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STM study of superstructures formed in the Pd/Si(111) system

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The structure of the low-coverage $(\sqrt{3}\times\sqrt{3})R\pm30^\circ$ Pd phase, produced upon mild annealing of a Pd layer deposited at room temperature, has been examined by scanning tunneling microscopy (STM). The STM images have revealed a rather inhomogeneous surface that contains large $(\sqrt{3}\times\sqrt{3})R\pm30^\circ$ domains, mixed with features assigned to a transition state from a $(\sqrt{3}\times\sqrt{3})R\pm30^\circ$ to a $(3\sqrt{3}\times3\sqrt{3})R\pm30^\circ$ structure, and areas of disordered Si phase. The structural units of both the $(\sqrt{3}\times\sqrt{3})R\pm30^\circ$ and $(3\sqrt{3}\times3\sqrt{3})R\pm30^\circ$ structures are protrusions of $\simeq 5.5$ Å average diameter described as Pd trimers chemisorbed on a (1×1) Si(111) surface. A structural model for the possible surface atomic arrangements in the $(\sqrt{3}\times\sqrt{3})R\pm30^\circ$ and $(3\sqrt{3}\times3\sqrt{3})R\pm30^\circ$ phases is suggested and discussed.

Formation of silicides is a common phenomenon when d metals are deposited on Si surfaces.[1,2] One of the systems studied in more detail is the reaction of Pd with Si(111) which yields a single product Pd_2Si. The intermixing of Pd and Si occurs readily at room temperature and the formation of a silicidelike nucleus at room temperature was evidenced even at Pd coverage of less than one monolayer.[3–9] The effects of increasing the temperature on the deposited layers have been described in a number of papers.[6–11] We were interested in mild annealing which produces a layer characterized by a $(\sqrt{3}\times\sqrt{3})R\pm30^\circ$ low-energy electron diffraction (LEED) pattern. The basic consideration of the models proposed to explain the origin of this pattern is the correspondence between the (1×1) $Pd_2Si(0001)$ alternating basal planes and the $(\sqrt{3}\times\sqrt{3})R\pm30^\circ$ structure of the (1×1) Si(111) surface.[1,2,6,8,10] A slightly different model for the $(\sqrt{3}\times\sqrt{3})R\pm30^\circ$ Pd /Si phase was given by Akiyama, Takayanagi, and Tanishiro on the basis of a transmission electron microscopy/transmission electron diffraction (TEM/TED) study.[11] They described the $(\sqrt{3}\times\sqrt{3})R\pm30^\circ$ structure in terms of a "twist model" where the Pd coverage is 1 ML and the arrangement of the atoms is not much different from that of a crystalline Pd_2Si. To our knowledge there is no scanning tunneling microscopy (STM) report on this Pd-related superstructure which can verify the guessed models.

Here we report our STM observations of the interfacial $(\sqrt{3}\times\sqrt{3})R\pm30^\circ$ layer produced by annealing of room-temperature-deposited Pd layers. On the basis of the features in the STM images we propose a model for describing the $(\sqrt{3}\times\sqrt{3})R\pm30^\circ$ and $(3\sqrt{3}\times3\sqrt{3})R\pm30^\circ$ phases.

The measurements were carried out in a ultrahigh vacuum chamber (base pressure $< 10^{-10}$ torr) equipped with a scanning tunneling microscope (WA Technology), LEED optics, a cylindrical mirror analyzer, and a metal evaporator. The samples of $10\times5\times0.4$ mm^3 were cut from p-type Si(111) wafers and mounted onto a special sample holder which allowed direct resistive heating to 1500 K. The sample holder, designed by WA Technology, can be transferred from the fast-entry lock to the manipulator and STM stage. The sample cleaning procedure involved flashing to 1470 K to remove the native oxide layer, followed by several cycles of annealing and slow cooling which resulted in a sharp 7×7 LEED pattern and an Auger spectrum showing no impurities within the detection limit. Pd was deposited always at room-temperature. The Pd coverage was estimated using the $Pd(MNN)/Si(LVV)$ ratio of the integral Auger spectra and from the STM images by direct counting of the Pd related features. 1 ML is defined as the density of the Si atoms on the Si(111) surface: 7.8×10^{14} atoms/cm^2. More details of the calibration method and the evolution of the Pd coverage after room-temperature deposition and after annealing are given in Ref. 13. All STM images were taken at room temperature.

The $(\sqrt{3}\times\sqrt{3})R\pm30^\circ$ LEED pattern was formed by annealing of a Si sample with $\simeq 3$ ML of Pd deposited at room temperature to $\simeq 550$ K for 30 sec. Large area scans showed that the surface morphology is not uniform: large bright and dark areas with irregular shapes coexist. The size of the bright areas ranges from 1.9×10^5 Å^2 to 9×10^5 Å^2 and they cover $\simeq 45$ % of the surface. The small area scans [Figs. 1(a) and 1(b)] reveal that the bright areas are an ordered phase: they consist of islands located at adjacent terraces separated by monoatomic steps with a random orientation. Two types of features can be distinguished in these islands: domains with a hexagonal structure and peculiar triangular and rhomboid features which do not show a definite long-range order.

The structural units of the predominant hexagonal phase are protrusions with an average cross section of $\simeq 5.5$ Å which is an indication that they consist of more than one atom. From the line profiles we derived a lattice constant of 6.4 ± 0.15 Å consistent with the $\sqrt{3}$ unit cell. The separation between the protrusions along the $[11\bar{2}]$ direction is $\simeq 1$ Å. The corrugation measured along the $[1\bar{1}0]$ direction is 0.5 ± 0.2 Å. Since a change in the sample bias from -2 to 2.5 eV affected the contrast slightly, we believe that topographic effects are dominant. The domain boundaries within the same plane appear as a line of brighter protrusions. Closer inspection shows that the main defects are missing protrusions which are imaged

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as depressions within the $(\sqrt{3} \times \sqrt{3})R \pm 30^\circ$ areas showing corrugation of 0.7 ± 0.2 Å. We tentatively assign the protrusions as Pd clusters located on top of the Si layer.

The second type of features which share 10–15 % of the brighter areas with the $(\sqrt{3} \times \sqrt{3})R \pm 30^\circ$ phase are rather peculiar. They do not show a particular long-range order. Most of these features can be described as 60° triangles or rhomboids formed by removal of some of the $(\sqrt{3} \times \sqrt{3})R \pm 30^\circ$ protrusions. Closer inspection shows that triangles and rhomboids, each side of which consists of four protrusions, predominate. The line profiles along the protrusions forming the sides show the same separation and cross section measured for the protrusions constructing the $(\sqrt{3} \times \sqrt{3})R \pm 30^\circ$ phase. According to the height profile measurements along line A (perpendicular to the triangles' sides) the corrugation is the same (0.7 ± 0.2 Å) as that measured across the areas of absent protrusion in the $(\sqrt{3} \times \sqrt{3})R \pm 30^\circ$ islands. The in-registry of the protrusion's rows, forming the sides of the triangles and rhombi, with the adjacent in-plane $(\sqrt{3} \times \sqrt{3})R \pm 30^\circ$ domains reveals that these features should be formed by destruction of the $(\sqrt{3} \times \sqrt{3})R \pm 30^\circ$ domains due to penetration of Pd into the Si lattice. The predominant side's length of 19.2 ± 0.2 Å, which equals the $(3\sqrt{3} \times 3\sqrt{3})R \pm 30^\circ$ lattice constant, and the shape of these features prompts us to propose that they are an intermediate state of a $(\sqrt{3} \times \sqrt{3})R \pm 30^\circ$ to $(3\sqrt{3} \times 3\sqrt{3})R \pm 30^\circ$ phase transition.

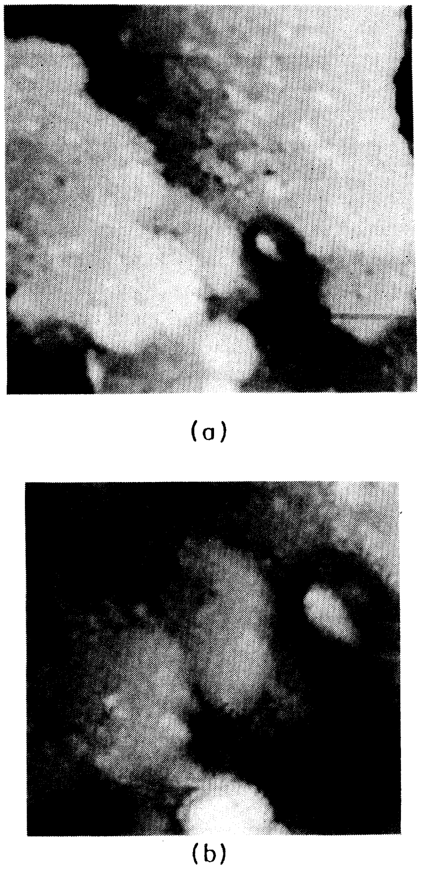

FIG. 1. STM images which shows brighter areas containing $(\sqrt{3} \times \sqrt{3})R \pm 30^\circ$ domains mixed with features related to formation of a Si-rich $(3\sqrt{3} \times 3\sqrt{3})R \pm 30^\circ$ phase. (a) 450×450 Å^2; (b) 190×190 Å^2. Bias 2.5 V, current 1 nA.

No in-registry features were observed in the large dark areas and the tip performance worsened after several scans. These areas should be considered as an amorphouslike Si phase which contributes to the enhanced background in LEED. The average roughness measured in these areas is about 2 Å. Very similar images were obtained after annealing for longer periods, when the $(\sqrt{3} \times \sqrt{3})R \pm 30^\circ$ LEED pattern was dissolved into the enhanced background and the Pd peak in the Auger spectrum attenuated to the noise level. This finding supports the assignment of the protrusions as Pd-related features.

On the basis of the present results we suggest the structural model shown in Fig. 2 which can satisfactorily describe the $(\sqrt{3} \times \sqrt{3})R \pm 30^\circ$ structure formed at elevated temperatures. In this model the $(\sqrt{3} \times \sqrt{3})R \pm 30^\circ$ structure only resembles a basal plane of Pd_2Si but it is actually an intermediate state of Pd chemisorbed on (1×1) Si(111) which precedes the formation of a true Pd_2Si phase. The arrangement and bonding of the Pd adatoms is similar to that of the Si-rich Pd_3 Si_2 plane which justifies the ultraviolet photoemission spectroscopy results for early formation of a silicidelike phase.[3–9] The model in Fig. 2 is in general agreement with the twist structure suggested on the basis of TEM/TED data where the $(\sqrt{3} \times \sqrt{3})R \pm 30^\circ$ structure, produced by deposition of a submonolayer of Pd at 570 K, is suggested to be a single Pd overlayer on top of (1×1) Si(111). According to the structural model suggested here the growth mechanism of an epitaxial (1×1) Pd_2 Si(0001) film observed at elevated temperatures involves an initial "chemisorption stage": Pd trimers form an adsorption complex with three Si atoms of the (1×1) Si(111) surface without causing a substantial disruption of the Si lattice. The suggested atomic arrangement of the $(\sqrt{3} \times \sqrt{3})R \pm 30^\circ$ stage is supported by the shape and size of the protrusions in the STM images which we relate to imaging of the Pd trimers. If the effects of the electronic structure are ignored, the corrugation of 0.5–0.7 Å measured along the $[1\bar{1}0]$ direction and across the sites of absent protrusions indicates that the Pd trimer is located on top of the (1×1) Si(111) bilayer. The validity of this suggestion is also supported by the 0.7 Å corrugation measured along line A in the region of the "$3\sqrt{3}$"-like features.

The structural model presented in Fig. 2 also accounts for the mechanism of formation of the Si-rich $(3\sqrt{3} \times 3\sqrt{3})R \pm 30^\circ$ phase as a result of temperature induced penetration of Pd trimers into the bulk. The $(3\sqrt{3} \times 3\sqrt{3})R \pm 30^\circ$ structure is formed by the remaining Pd trimers which tend to arrange themselves in rhombic structural units. Our STM images reveal the $(3\sqrt{3} \times 3\sqrt{3})R \pm 30^\circ$ structural units: they appear as single rhombi with sides built by four Pd trimers which gives a side length of 19.2 ± 0.2 Å equal to the $(3\sqrt{3} \times 3\sqrt{3})R \pm 30^\circ$ lattice constant. This structure is an intermediate and, as evidenced by LEED, converts to a (1×1) Si(111) with further increasing of temperature when all Pd is buried into the bulk. At the

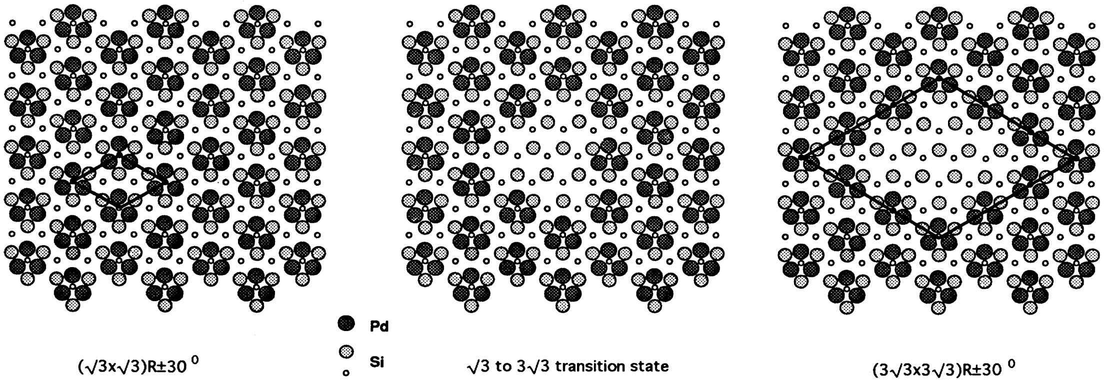

FIG. 2. Tentative structural models proposed to explain the formation of $(\sqrt{3} \times \sqrt{3})R \pm 30°$ and $(3\sqrt{3} \times 3\sqrt{3})R \pm 30°$ phases.

present stage of knowledge, when no serious investigations of the electronic structure exist, we are not able to offer a satisfactory explanation of the mechanism of the $(3\sqrt{3} \times 3\sqrt{3})R \pm 30°$ structure stabilization. We assume that there are strongly coverage-dependent kinetic and energetic factors ruling the processes of Pd diffusion subsurface and critical conditions for interconversion between the different intermediate phases preceding the formation of a true $\mathrm{Pd_2Si}$ film.

The model in Fig. 2 is also supported by the evaluations of the Pd coverage using both STM and Auger data.[13] Considering the bright areas covered by the $(\sqrt{3} \times \sqrt{3})R \pm 30°$ structure with local Pd coverage of 1 ML, we evaluated from the STM data Pd coverage of 0.45 ML. Taking into account the lower Pd concentration in the areas of the "$3\sqrt{3}$" features where $\simeq 50\%$ of the Pd related protrusions are absent leads to small reduction of the STM values down to $\simeq 0.40$ ML. Fair agreement with this value can be obtained from the Auger electron spectroscopy data supposing that the calibration factor, for the conversion of layer thickness (Å) to coverage (ML), for the $(\sqrt{3} \times \sqrt{3})R \pm 30°$ phase is of the order of the measured corrugation by STM, i.e., 0.7 Å per 1 ML. This leads to Pd coverage of 0.48 ML, fairly close to that obtained by STM. This result supports our model where the $(\sqrt{3} \times \sqrt{3})R \pm 30°$ structure is considered as a "chemisorption intermediate stage," because for an epitaxial (1 × 1) $\mathrm{Pd_2Si}(0001)$ layer the calibration factor, evaluated using STM and Auger or Rutherford backscattering data is 1.7 Å per 1 ML.[12,13]

In conclusion we have found that the low-coverage $(\sqrt{3} \times \sqrt{3})R \pm 30°$ and $(3\sqrt{3} \times 3\sqrt{3})R \pm 30°$ Pd phases formed after mild annealing should be considered as a Pd "chemisorption state" on a (1 × 1) Si(111) surface. The stoichiometry of the $(\sqrt{3} \times \sqrt{3})R \pm 30°$ structure is PdSi which mediates the formation of an epitaxial (1 × 1) $\mathrm{Pd_2Si}(0001)$ film. The $(\sqrt{3} \times \sqrt{3})R \pm 30°$ structural units are suggested to be Pd trimers located on top of (1 × 1) Si(111) forming a hexagonal structure. The Si-rich $(3\sqrt{3} \times 3\sqrt{3})R \pm 30°$ phase has been described as a result of temperature-induced penetration of some of the Pd trimers into the bulk. The remaining Pd trimers tend to form 60° rhombi the sides of which are built by four Pd trimers.

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[1] L. Braicovich, in *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, edited by D.A. King and D.P. Woodruff (Elsevier, Amsterdam, 1988), Vol. 5, p. 266.

[2] C. Calandra, O. Bisi, and G. Ottaviani, Surf. Sci. Rep. **4**, 271 (1984)

[3] P.S. Ho, G.W. Rubloff, J.E. Lewis, V.L. Moruzzi, and A.R. Williams, Phys. Rev. B **22**, 4784 (1980).

[4] G.W. Rubloff, P.S. Ho, J.F. Freeouf, and J.E. Lewis, Phys. Rev. B **23**, 4183 (1981).

[5] R.M. Tromp, E.J. van Loenen, M. Iwami, R.G. Smeenk, and F.W. Saris, Surf. Sci. **124**, 1 (1983).

[6] O. Bisi, O. Jepsen, and O.K. Andersen, Phys. Rev. B **36**, 9439 (1987).

[7] S. Nishigaki, T. Komatsu, M. Arimoto, and M. Sugihara, Surf. Sci. **167**, 27 (1986).

[8] S. Okada, K. Oura, T. Hanawa, and K. Saton, Surf. Sci. **97**, 88 (1980).

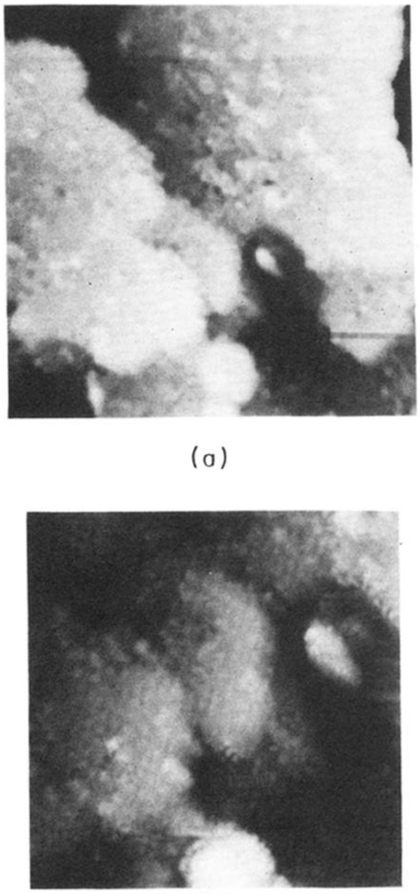
[9] J. Stohr and R. Jaeger, J. Vac. Sci. Technol. **21**, 619 (1982).

[10] J.G. Clabes, Surf. Sci. **145**, 87 (1984).

[11] K. Akiyama, K. Takayanagi, and Y. Tanishiro, Surf. Sci. **205**, 177 (1988).

[12] U.K. Köhler, J.E. Demuth, and R.J. Hamers, Phys. Rev. Lett. **60**, 2499 (1988).

[13] L. Casalis, C. Casati, R. Rosei, and M. Kiskinova (unpublished).



(a)

(b)

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