Trimer adatom structure of phosphorus on Ge(111)

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(Received 28 August 2000; published 4 April 2001)

The surface structures of phosphorus on a Ge(111)c(2×8) surface have been investigated by scanning tunneling microscopy (STM), low-energy electron diffraction, and Auger electron spectroscopy. Phosphorus adatoms are stable on the Ge(111) surface up to ~350 °C, where desorption and/or diffusion into the bulk sets in. The P adatoms cluster into small islands and form a local (v3×v3)R30° structure. The stable bonding configuration of phosphorus on Ge(111) between room temperature and ~260 °C is the so-called T4 trimer geometry, where the P adatoms form triangular trimer units above second-layer Ge atoms, thus saturating all the Ge surface dangling bonds in the local (v3×v3)R30° array. However, only poor long-range order is obtained. The P3 trimers replace the Ge adatoms of the c(2×8) reconstruction as revealed in atomically resolved STM images. The P trimer structure on Ge(111) is discussed in relation to the substitutional adsorption geometry of P on Si(111), and it is argued that the Ge(111)(v3×v3)R30°-P3 structure is the result of the larger tensile stress on the Ge surface and the weaker Ge-P bond strength as compared to the Si case.

DOI: 10.1103/PhysRevB.63.165320 PACS number(s): 68.35.Bs, 68.37.Ef, 81.05.Cy, 68.43.–h

I. INTRODUCTION

The study of the adsorption properties of group-V elements on Si and Ge surfaces may provide important insights into the atomic-level processes that govern the heteroepitaxial growth of thin films on group-IV semiconductor surfaces. The discovery that As and Sb may act as surfactants to enable the layer-by-layer growth of Ge on Si(111) surfaces1–3 has prompted research in this direction with direct technological relevance. From a more fundamental point of view the adatom-induced surface reconstructions of group-V elements demonstrate the delicate interplay of electronic versus elastic effects that determines the lowest-energy surface structure. The adsorption of group-V atoms on Si and Ge surfaces has therefore been investigated frequently as prototypical model systems by both experimental and theoretical means,4–6 but most studies have concentrated on the heavier elements of this group, viz., As, Sb, and Bi. Phosphorus is a common dopant for Si and Ge bulk materials, but few studies have addressed the adsorption of P on Si surfaces,7 and none, to the best of our knowledge, the adsorption of P on germanium. In this paper we attempt to fill in this gap of knowledge concerning group-V–group-IV interface systems and report experimental data on the adsorption of phosphorus on a Ge(111) surface.

The most common surface structures observed for group-V elements on Si(111) and Ge(111) surfaces are the (1×1) and (v3×v3)R30° structures. For example, As adopts a substitutional (1×1) adsorption geometry on Si(111) and Ge(111) surfaces,8,9 whereas Bi forms (v3×v3)R30° reconstructions on both surfaces.10,11 In the latter case two different types of (v3×v3)R30° structure were found at coverages of 1/3 of a monolayer and at 1 monolayer. Sb also generates (v3×v3)R30° structures on Si(111),12 but a (2×1) reconstruction on Ge(111). The higher-coverge (v3×v3)R30° structures have been shown to consist of triangular trimer building units,14 which occupy either H3 or T4 surface positions. In the so-called “milking stool” model of these (v3×v3)R30° structures, an adatom is adsorbed on top of each surface atom of the substrate and three nearest-neighbor adatoms form a trimer in a (v3×v3)R30° periodicity, thus accounting for the 1 monolayer coverage.4

For phosphorus on Si(111) our recent scanning tunneling microscopy (STM) work7 showed that the P adatoms occupy the substitutional adsorption geometry, replacing the Si atoms of the topmost surface layer, as predicted theoretically.3 At elevated temperature a (6v3×6v3)R30° surface reconstruction was observed, consisting of a domain-wall structure containing the P adatoms in hexagonal (1×1) domains in a substitutional adsorbate geometry.7 This structure has been interpreted as the result of the competition between the strong P-Si bond, which favors the substitutional (1×1) adsorption geometry, and the tensile surface stress, which is introduced by the P-Si bond topology and creates the domain walls as a means of stress relief.

The replacement of the Si(111) surface by a Ge(111) surface as the substrate for the adsorption of phosphorus provides an experimental testing ground for the concept of the interplay of electronic versus elastic effects in determining the surface structure of epitaxial overlayers. The lattice constant of Ge is ~4% larger than that of Si, but the P-Ge bond is weaker than the P-Si bond.13 The substitutional adsorption geometry is expected to be unstable for P on Ge(111), since the tensile stress for substitutional P on Ge(111) will be larger than for P on Si(111) and will not be overcompensated by the smaller P-Ge bond energy. A different adsorbate structure is therefore expected.

In this paper we report an investigation of the surface structure of P on a Ge(111)c(2×8) surface by STM; the STM experiments were supplemented by low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) measurements. Our results show that indeed a trimer configuration of P adatoms in a (v3×v3)R30° structure forms the stable adsorption geometry of phosphorus on the Ge(111) surface. The T4 surface sites have been unambiguously identified in high-resolution STM images as the central positions of the phosphorus trimer units.

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II. EXPERIMENT

The experiments were performed in a custom-designed three-chamber UHV system equipped with STM (Omicron micro-STM) and LEED/AES facilities as described previously.\textsuperscript{16} Clean, well-ordered Ge(111)c(2 \times 8) surfaces were prepared by Ar ion bombardment (0.5 kV) and annealing at 800 °C. The surface order and cleanliness of the Ge surfaces were checked by LEED, AES, and STM. Vapor-phase P\textsubscript{2} was generated by incongruent Langmuir evaporation of InP from a boron nitride evaporator, with the shutter closed and the sample out of sight of the evaporator to avoid In coadsorption. The absence of coadsorbed In impurities was confirmed by AES. Beyond the critical temperature for congruent evaporation P\textsubscript{2} constitutes the dominant gas-phase species.\textsuperscript{17}\textsuperscript{17} The P\textsubscript{2} exposures are given in langmuirs (1 L = 1 × 10^{-6} torr sec) as derived from uncorrected ionization gauge readings (i.e., not corrected for the ionization cross section of P\textsubscript{2}).

III. RESULTS AND DISCUSSION

A. General adsorption properties of phosphorus on Ge(111)c(2\times8)

Figure 1 gives a general impression of the adsorption characteristics of phosphorus on the Ge(111)c(2 \times 8) surface. In Fig. 1(a) the amplitudes of the P LVV and Ge MVV Auger transitions (peak-to-peak heights) are plotted against the P\textsubscript{2} dose at room temperature, illustrating the phosphorus uptake of the surface. The P uptake is rapid initially and slows down after exposures of \(\sim 5–6\) L; full saturation of the surface is reached after a P\textsubscript{2} dose of \(\sim 50\) L. The shape of the AES uptake curve together with STM observations [Fig. 2(c) below] suggest that the room-temperature saturation coverage of P is of the order of 1 monolayer. The P and Ge Auger peak intensities of a room-temperature P-saturated Ge(111) surface as a function of the surface temperature are shown in Fig. 1(b). The P adsorbate coverage is approximately stable up to \(\sim 300\) °C, where the P surface concentration starts to decrease as a result of desorption and/or diffusion into the bulk. The clean Ge(111)c(2 \times 8) surface is recovered after annealing to \(\sim 500\) °C.

The Ge(111)c(2 \times 8) LEED pattern decreases in intensity on P\textsubscript{2} dosing and after 1.5–2 L exposure a LEED pattern as reproduced in Fig. 1(c) is observed. This pattern consists of the overlapping contributions of a diffuse \((\sqrt{3} \times \sqrt{3})R30°\) structure and a diffuse \((2 \times 2)\) structure with split spots [see arrows in Fig. 1(c)], the latter due to modified Ge substrate regions as discussed below. The \(\sqrt{3}\) structure remains diffuse up to saturation adsorption conditions and indicates poor long-range ordering of the adsorbate layer; this is also confirmed by the STM images. On annealing, the \((\sqrt{3} \times \sqrt{3})\) pattern fades away at temperatures \(\sim 260\) °C. In the temperature range from 260 to 350 °C, i.e., prior to P desorption, STM observations reveal a surface that displays short chains of dimer structures irregularly distributed over the surface or in small domains on a partially disrupted Ge substrate surface.\textsuperscript{18} This surface shows no long-range order and consequently only a diffuse \((1 \times 1)\) pattern from the Ge(111) substrate is observed in LEED.

The morphology of the P-covered Ge(111)c(2 \times 8) surface after room-temperature deposition is illustrated in the large-scale STM images of Fig. 2, which show a characteristic monatomic step of the Ge substrate running across the images. The images demonstrate that the adsorbate atoms tend to cluster into small agglomerates with a uniform distribution over the surface, without preferential adsorption or decoration of step edges. In Fig. 2(c), obtained after a P\textsubscript{2} dose of 7 L, the surface appears to be uniformly covered with the adsorbate, but the surface displays a “grainy” contrast that is indicative of a rough morphology. As shown by the STM images at higher resolution, the P adsorbate forms a heterogeneous surface with adsorbate-covered areas and re-
regions of the uncovered but perturbed substrate surface in between, and this is also suggested by the diffuse LEED patterns observed.

In the following, it is convenient to separate the presentation into two parts: in the first part we will discuss the data for low adsorbate coverages, where the individual adspecies can be identified, whereas in the second part we will concentrate on the \((\sqrt{3}\times\sqrt{3})R30^\circ-P\) surface reconstruction.

B. Phosphorus trimer formation and the adsorption site

Figure 3 shows filled (a) and empty (b) state STM images of the Ge(111)\(c(2\times8)\) surface after exposure to 0.7 L P\(_2\) at room temperature followed by annealing at \(\sim200^\circ\text{C}\). The two images were recorded from the same area of the surface and the three rectangular \(c(2\times8)\) units cells are drawn in both images at the same position. In Fig. 3(a) a bright triangular feature consisting of three maxima is visible in the filled state image at the boundary of the marked unit cells, which appears as a dark depression in the empty state image of Fig. 3(b) (see arrows on both images). In empty state STM images of the Ge(111) surface the maxima have been principally associated with the adatoms of the \(c(2\times8)\) reconstruction, whereas in the filled state images the rest atoms are better expressed\(^{19}\). Comparison of images 3(a) and 3(b) thus allows one to locate the bright trimer in (a) at a Ge adatom

![FIG. 2. Constant-current topographical STM images of the Ge(111)\(c(2\times8)\) surface exposed to 0.5 (a), 2 (b), and 7 L (c) P\(_2\) at room temperature. 1500×1500 Å\(^2\); sample bias −2 V; tunneling current 1 nA.](image)

![FIG. 3. Filled (a) and empty (b) state high-resolution STM images of Ge(111)\(c(2\times8)\) exposed to 0.7 L P\(_2\) at room temperature followed by annealing at \(\sim200^\circ\text{C}\). The two images were taken from the same surface area and the three \(c(2\times8)\) unit cells indicated are drawn at the same position. (a) 63×51 Å; −2.1 V; 1.9 nA; (b) 63×51 Å; +2.1 V, 1.9 nA. (c) Line scan across two atoms of the trimer along the dotted line in image (a). (d) Schematic model of the \(T_4\) trimer geometry (filled circles, P; empty circles, Ge).](image)
position. The bright trimers seen in the filled state images increase in numbers with increasing P$_2$ exposure and are therefore identified as P trimer units. Their contrast dependence in STM on the sample bias polarity provides strong support for this assignment: each P adatom in the trimer has two bonds to two other P atoms of the trimer and one bond to the Ge surface [see Fig. 3(c)], leaving each P atom with a filled dangling-bond state standing proud of the surface. These filled lone-pair orbital states are imaged as maxima in the trimer units in the STM. Figure 3(c) shows a line scan across the trimer as indicated by the dotted line in Fig. 3(a). The maxima of the trimer display a corrugation of ~0.9 Å above the Ge rest atoms in the filled state image, and their separation suggests a P-P bond length of 2.9 Å in the trimer. This is considerably longer than the 2.2 Å bond distance in the P$_4$ cluster. It presumably reflects the influence of the P-Ge bonds and the Coulomb repulsion of the lone-pair orbitals in the planar trimer arrangement.

The empty state image Fig. 3(b) indicates that the P$_3$ units replace the Ge adatoms of the c(2×8) reconstruction. This allows us to unambiguously identify the T$_4$ surface sites as the adsorbate positions, i.e., the P trimers are centered above second-layer Ge atoms. Figure 3(d) illustrates this T$_4$ trimer geometry schematically.

The dual-polarity STM images of Figs. 4(a) and 4(b) show a larger area of the Ge c(2×8) surface after exposure to 0.7 L P$_2$ at ~200°C. Both isolated trimers (arrows) and aggregations of trimers (region of light-gray contrast, dotted arrow) are seen in the filled state image (a); in addition a number of bright single maxima and dimers is recognized in both images (a) and (b), which maintain the same contrast at positive and negative bias polarity. This different contrast behavior with sample bias as compared to the P trimer units suggests that these maxima (dimers) may possibly be associated with displaced Ge atoms. The long-range order of the Ge(111)c(2×8) surface reconstruction is lost after the adsorption of phosphorus, but the building blocks of the c(2×8) structure, the (2×2) and (4×2) units, seem to be still maintained. The Ge c(2×8) structure may be regarded as a periodic and alternating sequence of c(4×2) and (2×2) unit cells [see Fig. 4(c)]. On the uncovered Ge areas in Figs. 4(a) and 4(b) these building blocks of the c(2×8) structure can still be discerned, but their periodic order is removed: the (2×2) unit cells are arranged in small domains, which are in antiphase relation to each other and which are separated by rows of c(4×2) unit cells. Figure 4(d) gives a schematic representation of the surface imaged in Figs. 4(a) and 4(b), where the Ge (2×2) and c(4×2) unit cells are outlined by solid and dashed lines, respectively. The black dots indicate the positions of single P trimers. It is noticeable that the individual trimers are preferentially located at the boundaries between (2×2) and c(4×2) regions, where they replace Ge adatoms in T$_4$ positions, as discussed above.

The clean Ge(111)c(2×8) surface reconstruction undergoes a reversible transition to an incommensurate (2×2) phase in the temperature range 240–300 °C. This phase transition has been interpreted in terms of a local order-disorder transition involving a correlated shifting of adatom rows and the transformation of c(4×2) unit cells into (2×2) unit cells, and vice versa. The incommensurate (2×2) phase of germanium is stable only at elevated temperatures and the c(2×8) surface is restored if the surface is cooled to room temperature. The RT surface observed here is thus the result of both phosphorus adsorption and the annealing. It has been observed that the presence of group-III and group-IV adsorbate atoms stabilizes the incommensurate phase at room temperature and it has been suggested that the adatoms pin the (2×2) domains thus preventing the reordering of the surface into the c(2×8) structure. This phenomenon is also clearly seen here, where the P$_3$ units seem to pin the (2×2) domains by replacing Ge adatoms at the boundaries, thus inhibiting the transformation of (2×2) into c(4×2) units and their periodic rearrangement by a concerted shift of Ge adatom rows.

**C. The Ge(111)(v3×v3)R30°-P$_3$ structure**

With increasing phosphorus coverage the P$_3$ trimers condense into a (v3×v3)R30° structure as shown in Figs. 5(a)
and 5(b). The STM images reveal regions of local $\sqrt{3}$ structure separated by uncovered Ge(111)c(2\times 8) surface regions. On top of the $\sqrt{3}$ areas bright maxima are seen, which are most likely associated with displaced Ge adatoms. The long-range order of the $\sqrt{3}$-P$_3$ surface structure remains poor up to saturation adsorption conditions as evidenced also by LEED (see Sec. III A). The $\sqrt{3}$-P-covered areas, with a local surface coverage of 1 monolayer, coexisting with bare Ge(111) surface areas indicate an attractive interaction between P trimers. The surface energetics of an adsorbate with two domains with distinctly different structures on the surface has been investigated recently for Ga and As on the Ge(111) surface. A phase separation into a high-coverage (1\times1) structure and bare substrate areas instead of a more uniform adsorbate distribution has been found favorable for As on Ge(111). A similar situation seems to occur for P on Ge(111), where the high-coverage $\sqrt{3}$ trimer structure provides the most stable adsorbate configuration.

Figure 6 shows scanning tunneling spectra (STS) in $d\ln I/d\ln V$ versus $V$ form for the clean Ge(111)c(2\times 8) and the Ge(111)$\sqrt{3}$-P surfaces. The spectra were recorded with the tip stabilized at the setpoint parameters $-2$ V and 2 nA (feedback loop switched off), and many points from the tops of clean Ge and $\sqrt{3}$-P areas were averaged. The major differences between the STS of the Ge(111)c(2\times 8) and the $\sqrt{3}$-P surfaces are the disappearance of the clean surface peak at $-0.5$ V and the opening of a surface band gap of $\sim1.4$ eV in the latter case. The STS peak at $+0.5$ V on clean Ge(111)c(2\times 8) has been associated with the empty dangling-bond surface states of the Ge adatoms. Its absence on the $\sqrt{3}$-P surface provides strong support for the notion that the P$_3$ trimers replace the Ge adatoms, thereby opening the gap.

Figure 7(a) shows a higher-resolution STM image of the $\sqrt{3}$-P structure where most of the triangular P$_3$ units are oriented with their vertices pointing downward, but occasionally trimers with a slightly higher contrast are detected, which are rotated by 60° with respect to the majority trimers (see arrow). These minority trimers are laterally displaced from the stacking sequence of the majority trimers, as indicated by the dashed lines on the image, suggesting that they are located on different adsorption sites. A schematic model of the ($\sqrt{3}\times\sqrt{3}$)R30°-P$_3$ trimer structure is displayed in Fig. 7(b). The phosphorus trimer units in the ($\sqrt{3}\times\sqrt{3}$) array substitute for the Ge adatoms of the c(2\times 8) structure and are thus located at the $T_4$ surface sites, i.e., on top of second-layer Ge atoms. The observation of some minority trimer species [Fig. 7(a)] may be due to the accidental occupation of $H_3$ surface sites. In $H_3$ sites the trimers are centered above a hexagon composed of first- and second-layer substrate atoms as shown in Fig. 7(b). As seen in the drawing these trimers are rotated by 60° with respect to the majority species and are laterally displaced from the stacking sequence of the $T_4$ trimers.

It is of interest to investigate the origin of the $T_4$ trimer geometry observed here by comparing it with the substitutional adsorption geometry of P on Si(111) and of As on Si(111) and Ge(111) surfaces. Unfortunately, no theoretical treatment of the adsorption of P on Ge(111) has been reported so far. However, some guidance may be obtained from the first-principles total-energy calculations of Kaxiras on structural configurations of group-V adatoms on Si(111). For phosphorus on Si(111) Kaxiras predicts the substitutional geometry as the most stable adsorbate configuration, in agreement with the experimental findings. This structure also introduces the highest adsorbate bond strain, which is offset, however, by the strong P-Si bond; this results in a geometry that maximizes the number of P-Si bonds, i.e., the substitutional geometry. For the $T_4$ trimer geometry of P on Si(111) a much lower bond strain has been calculated. In particular, the P-P bond lengths in P$_4$ and in the calculated $T_4$ trimer structure on Si(111) are very similar (2.2 versus 2.23 Å, respectively). Extrapolation to P on Ge(111) leads us to suggest that the $T_4$ trimer geometry should also have a relatively low bond strain, although the measured P-P bond lengths in the P trimer appear to be re-
IV. CONCLUSIONS

The adsorption of phosphorus on Ge(111) provides an intriguing testing ground for studying the interplay between surface strain and adsorbate bond energetics in determining the most stable adsorbate configuration. It is argued that the experimentally observed $T_4$ trimer structure of P on Ge(111) may be rationalized by investigating the trends found for group-V adsorbates on Si(111) surfaces. The larger size of the Ge atom gives rise to a larger tensile surface stress as a result of the P adatom bonding than on the corresponding Si surface. Moreover, the P-Ge bond is weaker than the P-Si bond. As a result the balance between elastic strain energy and electronic bond energy in the P/Ge(111) system is altered as compared to the P/Si(111) system. It appears that the surface structure with the lowest strain wins the competition for the most stable adsorption geometry, and that is the $T_4$ trimer configuration. In contrast, the substitutional adsorption geometry has been observed for P on Si(111). The present STM study shows that the $(\sqrt{3} \times \sqrt{3})R30^\circ-P_4$ structure on Ge(111) is established locally, but that a uniform coverage over the entire surface is not obtained between room temperature and $\approx 260^\circ$C. It is likely that the weakness of the P-Ge bonding in the trimer configuration is detrimental to the ordering process on this surface: the P trimers dissociate (at $T>260^\circ$C) before the disruption of the Ge surface caused by the replacement of the Ge adatoms has time to heal out by annealing.

In summary, the adsorption of phosphorus on the Ge(111)$_c(2 \times 8)$ surface has been studied in the temperature range from room temperature to 500°C by STM, STS, LEED, and AES. The P adatoms tend to cluster and form islands of a local $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure up to $\approx 260^\circ$C. The stable adsorbate configuration at temperatures below 260°C is the so-called $T_4$ trimer geometry, in which the P adatoms are arranged in trimers above second-layer Ge atoms, thus replacing the Ge adatoms of the $c(2 \times 8)$ reconstruction. The $T_4$ trimer sites are more stable than the $H_3$ trimer sites, but the energy difference must be small, since the latter are also observed to be occupied by minority trimer species. In the temperature range 260–350°C the P adatoms form a poorly ordered overlayer with short chains of dimers irregularly distributed over the surface. For temperatures above 400°C the P adatoms disappear from the Ge surface via desorption into the gas phase and/or diffusion into the bulk.

ACKNOWLEDGMENTS

This work was supported in part by the Austrian Science Foundation. F.P.N. acknowledges with pleasure the hospitality of Professor G. A. Somorjai, University of California, Berkeley, during his sabbatical stay at Berkeley, where this manuscript was prepared.

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PHYSICAL REVIEW B 63 165320


