# Initial growth of silver on Ge(111) studied by scanning tunneling microscopy

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Scanning tunneling microscopy (STM) has been used to study the Ge(111) surface after submonolayer depositions of Ag. At the lowest coverages a $(4\times4)$ reconstruction, with small insets of a $(3\times1)$ edge structure, is observed. Based on the STM images we propose a mixed Ag and Ge adatom structure for the $(4\times4)$ reconstruction, in which the adatoms have local $(1\times1)$ and $(2\times2)$ arrangements corresponding to a Ag coverage of $\frac{6}{16}$ monolayers. The $(3\times1)$ structure appears to have a configuration similar to the Si(111)/Ag-$(3\times1)$ reconstruction, although in this case it has a much more limited extension, restricted to a few unit cells in the near vicinity of step edges and phase boundaries. At higher coverages, after the completion of a full $(4\times4)/(3\times1)$ surface, a $(\sqrt{3}\times\sqrt{3})R30°$ structure appears showing STM images similar to those previously published for the Si(111)/Ag system.

## I. INTRODUCTION

The initial growth of metals on semiconductor surfaces has been the subject of extensive research in recent years.[1] These efforts have been motivated from both technological and scientific viewpoints, and the importance of understanding the influence of the detailed atomic structure upon surface and interface properties such as Schottky-barrier formation, surface states, etc. has been emphasized.[2,3] The application of scanning tunneling microscopy (STM) has been of great importance in this research and a larger number of systems, e.g., several involving group III and IV element metals on silicon, can now be considered as more or less well known.[4] This is, however, not the case for the growth of noble metals on silicon and germanium. In particular, the atomic arrangement of the Si(111)/Ag$(\sqrt{3}\times\sqrt{3})R30°$ reconstruction as seen in low-energy electron diffraction (LEED) is still controversial despite the application of almost every surface-sensitive technique available, including several STM investigations.[5–9] Silver also induces a $(\sqrt{3}\times\sqrt{3})R30°$ reconstruction on Ge(111). The origin of this reconstruction has been assumed to be similar to the case of Si, but this has recently been questioned in a x-ray diffraction (XRD) study which predicted rather different atomic geometries between these surfaces.[10] At lower Ag coverages $(3\times1)$ and $(4\times4)$ superstructures have been reported for the Si and Ge(111) surfaces, respectively.[11] The Si(111)/Ag-$(3\times1)$ structure has recently been imaged with high resolution with STM by Wan, Lin, and Nogami,[12] who proposed a structural model closely related to the honeycomb-chain-trimer (HCT) model[13] suggested for the Si(111)/Ag-$(\sqrt{3}\times\sqrt{3})R30°$ reconstruction, but no model has yet been proposed for the $(4\times4)$, or according to Ref. 14 a $(4\times2)$, Ge(111)/Ag surface. However, knowledge of these low-coverage phases can be assumed to provide valuable insight to the complex $(\sqrt{3}\times\sqrt{3})R30°$ reconstructions, and in a wider perspective, a better understanding of the interaction between noble-metal atoms and semiconductor surfaces.

In this paper we report STM observations of the initial growth of Ag on Ge(111) at elevated temperatures. At the lowest coverages, we find a $(4\times4)$ reconstruction, with small insets of a $(3\times1)$ structure, growing from the step edges of the $c(2\times8)$ reconstructed Ge surface. The interpretation of the images is not straightforward, but they lead us to propose an adatom model for the $(4\times4)$ reconstruction with both Ge and Ag atoms on the surface. Images of the $(3\times1)$ and $(\sqrt{3}\times\sqrt{3})R30°$ structures are similar to the case of Si(111)/Ag, suggesting a close relationship between these systems.

## II. EXPERIMENTAL DETAILS

The experiments were performed in an ultrahigh-vacuum system with a base pressure of approximately $1\times10^{-10}$ Torr in which a commercial STM (Ref. 15) is incorporated. Cycles of sputtering (1-keV Ar ions) and annealing ($\approx650$ °C) of the Ga-doped (0.004–0.01 Ω cm) Ge(111) sample resulted in a sharp $c(2\times8)$ LEED pattern, and subsequent STM images revealed a well-ordered surface. Ag was evaporated from a tungsten filament onto the surface which was held at approximately 400 °C, the temperature measured with a pyrometer. For increasing Ag coverage the Ge(111) surface showed a sequence of $c(2\times8)\rightarrow(4\times4)\rightarrow(\sqrt{3}\times\sqrt{3})R30°$ LEED patterns, in agreement with previous reports.[16] The STM images were acquired with electrochemically etched tungsten tips, and all images presented in this study could be reproduced with several different tips and tunneling conditions.

## III. RESULTS AND DISCUSSION

Figure 1 provides an overview empty-state image (positive sample voltage) of the surface after evaporation leading to a mixed $c(2\times8)/(4\times4)$ LEED pattern. The two different surface structures are observed on different terraces separated by step heights of approximately 1.5 Å or half a Ge(111) double layer. The appearance of the $c(2\times8)$ reconstruction is similar to the case of the clean Ge(111) surface.[17] There is some disorder present in

 

FIG. 1. A 1320×550 Å$^2$ STM image of the Ge(111) surface at an Ag coverage of about 0.1 ML. The sample bias was 2.0 V at a tunneling current of 0.5 nA.

these areas, mainly in the form of small patches of $(2\times2)$ units, which usually are located in the vicinity of the steps or at the domain boundaries between different regions of the threefold-symmetric $c(2\times8)$ structure. However, the disorder is comparable to the clean Ge(111)-$c(2\times8)$ surface, which is known to have an easily disturbed structure with a higher percentage $(2\times2)$ than $c(2\times4)$, the subunits of the full $c(2\times8)$ unit cell.[18] In general, no traces of silver were observed on the $c(2\times8)$ terraces. The threefold-symmetric pattern on the remaining terraces corresponds to the $(4\times4)$ reconstruction, but there also exist streaks of a twofold-symmetric structure. This latter structure, which could be deduced from the images to have a $(3\times1)$ periodicity, is located at the domain boundaries between the $(4\times4)$ and $c(2\times8)$ areas and between different phases of the $(4\times4)$ structure. This edge structure is clearly a minority effect, not more than three unit cells in the direction of the longer periodicity was observed, and it could not be detected by LEED. We also note that none of the observations in this study confirms the report of a $(4\times2)$ superstructure by Suliga and Henzler.[14]

Images recorded as a function of the Ag coverage showed that the $(4\times4)$ phase grows continuously from the step edges of the $c(2\times8)$ reconstructed Ge surface until the $c(2\times8)$ terraces are totally consumed. This is illustrated in Fig. 2 where the (a) initial and (b) almost completed growth of the $(4\times4)$ phase is shown. We did not observe any coexistence of the $c(2\times8)$ and the $(\sqrt{3}\times\sqrt{3})R30°$ reconstructions, where the latter corresponds to a slightly higher Ag coverage than the $(4\times4)$ structure. The saturation coverages of these superstructures have been estimated from Auger electron spectroscopy (AES) measurements to 0.27 and 0.85 monolayers[19] [(ML) 1ML$=7.2\times10^{14}$ atoms per cm$^2$, the density of atoms in the ideal Ge(111) surface plane]. After the completion of the $(4\times4)$ surface, the $(\sqrt{3}\times\sqrt{3})R30°$ structure started to develop in a similar fashion from the step edges of the surface. These observations seem consistent with the initial stages of the Stransky-Krastanov growth mechanism believed to be valid for this system,[20] but we did not examine the case of higher-coverage depositions. The continuous evolution of the superstructures from the step edges is also well in agreement with the predictions of Suliga and Henzler,[14] who, using LEED and AES, observed a preferred adsorption of Ag at step sites and a strongly increased diffusity of Ag along steps on this surface.

The simultaneously acquired filled- and empty-state images in Fig. 3 show that each $(4\times4)$ unit cell consists of two triangular subunits. The apparent heights of these subunits show a reversal with the tunneling voltage, with one side being higher for positive sample bias and the other being higher for negative bias; see Figs. 3(a) and 3(b). For a sample-to-tip bias of $\pm2.5$ V the height difference is approximately 0.5 and 0.3 Å, respectively. Furthermore, the structure within these subunits, at the two sides and at the different bias conditions, are quite different. In the filled-state image of Fig. 3(a), the apparent higher subunit contains six protrusions with the periodicity of the Ge substrate, whereas the lower halves show three broader features. However, in the empty-state image of Fig. 3(b), there are three protrusions in the middle of the higher subunit, whereas the lower half, which showed six well-defined protrusions in the filled-state image, now have a deep depression in the middle. In order to establish the lateral registration of the resolved features in the $(4\times4)$ unit cells, the registry between adjacent $(4\times4)$ and $c(2\times8)$ domains was carefully examined. It could thereby be shown that the six maxi-

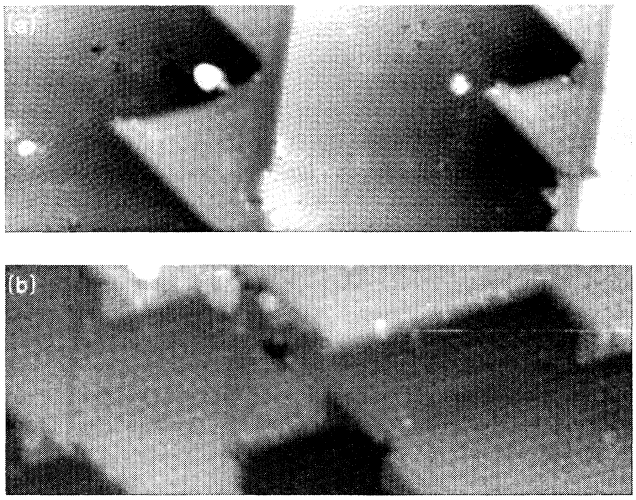


FIG. 2. (a) Tunneling image showing the very initial formation of the $(4\times4)$ structure which is seen at the step edges of the substrate. The $c(2\times8)$ reconstruction is preserved without any sign of Ag atoms. (b) Image of the almost completed $(4\times4)$ phase with only small fractions of the Ge terraces left. No $(\sqrt{3}\times\sqrt{3})R30°$ structure is present.

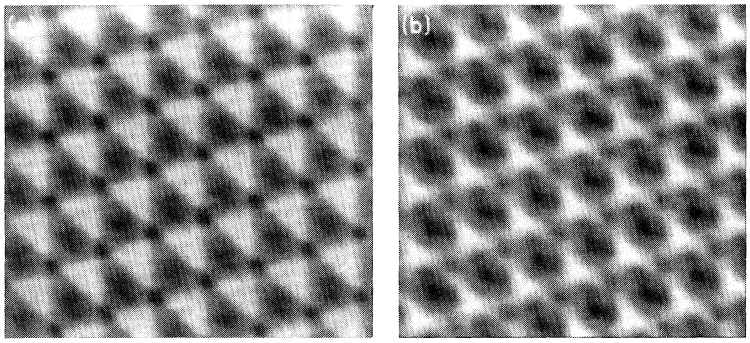


FIG. 3. (a) Filled- and (b) empty-state images of the same Ge(111)/Ag(4×4) unit cells acquired with $V_T=-1.5$ and $+2.0$ V at $I_T=0.5$ nA.

ma in the higher subunit of the filled state image correspond to top sites of the underlying Ge(111) lattice. This identification relies on an assignment of the adatoms in the $c(2\times8)$ structure to $T_4$ positions, the threefold-coordinated hollow sites directly over second-layer substrate atoms.[17]

A tempting explanation for the difference in apparent height of the subunits would be the presence of both Ge and Ag atoms in the topmost layer, one kind in each subunit. In that case it can be assumed to be a difference in the density of occupied and unoccupied states over the different atoms, connected with a transfer of charge from one kind of atom to the other. This would then make one kind of atom appear higher at positive bias and the other kind appear higher at negative bias similar to what has been found in several previous STM studies, e.g., in the case of the Al-induced $(\sqrt{3}\times\sqrt{3})R30°$ reconstruction on Si(111),[21] where the Al or the Si adatoms appear higher depending on the polarity of the tunneling voltage.

A weakness of the STM technique is the inability to perform chemical identification, and it is thus not possible to determine the atomic species of the (4×4) reconstruction in a straightforward manner. However, some insight into the problem might be gained from the expected direction of charge transfer between the atoms. Photoelectron spectroscopy data on low-coverage phases of Ag on Ge(111), and Si(111), have revealed surface-shifted Ge $3d$,[22] and in particular Si $2p$,[23] core-level components to higher binding energies. Disregarding possible final-state effects, this would indicate a charge transfer from the Ge, or Si, atoms to the Ag atoms. As a consequence, one might assume that the brighter atoms in the empty-state images of the (4×4) reconstruction are Ge and that the brighter atoms in the filled-state images are Ag. Such a correspondence between the Ag atoms and the maxima in the filled-state images would also be in agreement with what previously has been suggested for the Si(111)/Ag surface.[9,12]

A direct interpretation of the images, assuming that the protrusions correspond to the atomic positions and that the chemical identities differ between the different subunits in the way discussed above, leads to the model for the (4×4) reconstruction presented in Fig. 4. Here, every second triangular subunit of the (4×4) reconstruction is assumed to house six Ag atoms in a (1×1) arrangement occupying top sites. In this way, each Ag atom eliminates one dangling bond of the substrate. In the other half, there are three Ge adatoms in $T_4$ positions binding with nine of the remaining ten dangling bonds, and thus leaving one rest atom in the middle.

This model reflects the STM images reasonably well. If one assumes a charge transfer from the Ge to the Ag atoms, one would expect to find maxima in the empty-state image over the Ge unit with three adatoms and over the Ag atoms in the filled-state image. In the filled-state image, all Ag atoms are resolved at their expected position according to the model. This also holds for the Ge adatoms, which manifest themselves as the slightly broader features in the lower height subunit. In the empty-state image, there is no real resolution over the Ag subunit but just a deep depression in the middle indicating a low density of unoccupied states in the region. In the Ge subunit, there are three protrusions which can be attributed to the adatoms. These protrusions are, however, slightly centered as compared to what is expected from the model. We attribute this discrepancy to the presence of the rest atom in the middle of the subunit,

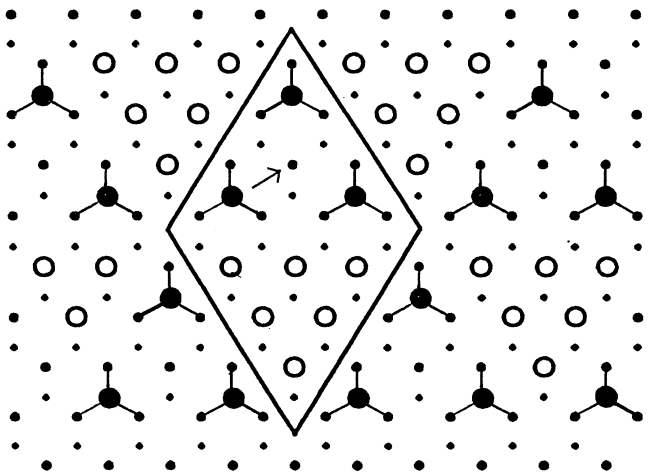

FIG. 4. Proposed geometrical model for the Ge(111)/Ag(4×4) reconstruction consisting of Ge and Ag adatoms in local (2×2) and (1×1) arrangements. Large open and filled circles denote Ag and Ge adatoms, respectively. The rest atom is indicated by an arrow.

which is likely to peak the state density so as to cause a slight asymmetry in the image.

Although somewhat speculative, the model is appealing for at least two reasons. First, the associated Ag coverage of $\frac{6}{16}$ ML is reasonably close to previous estimates of approximately 0.27 ML,[17] and second, in the light of recent results on the Si(111)/Ag($\sqrt{3}\times\sqrt{3}$)$R$30° structure,[9,12,24,25] the Ag atoms can be expected to remain on the surface rather than being incorporated in underlying layers for these low-coverage phases. This, of course, assumes that the Si(111)/Ag and Ge(111)/Ag systems resemble each other in this respect, even though it should be noted that several earlier models for the Si(111)Ag($\sqrt{3}\times\sqrt{3}$)$R$30° reconstruction have Si in the topmost layer,[26] and that Ge segregation to the surface is found in the case of growth of thicker Ag films on Ge(111).[27]

The measured step height between the $c(2\times8)$ and $(4\times4)$ domains was only slightly bias dependent and typically around 1.5 Å. Since the local geometry and chemical composition differ between these domains, this step height contains both geometric and electronic contributions and does not provide any conclusive test on the validity of the model. It has indeed been pointed out that the corrugation on semiconductor surfaces as measured by STM is dominated by the electronic contribution rather than geometrical height differences.[28] Anyway, a rough estimate of the pure geometrical contribution can be of interest as a comparison. Adopting the adatom height from the case of the Si(111)(7×7) system of 1.2 Å,[29] and taking the height of the top-bonded Ag atom as the sum of the Ge and Ag tetrahedral covalent radii 2.74 Å,[30] a value close to the measured 1.5 Å is actually obtained.

The $(3\times1)$ structure is shown on the right-hand side of the dual polarity images of Fig. 5, which show the (a) filled and (b) empty state acquired at tunneling biases of −1.5 and 2.0 V, respectively. The registration between the filled and empty states is indicated by the outlined $(3\times1)$ unit cell which is located at the same position in both images. In the filled-state image the structure appears as double rows separated by $3a$ running along $[1\bar{1}0]$-type directions, $a$ being the surface lattice parameter. There is also some striation along the rows with a periodicity of $1a$. The image seems to well resemble the filled-state image acquired on the Si(111)/Ag-$(3\times1)$ reconstruction by Wan, Lin, and Nogami.[12] One exception is that the periodicity here actually seems to be $(3\times1)$ and not $(6\times1)$ as deduced from a significant difference in the striation of adjacent-row pairs in the filled-state images on the Si surface. [The Si(111)/Ag-$(3\times1)$ reconstruction converts upon cooling to room temperature to a $(6\times1)$ structure, but it is still usually referred to as a $(3\times1)$ reconstruction[11].] The contrast in the empty-state image is not as good and it is harder to recognize the resolved features, but a careful examination of the image in Fig. 5(b) and other empty-state images acquired on this structure reveals that also for this polarity there is a strong similarity with the Si(111)/Ag system.[12] As in that case, the empty-state images consist of bright stripes running in $[1\bar{1}0]$-type directions separated by $3a$, of which the lateral position correspond to the center of the rows in the filled-state image. Between these stripes there are two rows of protrusions with a periodicity of $1a$ along the rows and with protrusions at each side of the stripes pointing in a non-high-symmetry direction.

These results imply that the atomic geometries of the Ge(111)/Ag- and Si(111)/Ag-$(3\times1)$ structures are similar. For the latter case, Wan, Lin, and Nogami[12] proposed a structural model closely related to the HCT model recently suggested for the Si(111)/Ag-($\sqrt{3}\times\sqrt{3}$)$R$30° reconstruction.[13] They based their model on the correlation between the atom positions of coexisting $(3\times1)$, $(\sqrt{3}\times\sqrt{3})$, and $(7\times7)$ geometries, the height difference between these reconstructions, and the bias dependency of the STM images as well as an assumption that the HCT model is valid for the $(\sqrt{3}\times\sqrt{3})$ structure. In the model, $\frac{2}{3}$ ML of Si atoms form zigzag chains separated by $3a$ and running in $[1\bar{1}0]$-type directions on the bulk terminated Si(111) surface. In this way, there is one dangling bond on each Si atom along the chains and one row of atoms with dangling bonds between the chains. The Ag layer is then formed by bonding $\frac{2}{3}$ ML of Ag atoms to the dangling bonds of the chain atoms in such a way that the Ag atoms on each chain approximately point towards the Ag atoms on adjacent chains. In the filled-state STM images, the protrusions are thought to correspond to the positions of the Ag atoms, whereas the correspondence of the features in the empty-state images is less clear. The present data do not allow us to clarify the validity of this model for the Ge(111)/Ag system, but there are some concerns of the consistency with the model proposed here for the $(4\times4)$ structure which are worthwhile to consider. First it is noted that the $(4\times4)$ and $(3\times1)$ structures are approximately level in height, which would be expect-

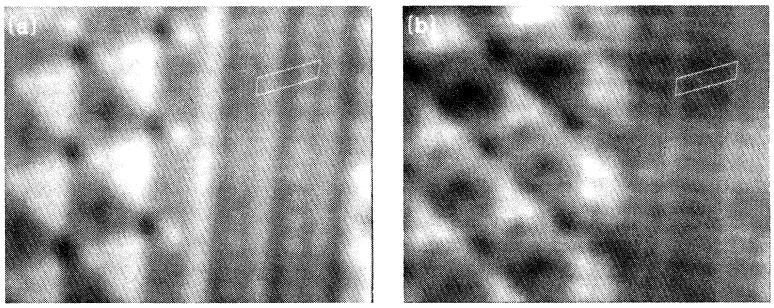


FIG. 5. (a) Filled- and (b) empty-state image (−1.5 and +2.0 V sample bias) showing the $(3\times1)$ reconstruction.

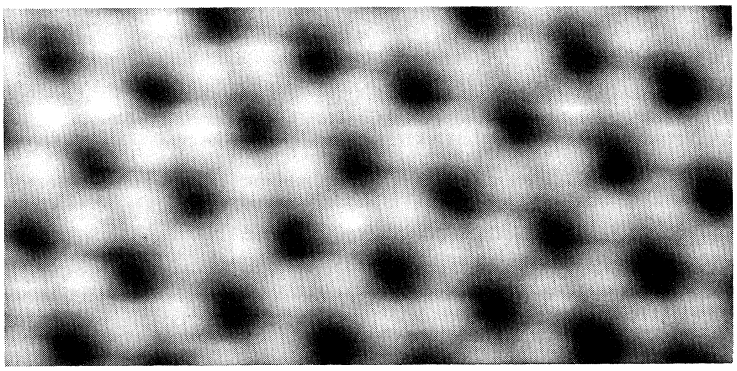

FIG. 6. Empty-state image of the $(\sqrt{3}\times\sqrt{3})R30°$ reconstruction. The sample bias was 0.5 V at a tunneling current of 0.1 nA.

ed from strict geometrical considerations if both models are valid. Second, both models are based on the same bias dependency of the Ag atoms, i.e., a correspondence to a high density of unoccupied states. A final consideration would concern the registration between the phases. The protrusions of the filled-state image of the Si(111)Ag-$(3\times1)$ reconstruction was found to approximately correspond to $T_4$ sites,[12] and it is thus of interest to see if this is consistent with the sites found here for the $(4\times4)$ structure. However, limitations in the resolution prevent us from unambiguously performing this identification.

From the evolution of the different structures during the growth process it was concluded that the surface energy of the $(3\times1)$ phase probably is higher than the $(7\times7)$ or $(\sqrt{3}\times\sqrt{3})$ phases on the Si(111)/Ag surface.[12] This seems to be even more pronounced on the Ge(111)/Ag surface, regarding the surface energy of $(3\times1)$ as compared to $c(2\times8)$, $(4\times4)$, and $(\sqrt{3}\times\sqrt{3})$, where the $(3\times1)$ structure is never observed over any extended areas.

We now turn to the $(\sqrt{3}\times\sqrt{3})R30°$ reconstruction, which is obtained at slightly higher Ag coverages and has been found to be saturated at about 0.85 ML.[19] From, e.g., photoelectron spectroscopy[31] and LEED $I/V$ (Ref. 32) measurements, it has been assumed that this reconstruction has a similar atomic configuration to Si(111)/Ag-$(\sqrt{3}\times\sqrt{3})R30°$. On the other hand, in a recent XRD study Dornisch *et al.*[10] found similarities to the $(\sqrt{3}\times\sqrt{3})R30°$ reconstruction of Si(111)/Au rather than that of Si(111)/Ag, and it is thus of interest to see how the STM images can distinguish between these cases. This distinction can be accommodated by a comparison with previous STM results on the Si(111)/Ag- and Si(111)/Au-$(\sqrt{3}\times\sqrt{3})R30°$ reconstructions, which are rather different. The sixfold honeycomb structure in the STM image of Fig. 6 is in close conformity with the observations for the Si(111)/Ag system,[5–9] but does not resemble the results on Si(111)/Au,[33] which instead have shown a centered hexagonal array of dots, each possibly corresponding to a Au adatom trimer, and the idea of a similar atomic configuration to that in the Si(111)/Ag case is strongly supported.

It was generally more difficult to achieve stable tunneling conditions on this reconstruction, and the best images were obtained with the rather low tunneling bias of $\pm0.5$ V. At this bias, empty- and filled-state images were similar, and we could not see any asymmetry of the kind discussed in the recent paper by Wan, Lin, and Nogami[9] for the case of Si(111)/Ag at tunneling voltages $|V_T|>0.8$ V. However, the low contrast in the images acquired at higher voltages prevents any confirmation if this also holds for the Ge(111)/Ag system, and we have to conclude that the observations in this study do not allow us to further distinguish between the various models proposed for the $(\sqrt{3}\times\sqrt{3})R30°$ reconstruction.[26]

## IV. CONCLUSION

We have reported the application of STM to studying the growth and structure of the low-coverage phases of the Ge(111)/Ag system. The images show a well-ordered surface with a continuous growth of Ag induced reconstructions from the step edges. Initially, a $(4\times4)$ reconstruction with insets of a $(3\times1)$ edge structure starts to develop on the $c(2\times8)$ reconstructed Ge(111) surface. The complexity and strong bias dependency of the images makes the analysis nontrivial, but we speculate over a possible model for the $(4\times4)$ phase, which is in qualitative agreement with the bias dependency, the measured registration, and previous estimates of the related Ag coverage. The $(3\times1)$ structure was compared with recent STM results on Si(111)/Ag-$(3\times1)$ and it can be believed to have a similar atomic geometry. Finally, it was concluded that the $(\sqrt{3}\times\sqrt{3})R30°$ reconstruction, which starts to develop for higher Ag coverages on the completed $(4\times4)/(3\times1)$ surface, also is likely to be similar to the one on Si(111)/Ag.

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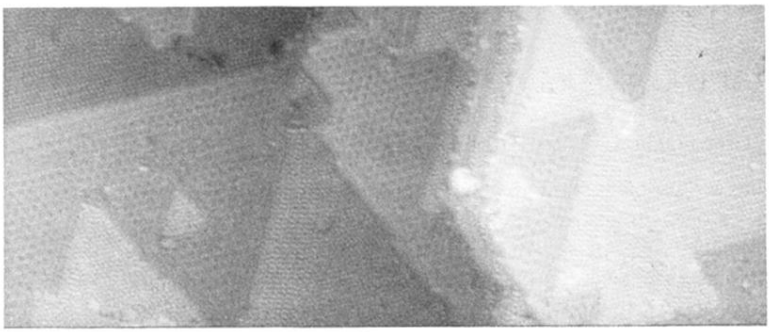

FIG. 1. A 1320×550 Å$^2$ STM image of the Ge(111) surface at an Ag coverage of about 0.1 ML. The sample bias was 2.0 V at a tunneling current of 0.5 nA.

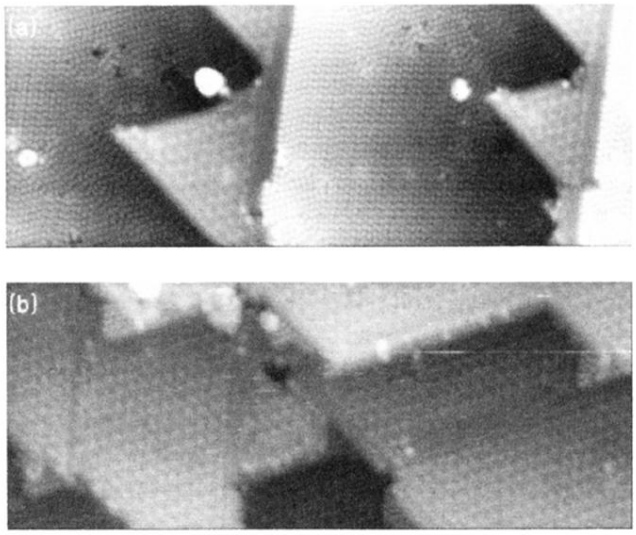


FIG. 2. (a) Tunneling image showing the very initial formation of the $(4\times4)$ structure which is seen at the step edges of the substrate. The $c(2\times8)$ reconstruction is preserved without any sign of Ag atoms. (b) Image of the almost completed $(4\times4)$ phase with only small fractions of the Ge terraces left. No $(\sqrt{3}\times\sqrt{3})R\,30°$ structure is present.

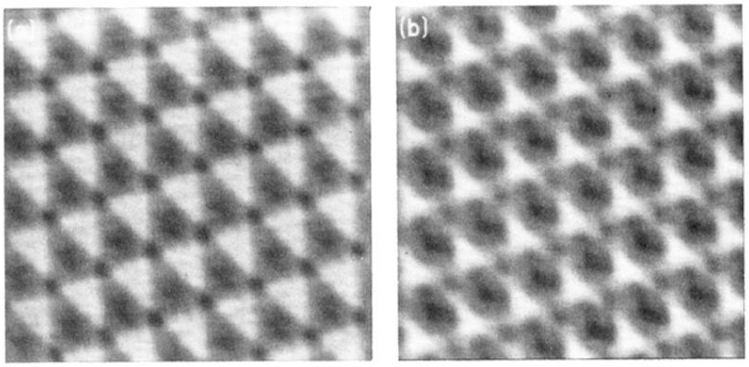


FIG. 3. (a) Filled- and (b) empty-state images of the same Ge(111)/Ag(4×4) unit cells acquired with $V_T = -1.5$ and $+2.0$ V at $I_T = 0.5$ nA.

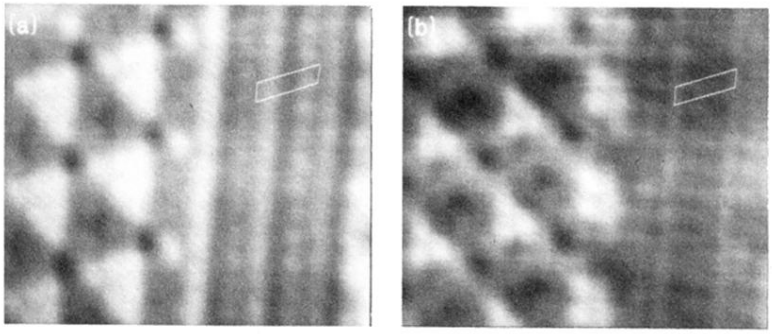


FIG. 5. (a) Filled- and (b) empty-state image ($-1.5$ and $+2.0$ V sample bias) showing the $(3\times1)$ reconstruction.

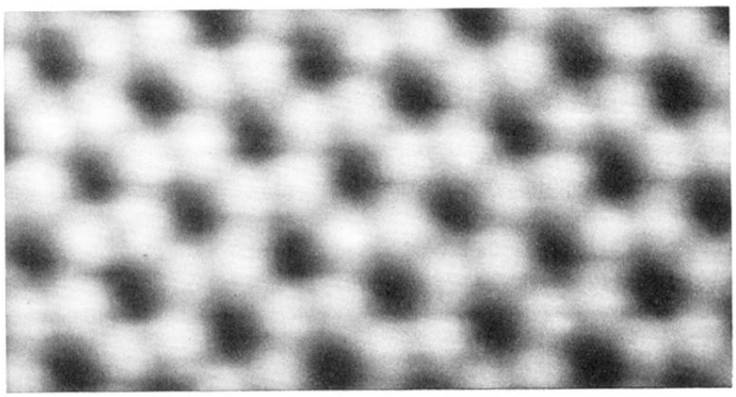

FIG. 6. Empty-state image of the $(\sqrt{3}\times\sqrt{3})R30°$ reconstruction. The sample bias was 0.5 V at a tunneling current of 0.1 nA.