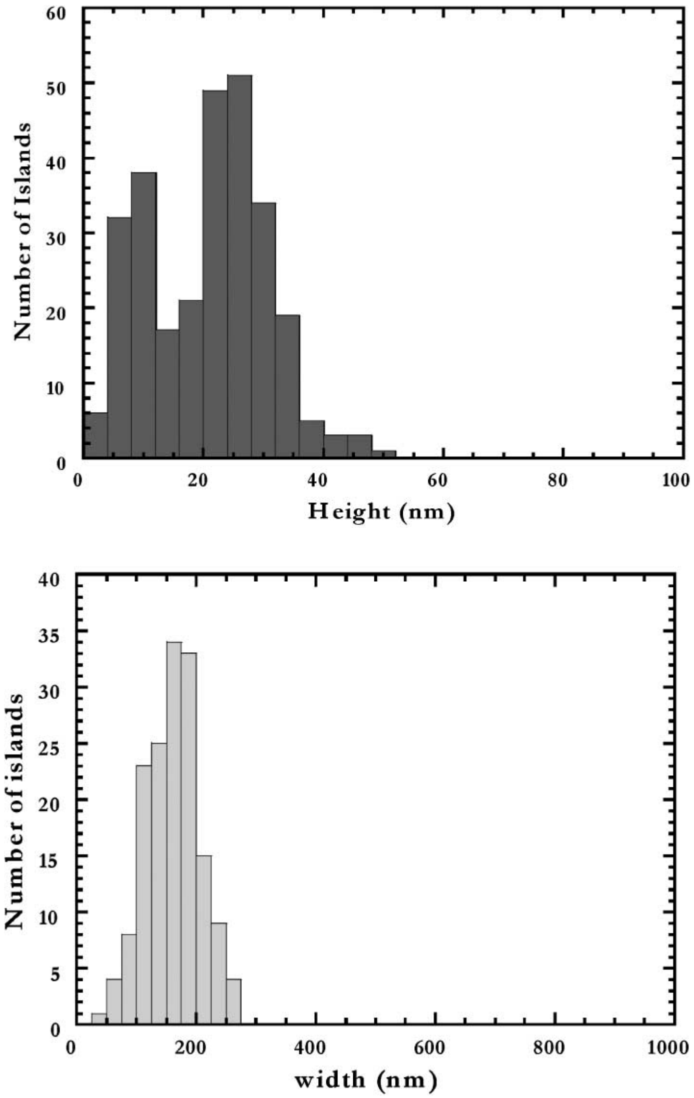


Fig. 2. Histograms of the islands height (left) and width (right) for a sample grown at 450 °C and with a total deposition of 2.5 nm Ge.

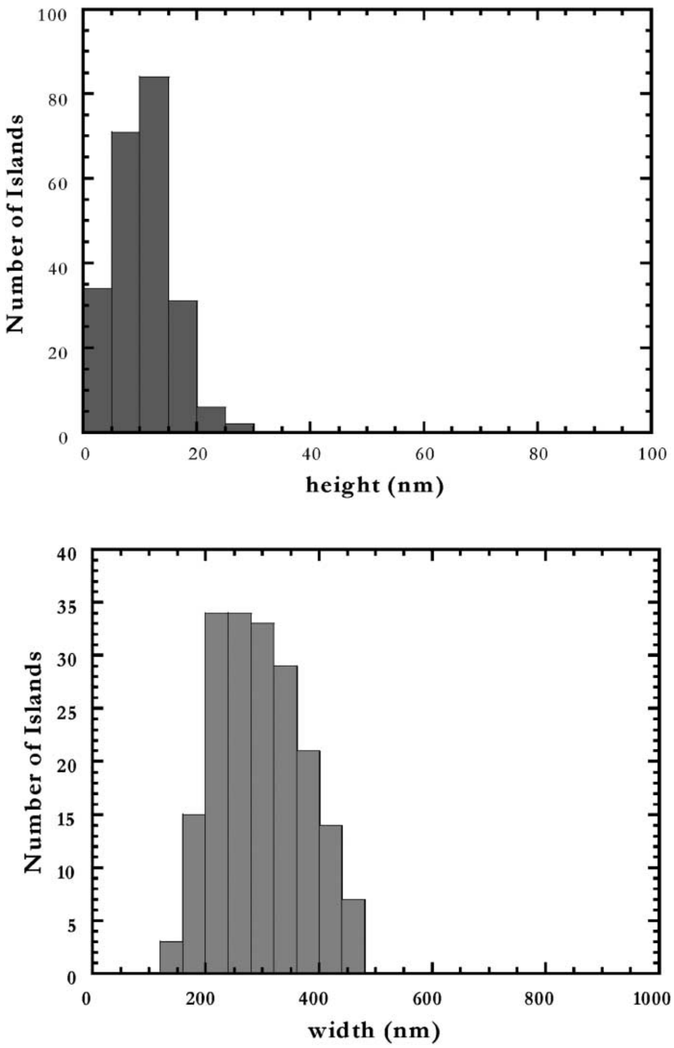


Fig. 3. Histograms of the islands height (left) and width (right) for a sample grown at 550 °C and with a total deposition of 2.0 nm Ge.

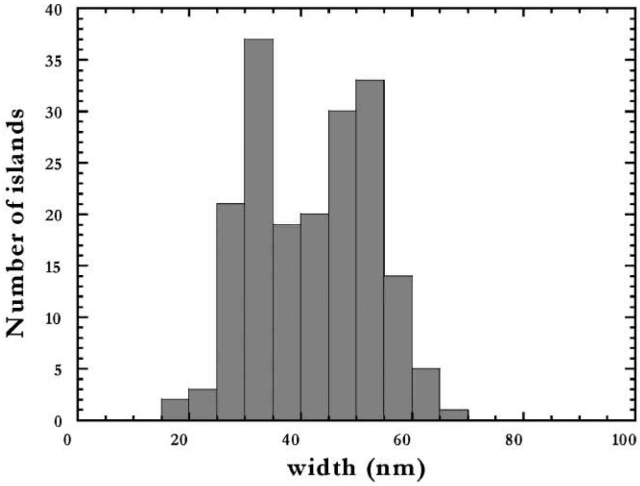
In Fig. 2, we report the histograms of the island height and width, respectively, for a sample with a total coverage of 2.5 nm Ge grown at $T = 450\,^{\circ}\mathrm{C}$. In these growth conditions, we find that the distribution of the islands' height is bimodal, whereas the width distribution is monomodal.

Fig. 3 shows the histograms of the island height and width, respectively, for a sample with a total coverage of 2.0 nm Ge grown at $T = 550\,^{\circ}\mathrm{C}$. Apparently, in these growth conditions both the distribution of the islands' height and width are monomodal.

Finally, in Fig. 4, we report the histograms of the island height and width, respectively, for a sample with a total coverage of 1.5 nm Ge grown at $T = 500\,^{\circ}\mathrm{C}$. Again in these conditions the distribution of the islands' height is bimodal, whereas the width distribution is monomodal. The different types of height distributions can be in principle ascribed to kinetic effects.

In sharp contrast to our findings, Lobo et al. report two *trimodal* distributions (shown in Fig. 3 from [1]) for the distribution of island height and width for their sample, which was grown at 450 °C and with a total coverage of 2.0 nm Ge.

Besides the different types of distributions we obtain for the width and height (in three different



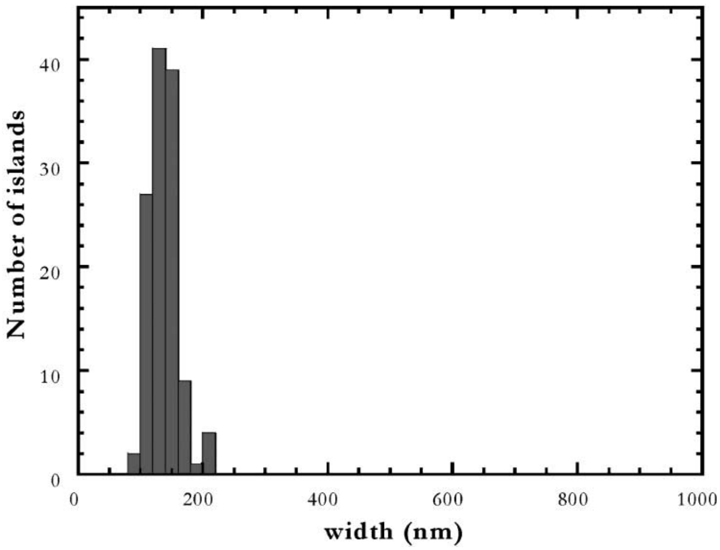


Fig. 4. Histograms of the islands height (left) and width (right) for a sample grown at 500 °C and with a total deposition of 1.5 nm Ge.

growth conditions), we would like to point out that all our histograms clearly show that the statistical distributions are significantly more *disperse* than those reported by Lobo et al. Remarkably, our results are qualitatively consistent with those reported recently by Capellini et al. [10]. The simultaneous presence of different types of islands on the surface is consistent with a recent theoretical model [11].

In conclusion, we believe that the discrepancies described above with respect to the results reported in Ref. [1] may have been caused mainly by two unorthodox approaches in the paper we are commenting on, namely that:

1. The data analysis may not have been performed appropriately, possibly due to ''software-induced'' artifacts, since it leads to statistical distributions which are suspected to be too narrow.
2. It appears from their article that Lobo et al. may have used the same samples for the XPS experiments *first* and subsequently for AFM analysis. This would basically lead to two further conclusions:

2.1. The samples were completely oxidized when studied ex situ by AFM; recently Kamins et al. [12] reported a comprehensive study of Ge deposited on Si(0 0 1) in which a clear imaging of the trenches around the islands (later reported clearly by other authors [13,14]) was not possible because of the oxidation of the samples, which were also measured ex situ by AFM in air.
2.2. If they did use the same samples for XPS and AFM as one could infer from their article, Lobo et al. did not discuss or take into account the likely damage induced by extended exposure of their samples to X-rays during XPS measurements, and which can be quite significant, as reported in the literature [2,3]. In principle, even the double-column islands they observe and which, to our knowledge, were never reported before, may have been induced by damaging from exposure to photons, unless they are to be attributed to tip artifacts.

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