

## Structure determination of the Ge(111)- $c(2\times 8)$ surface by medium-energy ion scattering

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The Ge(111)- $c(2\times 8)$  and the Si(111)- $(7\times 7)$  reconstructions are directly compared by medium-energy ion scattering. The  $c(2\times 8)$  surface is shown to induce considerably less atomic displacements than the  $(7\times 7)$  structure. The data are in good agreement with a simple adatom model for the  $c(2\times 8)$  reconstructed surface.

Since the first observation of the  $c(2\times 8)$  reconstruction of a clean Ge(111) surface by low-energy electron diffraction (LEED) (Ref. 1) many structure studies of this surface have been performed.<sup>2</sup> However, the atomic arrangement of the reconstructed surface remains controversial.<sup>3,4</sup>

Recent experiments revealed an intriguing relation between the reconstructions of (111) surfaces of group-IV semiconductors. A scanning tunneling microscopy (STM) study<sup>5</sup> showed that on a laser-annealed Si(111) surface  $(2\times 2)$  and  $c(4\times 2)$  structures coexist. After a partial thermal anneal,  $(5\times 5)$ ,  $(7\times 7)$ , and  $(9\times 9)$  ordered areas were found on this surface. In electron-diffraction studies of Sn deposited on Ge(111) (Ref. 6) and of Ge-Si(111) epitaxial heterostructures,<sup>7-12</sup> transitions between  $c(2\times 8)$ ,  $(7\times 7)$ , and  $(5\times 5)$  reconstructions were observed. There is experimental evidence<sup>9-12</sup> that the observed periodic structures are stabilized by lattice-mismatch-induced strains, as was suggested by Phillips.<sup>13</sup> The existence of a class of related reconstructions of Si and Ge(111) surfaces renewed the interest in the Ge(111)- $c(2\times 8)$  structure. It initiated the formulation of unified models<sup>3</sup> and a search for common structural characteristics<sup>10,14</sup> of the  $c(2\times 8)$  and  $(7\times 7)$  ordered surfaces. In this Rapid Communication, we describe the results of a structure study of Ge(111)- $c(2\times 8)$  by medium-energy ion scattering. The Ge(111)- $c(2\times 8)$  data are compared with the backscattered ion yield from a Si(111)- $(7\times 7)$  surface and with Monte Carlo simulations for various structure models for the  $c(2\times 8)$  reconstruction.

The medium-energy ion-scattering technique is described in Ref. 15. The Si(111)- $(7\times 7)$  reconstruction has been studied previously by this technique.<sup>16</sup>

Structural information about the atomic geometry at the surface is obtained by the use of shadowing and blocking effects. An energetic ion beam is aligned with a low-index crystallographic direction of the substrate. Since only the first atom in each row is fully exposed to the beam, backscattering occurs mainly in the surface region; atoms further along the row are shadowed. Static and dynamic displacements of the atoms reduce the shadowing effect, leading to a nonzero backscattering probability for

deeper-lying atoms. On their outgoing trajectories, backscattered ions are blocked by (near-)surface atoms in certain directions, giving rise to blocking minima in the detected yield.

Static displacements of atoms from bulklike positions are caused by surface reconstructions and strain fields. As a result, the yield of backscattered ions increases (reduced shadowing) and blocking minima possibly shift. Dynamic displacements are caused by thermal vibrations. The enhancement of the yield by vibrations scales with  $\rho/r_M$ ,<sup>17</sup> in which  $\rho$  is the two-dimensional (2D) rms thermal vibration amplitude and  $R_M$  is the shadow cone radius at the second atom along a row (calculated in the Molière approximation to the Thomas-Fermi potential). Since  $R_M$  is a known function of the nuclear charges of ion and atom, the interatomic distance along the incident direction and the primary ion energy  $E_0$ ,<sup>15</sup> it is possible to normalize the contribution of thermal vibrations in ion-scattering experiments on different substrates by a proper choice of  $E_0$ . In this way, the effects of reconstruction-induced atomic displacements in different surface structures on shadowing and blocking can be compared directly.

Since the ion-atom scattering potentials at the energies used (50–200 keV) are well known, the experiment can be simulated on a computer by a Monte Carlo procedure.<sup>18</sup> In the simulation, the surface atoms are arranged according to a certain structure model. Subsurface distortions are calculated by minimizing the elastic strain, using a force-constant model after Keating.<sup>16,19</sup> Thermal vibrations are modeled in the simulation by a Gaussian probability density of uncorrelated atomic displacements. In this way, experimental ion-scattering data can be compared with simulations for various reconstruction models.

Experiments were performed in a high-resolution ion-scattering system.<sup>15</sup> Samples were prepared in a molecular-beam-epitaxy (MBE) apparatus connected to this system.<sup>20</sup> Si(111) substrates were heated for 10 min at 480 °C and 3 min at 700 °C, cooled down to room temperature (RT), then mildly sputtered with 0.8-keV Ar<sup>+</sup> ions (a dose of  $4\times 10^{14}$  ions cm<sup>-2</sup> at an angle of 50° with the surface normal) and finally annealed for 2 min at 900 °C. Ge(111) substrates were heated for 10 min at 400 °C,

sputtered at RT with 0.8-keV Ar<sup>+</sup> ions (dose 8 × 10<sup>15</sup> ions cm<sup>-2</sup>, angle 50°), and heated for 5 min at 600°C. This sputter and anneal treatment was repeated two or three times, followed by an anneal at 700°C for 30 s. Finally, a Ge film of several nm thickness was grown at 500°C on the Ge substrates. After this cleaning procedure, sharp Si(111)-(7 × 7) and Ge(111)-c(2 × 8) reflection high-energy electron-diffraction (RHEED) patterns were observed. The samples were transferred through an ultrahigh vacuum (UHV) to the ion-scattering chamber and surface cleanliness was checked with Auger electron spectroscopy (AES) and Rutherford backscattering spectroscopy (RBS).

In the ion-scattering chamber, the (111)-oriented samples were mounted in a high-precision goniometer and accurately aligned such that the collimated beam of energetic H<sup>+</sup> ions coincided with the [00 $\bar{1}$ ] direction of the crystal. Backscattered ions were analyzed in energy and scattering angle with a toroidal electrostatic analyzer. Primary proton energies of 161.3 and 99.4 keV for Ge substrates ( $\rho_{\text{bulk, Ge}} = 0.126 \text{ \AA}$ ) and 99.4 and 63.7 keV for Si substrates ( $\rho_{\text{bulk, Si}} = 0.110 \text{ \AA}$ ) were used. In this way, two sets of mutually comparable (identical  $\rho/R_M$ ) angular distributions of the backscattered yield were obtained.

The yield of backscattered ions from Ge(111)-c(2 × 8) and Si(111)-(7 × 7) surfaces for  $\rho/R_M = 0.60$ , expressed as the number of atoms per [00 $\bar{1}$ ] row, is plotted as a function of scattering angle  $\theta$  in Fig. 1(a). Virtually identical results have been obtained for  $\rho/R_M = 0.50$ . A static bulk-terminated lattice would give a yield of exactly 1 atom/row. The much higher yield in the Ge and Si spectra is caused by atomic displacements. The minima at  $\theta = 54.74^\circ$  are caused by blocking in the [11 $\bar{1}$ ] direction. Since the contribution of thermal vibrations to the backscattering ion fraction is the same for Ge and Si, the spectra can be compared directly. The enhancement of the yield with respect to a simulated spectrum for a vibrating bulklike surface [Fig. 1(a)] indicates extensive static atomic displacements in the near-surface region for both crystals. The Si data are in good agreement with simulations for the dimer-atom-stacking (DAS) fault model.<sup>16,21</sup> The significantly lower yield from the Ge surface as compared to that from the Si surface reflects the presence of much smaller static displacements in the c(2 × 8) surface structure than in the (7 × 7) reconstruction, and in particular, it indicates the absence of stacking faults. This result is in striking contrast with the channeling data of Culbertson *et al.*,<sup>22</sup> which indicated equal displacements for both surfaces. The reason for the discrepancy is not yet clear. However, large uncertainties in the surface yield calibration may have affected their conclusions, since they are based on measurements performed with a low-resolution solid-state detector. Furthermore, their Ge surface preparation, which involved only sputtering and annealing, might have led to some disorder. Previous ion-scattering work has shown that sputtering of a semiconductor may lead to (sub)surface damage that cannot be annealed out.<sup>23</sup>

The symmetry of the Ge(111)-c(2 × 8) structure was found from an analysis of the LEED pattern,<sup>24,25</sup> using the extinction rule. The periodic arrangement of the

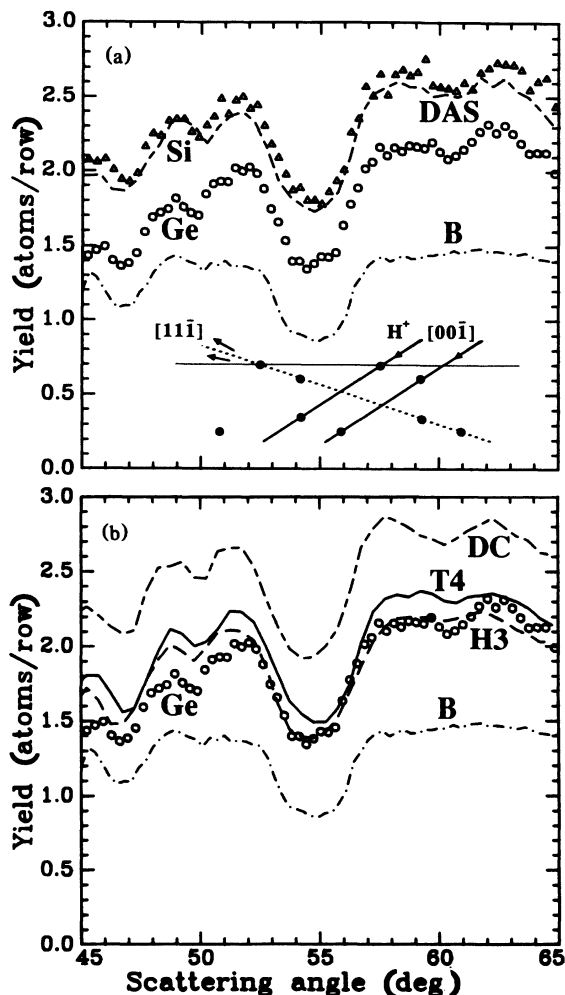


FIG. 1. (a) Medium-energy ion-scattering angular spectra of Si(111)-(7 × 7) and Ge(111)-c(2 × 8) reconstructed surfaces for  $\rho/R_M = 0.60$ . The contribution of thermal vibrations is normalized. Differences in backscattered ion yield reflect directly, therefore, the difference in static reconstruction-induced lattice distortions. Simulated spectra for the (7 × 7)-DAS structure and for a bulklike surface are also shown. The scattering geometry is shown in the inset. (b) Ion-scattering angular spectra of the Ge(111)-c(2 × 8) for  $E_0 = 161.3 \text{ keV}$  are compared with Monte Carlo simulations of a bulklike surface (B) and with dimer-chain (DC) and adatom model ( $T_4$  and  $H_3$ ). The scattering geometry is the same as in (a).

scattering centers derived from LEED is consistent with the observed protrusions in an STM study by Becker, Golovchenko, and Swartzentruber.<sup>14</sup> Adatoms are natural interpretation for the presence of the scattering centers and/or protrusions. The presence of adatoms can lower the total energy considerably by saturating a large fraction of the dangling bonds.<sup>26</sup> Takayanagi<sup>3</sup> has proposed a model for the Ge(111)-c(2 × 8) reconstructed surface containing dimers, adatoms, and stacking faults, in analogy with his successful DAS model of the (7 × 7) reconstruction.<sup>21</sup> This so-called dimer-chain model [Figs. 2(a) and 2(b)] contains as structure elements, walls and domains, which can be arranged in a network to form a c(2 × 8)

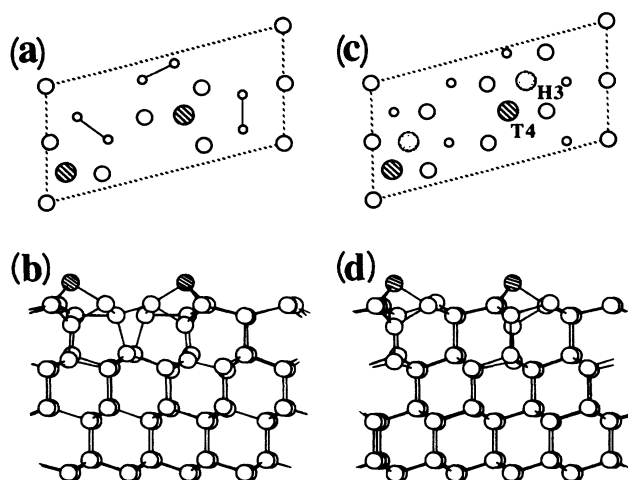


FIG. 2. Atomic arrangement of the dimer-chain model [(a), (b)] and the simple adatom models [(c), (d)]. Primitive unit meshes of the  $c(2\times 8)$  structure are shown schematically in top view [(a), (c)], where only adatoms (hatched), atoms in the first double-layer and dimer bonds are indicated. The two possible adatom positions for the adatom model ( $T_4$  and  $H_3$ ) are shown. Part of the elastically (Keating-) relaxed crystal structures are shown in side view [(b), (d)].

structure as well as  $(2\times 2)$ ,  $c(2\times 4)$ ,  $(5\times 5)$ , or  $(7\times 7)$  ordered structures. Another model for the  $c(2\times 8)$  reconstruction is the simple adatom model<sup>26</sup> [Figs. 2(c) and 2(d)]. Two different low-energy sites are available for the adatoms.<sup>27</sup> Both are threefold coordinated, but are either directly above a second-layer atom ( $T_4$  or filled site) or above a fourth-layer atom ( $H_3$  or hollow site). Pseudopotential calculations by Northrup and Cohen<sup>27,28</sup> have shown that in the  $7\times 7$  and  $\sqrt{3}\times\sqrt{3}$  structures the  $T_4$  site is preferred. In a rectangular  $(2\times 2)$  geometry, which is related to the  $c(2\times 8)$  structure, it is more difficult to indicate the most favorable site, since the energy is dependent on the lattice relaxation.

In Fig. 1(b), the results of the ion-scattering experiment are compared with Monte Carlo simulations<sup>18</sup> of the bulklike surface, the dimer-chain model and the adatom model (both the  $H_3$  and  $T_4$  version). The modeled surfaces are elastically relaxed.<sup>16,19</sup> The curves for the adatom model correspond to a simulation in which the thermal vibrations of the adatoms and the atoms in the outer double layer are enhanced by a factor  $\sqrt{2}$  with respect to  $\rho_{\text{bulk}}$ ;<sup>16</sup> the other simulations have been performed for bulklike surface-vibration amplitudes. The surface-vibration enhancement assumed in the adatom model raises the yield by only  $\sim 0.05$  atom/row. Resulting simulated spectra are averaged over the three possible domain orientations of the  $c(2\times 8)$  structure. From Fig. 1(b) it is evident that the simple adatom model gives the best agreement with the data. Of the two different versions of this model, the  $H_3$  version is slightly closer to the ion-scattering data than the  $T_4$  version (in absolute yield and position of the  $[11\bar{1}]$  blocking minimum), but no clear distinction can be made. The dimer-chain model gives

very similar results as the  $(7\times 7)$ -DAS model, which reflects the similarity in local geometry. Because of large strain fields and stacking faults the simulated backscattered yield for this model is much higher than the experimental Ge data. Therefore, the dimer-chain model for the  $c(2\times 8)$  structure can be ruled out.

In both adatom and dimer-chain models the total energy is reduced by a lowering of the dangling-bond density, but increased by the induced lattice-strain energy. The lattice distortions [Figs. 2(b) and 2(d)] form the main contribution to the enhancement of the yield in the ion-scattering experiments.<sup>16</sup> Total-energy calculations<sup>29</sup> have shown that the dimer-chain model has a very low energy for the  $(7\times 7)$  structure, but that the strain fields make it less favorable in case of the  $c(2\times 8)$  structure.

Any geometric model should not only explain observations made with surface structural techniques such as ion scattering but also the surface electronic properties as derived from (inverse) photoemission<sup>30</sup> and scanning tunneling microscopy<sup>14</sup> experiments. The surface electronic structure of Ge(111)- $c(2\times 8)$  is very similar to that of Si(111)- $(7\times 7)$ , with one important difference: the  $(7\times 7)$  surface has a metallic surface state, Ge(111)- $c(2\times 8)$  does not. Instead, the Ge surface is semiconducting, implying that all surface states are either completely occupied or empty. Partially filled states do not occur. In the adatom model supported by the ion-scattering experiments described above, the surface electronic structure can easily be explained in analogy with that of Si(111)- $(7\times 7)$  and in concordance with the theoretical work by Northrup and Cohen.<sup>27,28</sup> The  $c(2\times 8)$  primitive unit cell has four broken bonds. Two are localized on the adatoms and two on the remaining threefold-coordinated atoms in the first layer of the underlying crystal (the so-called rest atom; see Fig. 2). One electron is transferred from the adatom to the rest atom. The rest atom has a completely filled surface state (about 1 eV below the Fermi level) and the adatom has an empty surface state. The transfer of charge opens up a gap and the surface is semiconducting. [The Si(111)- $(7\times 7)$  surface is metallic because there are more adatoms than rest atoms and complete charge transfer from adatoms to rest atoms cannot occur.] Now consider Takayanagi's dimer-chain model. The  $c(2\times 8)$  unit cell contains two adatoms, but no rest atom (Fig. 2). Charge transfer from adatom to rest atom can therefore not occur. One might postulate transfer of charge from one adatom to the other in order to open a surface-state band gap. This appears to be very unlikely, however, because the two adatoms are geometrically equivalent, unlike adatom and rest atom. In addition, such a hypothesis would be inconsistent with the STM experiments by Becker, Golovchenko, and Swartzentruber.<sup>14</sup> In these experiments, electrons tunneled from the tip into the empty states of the sample. Per  $c(2\times 8)$  primitive unit cell, two distinct bumps were observed signifying two positions in the unit cell with an empty surface state to tunnel into. Now suppose that one adatom would transfer its dangling-bond electron to the other adatom. In that case, only one of the two adatoms would have an empty surface state, the other adatom would have a completely filled surface state, thus opening a gap. In this case the STM ex-

periment would only observe one bump per  $c(2\times 8)$  unit cell. This is in contradiction with experiment. The bumps observed in the STM experiments are naturally explained by the adatom model.

In conclusion, medium-energy ion-scattering experiments have shown that the  $c(2\times 8)$  structure exhibits considerably less lattice distortions compared to the  $(7\times 7)$  structure. A simple adatom model for the  $c(2\times 8)$  recon-

structed surface is in excellent agreement with the ion-scattering data and fully consistent with STM.

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<sup>1</sup>P. W. Palmberg and W. T. Peria, *Surf. Sci.* **6**, 57 (1967).

<sup>2</sup>D. Haneman, *Adv. Phys.* **31**, 165 (1982).

<sup>3</sup>K. Takayanagi and Y. Tanishiro, *Phys. Rev. B* **34**, 1034 (1986).

<sup>4</sup>D. Vanderbilt, *Bull. Am. Phys. Soc.* **32**, 571 (1987).

<sup>5</sup>R. S. Becker, J. A. Golovchenko, G. S. Higashi, and B. S. Swartzentruber, *Phys. Rev. Lett.* **57**, 1020 (1986).

<sup>6</sup>T. Ichikawa and S. Ino, *Surf. Sci.* **105**, 395 (1981).

<sup>7</sup>K. Shoji, M. Hyodo, H. Ueba, and C. Tatsuyama, *Jpn. J. Appl. Phys.* **22**, L200 (1983).

<sup>8</sup>E. G. McRae and R. A. Malic, *Surf. Sci.* **165**, 191 (1986).

<sup>9</sup>T. Ichikawa and S. Ino, *Surf. Sci.* **136**, 267 (1984).

<sup>10</sup>H.-J. Gossmann, J. C. Bean, L. C. Feldman, E. G. McRae, and I. K. Robinson, *Phys. Rev. Lett.* **55**, 1106 (1985).

<sup>11</sup>A. Ourmazd, D. W. Taylor, J. Bevk, B. A. Davidson, L. C. Feldman, and J. P. Mannaerts, *Phys. Rev. Lett.* **57**, 1332 (1986).

<sup>12</sup>K. Nakagawa, P. M. J. Marée, and J. F. van der Veen, in *Proceedings of the Eighteenth International Conference on the Physics of Semiconductors*, edited by O. Engström (World Scientific, Singapore, 1987), p. 93.

<sup>13</sup>J. C. Phillips, *Phys. Rev. Lett.* **45**, 905 (1980).

<sup>14</sup>R. S. Becker, J. A. Golovchenko, and B. S. Swartzentruber, *Phys. Rev. Lett.* **54**, 2678 (1985).

<sup>15</sup>J. F. van der Veen, *Surf. Sci. Rep.* **5**, 199 (1985).

<sup>16</sup>R. M. Tromp and E. J. van Loenen, *Surf. Sci.* **155**, 441 (1985).

<sup>17</sup>I. Stensgaard, L. C. Feldman, and P. J. Silverman, *Surf. Sci.* **77**, 513 (1978).

<sup>18</sup>J. W. M. Frenken, R. M. Tromp and J. F. van der Veen, *Nucl. Instrum. Methods B* **17**, 334 (1986).

<sup>19</sup>P. N. Keating, *Phys. Rev.* **145**, 637 (1966).

<sup>20</sup>P. M. J. Marée, A. P. de Jongh, J. W. Derks, and J. F. van der Veen, *Nucl. Instrum. Methods B* **28**, 76 (1987).

<sup>21</sup>K. Takayanagi, Y. Tanishiro, S. Takahashi, and M. Takahashi, *Surf. Sci.* **164**, 367 (1985).

<sup>22</sup>R. J. Culbertson, Y. Kuk, and L. C. Feldman, *Surf. Sci.* **167**, 127 (1986).

<sup>23</sup>I. Yamada, D. Marton, and F. W. Saris, *Appl. Phys. Lett.* **37**, 563 (1980).

<sup>24</sup>D. J. Chadi and C. Chiang, *Phys. Rev. B* **23**, 1843 (1981).

<sup>25</sup>W. S. Yang and F. Jona, *Phys. Rev. B* **29**, 899 (1984).

<sup>26</sup>W. A. Harrison, *Surf. Sci.* **55**, 1 (1976).

<sup>27</sup>J. E. Northrup and M. L. Cohen, *Phys. Rev. B* **29**, 1966 (1984).

<sup>28</sup>J. E. Northrup, *Phys. Rev. Lett.* **57**, 154 (1986).

<sup>29</sup>Guo-Xin Qian and D. J. Chadi, *Phys. Rev. B* **35**, 1288 (1987).

<sup>30</sup>F. J. Himpsel, D. E. Eastman, P. Heimann, B. Reichl, C. W. White, and D. M. Zehner, *Phys. Rev. B* **24**, 1120 (1981).