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Charge transfer and asymmetry on Ge(111)-$c(2\times8)$ studied by scanning tunneling microscopy

E. S. Hirschorn, D. S. Lin, F. M. Leibsle, A. Samsavar,* and T.-C. Chiang

Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801 and Materials Research Laboratory, University of Illinois at Urbana-Champaign, 104 South Goodwin Avenue, Urbana, Illinois 61801

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Scanning-tunneling-microscopy images of annealed Ge(111) show large $c(2\times8)$ domains with protrusions that match closely the arrangement of adatom and rest-atom dangling bonds in the simple adatom model. The unit cell, however, appears asymmetric or "buckled"; namely, the two adatoms or the two rest atoms within the unit cell show significant differences in apparent height. Both the adatom and rest-atom dangling bonds can be simultaneously observed with either bias polarity, indicating that both are partially filled. These results will be discussed in relation to the proposed charge transfer between the adatoms and rest atoms.

The Si(111)-(7×7) surface appears to be nearly fully understood, yet there remain unresolved issues for the closely related Ge(111)-$c(2\times8)$ surface. The geometrical structure of the Ge(111)-$c(2\times8)$ surface is generally considered to be optimally described by a simple adatom model in which the (1×1) substrate is decorated with germanium adatoms in alternating (2×2) and $c(2\times4)$ subunits. In this model, each $c(2\times8)$ primitive unit cell of eight (1×1) sites contains two adatoms and two rest atoms, totaling four dangling bonds. Verification of this model has been provided by studies using x-ray diffraction,[1] scanning tunneling microscopy (STM),[2] and medium-energy ion scattering.[3] In the STM study of Becker *et al.*, a pattern of protrusions was observed which matches the arrangement of either the rest atoms or the adatoms, depending of the sample-to-tip bias polarity, *but not both simultaneously.*[2] This observation, combined with information available from a model calculation,[2,4] lead to the following suggestions: (i) The simple adatom model is valid. (ii) There is a complete electron transfer from the adatoms to the rest atoms resulting in a fully occupied rest-atom dangling-bond state and a completely empty adatom dangling-bond state. A surface electronic band at a binding energy of about 0.8 eV observed by ultraviolet photoemission was ascribed to the occupied rest-atom dangling-bond state in analogy to the Si(111)-(7×7) case.[2] Two questions remain concerning the above model. The first question arose from a more recent photoemission study revealing the existence of another occupied surface-state band with a dangling-bond character,[5] which could not fit into the model. The second question had to do with the high Coulomb energy needed for a complete charge transfer from the adatoms to the rest atoms. A fully ionic surface appears to be highly unlikely.[6]

In the work reported here, we examined the Ge(111)-$c(2\times8)$ surface with STM under various bias conditions and found features not reported before, which could provide an explanation in connection with the above-mentioned questions. Our results confirm that the simple adatom model is valid except that the $c(2\times8)$ unit cell appears "buckled" or asymmetric; namely, the two adatoms or the two rest atoms in a unit cell show significant differences in apparent height depending on the imaging conditions. This observation is somewhat similar to the familiar case of a difference in height observed between the two halves of the (7×7) unit cell of Si(111),[2,7,8] although a stacking fault is not involved in the present case. With either a positive or a negative sample bias, both the adatom and rest-atom dangling bonds can be simultaneously observed. Therefore, both kinds of dangling bonds are partially filled and the surface is not fully ionic.

The STM measurements were performed in a vacuum chamber with a base pressure of 6×10^{-11} Torr. A gold-plated tungsten tip was used as the probe. Ge(111) samples were oriented with the Laue technique and polished to a mirror finish. The samples were etched in a CP-4 solution just prior to chamber insertion. Cleaning of the Ge(111) surfaces was performed by several cycles of 1-keV argon ion bombardment while the sample was kept at 900 °C, followed by annealing at the same temperature for another 5 min. This treatment resulted in a sharp $c(2\times8)$ reflection high-energy-electron-diffraction pattern with low background. The STM images were taken after a waiting period of at least 6 h after annealing to allow the sample to cool down to near room temperature. Large scale STM images revealed large flat areas ($\simeq500\times500$ Å^2) of single-domain $c(2\times8)$ interspersed with small patches of (2×2) units, usually located near the boundary between two different single-domain $c(2\times8)$ regions (the surface has threefold symmetry and all three possible domain orientations were observed). A typical scan also showed a small amount ($<2\%$) of unidentified debris. We saw no sign of extended regions of $c(2\times4)$ unit cells.

The simple adatom model is illustrated in Fig. 1, where the adatoms are shown occupying the T_4 sites which are on top of second layer atoms. The other two possible domain orientations, related by a rotation of 120° and 240°, are not shown. In this model, the patterns formed by the adatoms and the rest atoms in the surface plane are the same, and the two patterns are related by a spatial offset. These patterns and the spatial offset were observed by Becker *et al.* using a dual-polarity imaging technique,[2] in which applying a positive (negative) sample bias resulted in the observation of the adatom (rest atom) pattern

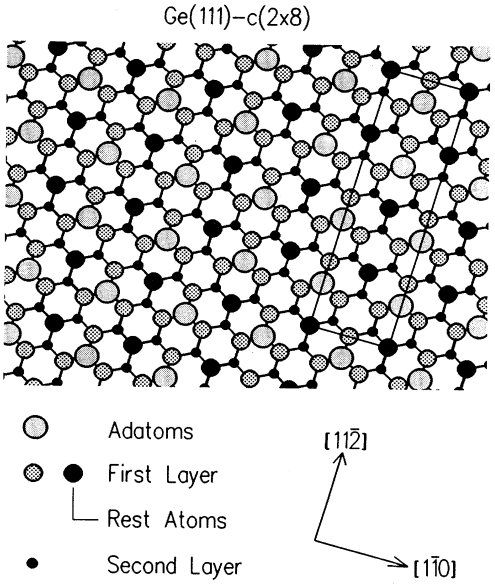

FIG. 1. Top view of an atomic model for the Ge(111)-$c(2\times8)$ surface. The first (top) layer of the diamond structure consists of two kinds of atoms: the ones with a dangling bond are the rest atoms, and the others are bonded to the adatoms and have no dangling bonds. On top of this first layer, the surface is decorated by adatoms as indicated; each adatom has a dangling bond. The second layer below the surface is also shown. The rectangle indicates a (2×8) conventional unit cell having an area twice as large as the $c(2\times8)$ primitive unit cell.

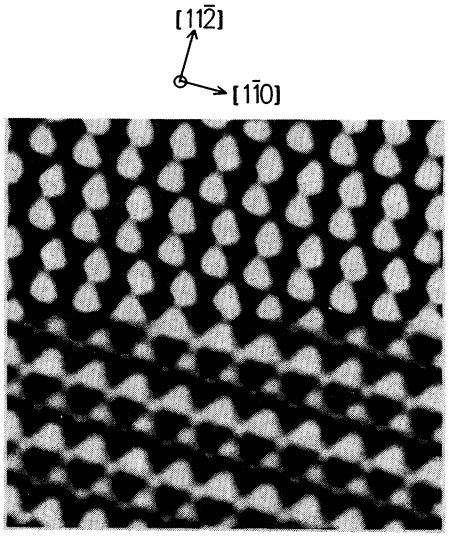

FIG. 2. A grey-scale STM image of Ge(111)-$c(2\times8)$ showing the partial distribution of occupied states. The bottom section was taken with a sample bias of -0.7 V, and the top section was taken with a sample bias of -1.2 V. The two sections were obtained during a single uninterrupted scan. The tick marks on the two sides indicate the position of bias voltage switching.

only. The adatom and rest-atom assignment was based on a calculation of the electronic properties of a related, hypothetical Si(111)-(2×2) surface which exhibited similar local structures for the dangling bonds. This calculation showed that the electron of the adatom dangling bond was transferred to the rest-atom dangling bond resulting in a filled rest-atom dangling bond and an empty adatom dangling bond.[4] A positive (negative) sample bias used in the STM will sense the distribution of the unoccupied (occupied) states only; thus, the observation of Becker *et al.* indicated a complete charge transfer in agreement with this model calculation.

In our study, we employed a multiple-voltage imaging technique similar to the technique of Becker *et al.* to retain spatial registry information for images taken with different bias voltages. This technique is illustrated by the grey-scale STM image in Fig. 2, in which protrusions are represented by white areas. The lower section of this image was taken with a sample bias voltage of -0.7 V and the upper section was taken with a sample bias voltage of -1.2 V during a single uninterrupted raster scan. The tick marks on the two sides of the image indicate the position of sample bias switching. In our experiment, the sample bias voltage was typically switched more than once during a single raster scan, and the starting and ending voltages were often chosen to be the same for verification of reproducibility. Figure 2 was cut out from a larger scan in which the reproducibility was verified.

The upper section of Fig. 2 looks very similar to the negative sample bias image of Becker *et al.*[2] Based on their assignment, the protrusions should correspond to the rest atoms, and the pattern does match the rest-atom arrangement seen in Fig. 1. The lower section of Fig. 2 is considerably more detailed. By following the transition between top and bottom sections we see that the rest-atom dangling bonds remain the dominant features in the lower section; however, the alternating rest-atom rows along the [1$\bar{1}$0] direction are no longer equally bright, suggesting a significant asymmetry between the two neighboring rest atoms along the [11$\bar{2}$] direction. Furthermore, additional secondary maxima are seen, which correspond closely to the locations of the adatom dangling bonds seen in Fig. 1. Again, the two neighboring adatoms along the [11$\bar{2}$] direction show a significant difference in apparent height. It is interesting to note that the rest-atom features in Fig. 2 exhibit a noncircular shape which was repeatedly observed with several different tips. It is likely that the shape has to do with the detailed spatial distribution of all of the electronic states involved in the tunneling process.[9]

Figure 3 illustrates the main results of this work. Figure 3(a) is a piece cut out from the bottom section of Fig. 2. Figure 3(b) is a piece, with the same area, cut out from the top section of Fig. 2; the grey scale has been adjusted in this case to emphasize the locations of dangling bonds. By design, the two pieces are related by a translation via a surface lattice vector to maintain the spatial registry. In each picture, a conventional unit cell, having an area twice as large as the $c(2\times8)$ unit cell, is drawn as a guide to the eye. Figure 3(c) is obtained from Fig. 3(a) by subtracting a constant intensity. Here, half of the rest atoms and all of the adatoms are no longer visible. This shows clearly that the two neighboring rest atoms along the [11$\bar{2}$] direction are not at the same apparent height (referred to as buckling). This buckling may reflect an asymmetric

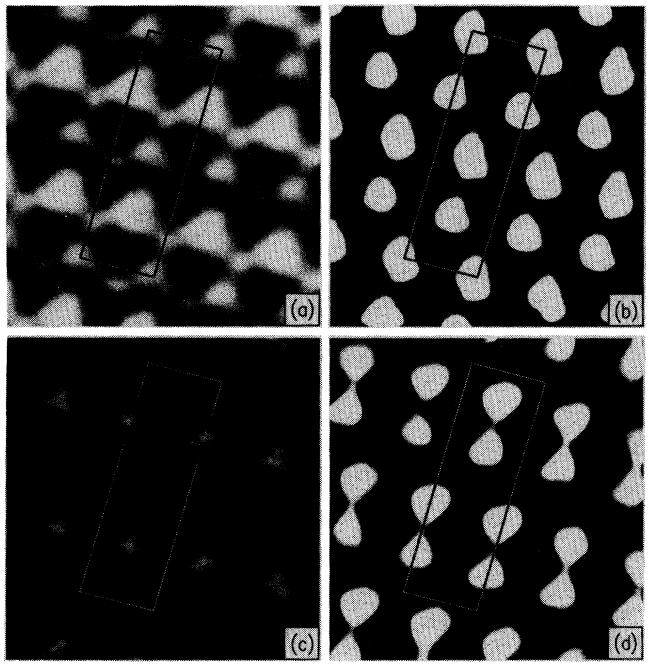

FIG. 3. Spatially-registered grey-scale STM images of Ge(111)-$c(2\times8)$. The four images (a)–(d) correspond to sample bias voltages of -0.7. -1.2, -0.7, and $+1.5$ V, respectively. (a) and (c) represent the same data but with different grey scales related by a constant intensity offset. The rectangles indicate the same conventional unit cell shown in Fig. 1. The images taken with a positive (negative) sample bias show the partial distribution of the unoccupied (occupied) states.

electronic-state density distribution, a geometric buckling, or both. Figure 3(d) is an image obtained with a sample bias of $+1.5$ V, constructed in the same manner as discussed above to maintain the spatial registry. Here, the protrusions clearly exhibit the same pattern as that seen in Fig. 3(b) except for an offset. Comparing these pictures with the model in Fig. 1 shows that the protrusions in Fig. 3(d) correspond to the adatoms.

The results of our observation can be summarized as follows. The STM images show that all of the observed protrusions correspond to either the adatoms or the rest atoms. The rest atoms are the dominant features in the images taken with a negative-sample bias voltage. The adatom contribution becomes more noticeable at a smaller absolute value of the negative bias as illustrated by comparing Figs. 3(a) and 3(b). As the sample bias polarity is switched to positive, the adatom dangling bonds become the dominant features seen, as illustrated by Fig. 3(d).

As discussed earlier,[2] the STM images of semiconductor surfaces mainly reflect the spatial distribution of the occupied and unoccupied electronic states. Previous angle-resolved photoemission studies of the Ge(111)-$c(2\times8)$ surface showed the presence of two occupied surface states (S1 and S2) with a dangling bond character and an apparent (1×1) periodicity.[5] Both states show considerable band dispersion; the top of the S1 (S2) band is at about 0.3 (0.8) eV below the Fermi level. The S2 state has been thought to correspond to the occupied rest-atom dangling bond, in analogy to the Si(111)-(7×7) case.[2,5,8] However, our image taken with a -0.7-V sample bias shows both the rest atoms and the adatoms as seen in Fig. 3(a), even though the S2 state cannot contribute to the image. A natural interpretation is that the occupied S1 state has a spatial distribution covering both the adatom and rest-atom sites, and therefore both sites are observed by STM simultaneously. As the bias voltage is made more negative, both S1 and S2 are contributing to the image, and it is likely that the rest-atom origin of the S2 state leads to the dominant appearance of the rest-atom features in the image. Note that two completely occupied surface bands (S1 and S2) with (1×1) periodicity would imply a total of four surface electrons per (1×1) site, while there are just four electrons derived from the four dangling bonds in a $c(2\times8)$ unit cell, or $\frac{1}{2}$ electron per (1×1) site. This apparent discrepancy in electron count can be simply explained by noting that the S1 and S2 bands can involve other valence electrons in addition to the dangling-bond electrons. In fact, significant portions of these bands can be surface resonances in that they overlap in energy with the bulk bands.[5]

In view of the findings reported here, the model calculation of the hypothetical Si(111)-(2×2) mentioned above cannot be applied quantitatively to the case of Ge(111)-$c(2\times8)$. However, the direction of charge transfer predicted by this model is likely to be correct. Our experimental results show the dominance of the rest atom and adatom features in typical STM images taken with a negative and positive bias, respectively, in agreement with the concept of a partial electron transfer from the adatom to the rest atom. An important point that should go into any comparison with theoretical calculations is the buckling observed here. This buckling may reflect an asymmetric distribution of the surface electronic-state density in addition to any possible geometric height differences. Thus, some charge transfer between the two inequivalent adatoms (rest atoms) in a unit cell may also occur.

In summary, STM results on Ge(111)-$c(2\times8)$ are reported. With spatially-registered images taken under various bias conditions, we see both adatom and rest-atom patterns in agreement with a buckled adatom model. There is a partial electron transfer from the adatom to the rest atom, but the surface is definitely not fully ionic as previously suggested.

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*Present address: IBM, T. J. Watson Research Center, Yorktown Heights, NY 10598.

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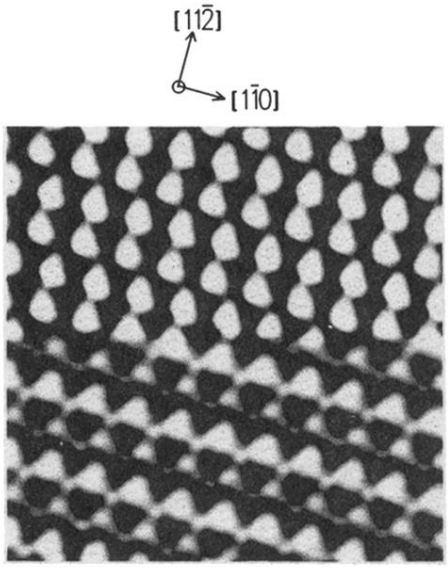
[9]All of the electronic states within the tunneling voltage range could contribute to the image, although the dangling bonds are the dominant ones in the present case. See Ref. 8 for a demonstration of an energy-resolved imaging technique.



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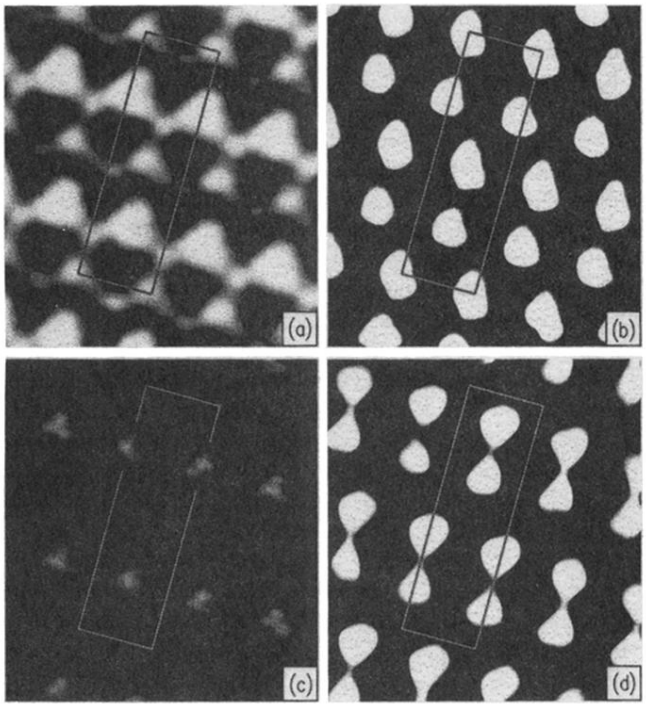

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