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Roles of defects induced by hydrogen and oxygen on the structural phase transition of Si(111)4×1-In

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The influences of surface defects created by hydrogen and oxygen adsorption on the $(4\times1)\rightarrow(8\times2)$ structural phase transition in an In/Si(111) system have been studied using low-energy electron diffraction. The transition temperature (T_c) decreased with the hydrogen exposure as compared to the clean surface, whereas it increased with the oxygen exposure. The H-induced decrease in the T_c is expected and explainable by the general destructive role of defects as random disorders in the transition. In contrast, the O-induced increase of the T_c is rather unusual. Mobile defects or doping effects may account for the assisting role of the O-induced defects in the condensation of the (8×2) low-temperature phase.

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I. INTRODUCTION

Recently, a number of metal-induced reconstructions formed on solid surfaces have drawn a fundamental interest by showing symmetry-breaking phase transitions.[1–8] Compared with the bulk, the surface reconstructions inherently possess reduced dimensionality and thus exhibit richer phenomena of the phase transitions. In addition, the role of defects and impurities (hereinafter referred to generically as defects) becomes increasingly important in the phase transition in these reduced-dimensional systems. A small amount of defects can affect the phase transition significantly by changing the global characteristics such as transition order and transition temperature (T_c). One prototypical example is a Sn/Ge(111) surface with one third of a monolayer (ML) of Sn, which shows a phase transition from a $\sqrt{3}\times\sqrt{3}$ structure at room temperature (RT) into a 3×3 structure at low temperature (LT).[9–14] It was suggested that the phase transition was mediated by defects and the T_c was shifted up by the presence of Ge-substituted Sn from the value expected for the ideal defect-free system.[9,10]

In chains on Si(111) formed with 1 ML of In are a quasi-one-dimensional (q-1D) model system where the effects of defects on the phase transition have also been studied.[2,15–23] This q-1D In/Si(111) system is known to undergo a phase transition from a 4×1 structure at RT (4×1-RT) to a symmetry-broken 8×2 structure at LT (8×2-LT) at about $120\sim130$ K. Simultaneously with this structural phase transition, an electronic transition also occurs as the electron density of states (DOS) at Fermi level vanishes[20] or dramatically drops[16,21,22] at LT. This transition has been attributed to the charge-density-wave (CDW) transition[2] due to the Peierls instability.[24]

For this q-1D system, a variety of influences of defects on the phase transition have been reported.[18,19,25,26] Ag and In atoms deposited on the 8×2-LT surface increased the surface conductivity at LT.[25] However, when In atoms were added to the system at RT, the conductivity measurement showed the phase transition occurring at a temperature higher than the T_c of the pristine surface.[19] Na impurities added at RT drove a metal-insulator transition by changing the metallic 4×1-RT system into the insulating 4×2-LT phase even at RT,[26] also suggesting the increase in T_c. Scanning tunneling microscopy (STM) studies also revealed different roles of defects in real space. Defects either locally pinned the 4×2-LT phase at temperatures above T_c,[21,27] or induced the 4×1-RT phase at temperatures below T_c.[21,23,27] On the other hand, hydrogen adsorption on the 4×1-RT surface also locally induced a period-doubling modulation in STM images.[18] This H-induced period-doubling modulation was found to be different from the symmetry-broken 8×2-LT phase in that the DOS at the Fermi level was hardly changed.

In this paper, we report on the contrasting influences of the defects created by two different gases, hydrogen and oxygen, on the phase transition of the In/Si(111) surface studied by using low-energy electron diffraction (LEED). The 4×1-RT surface exposed to hydrogen showed the transition to the 8×2-LT phase occurring at a lower temperature than that for the clean surface. This lowering of T_c indicates the suppression of condensation of the LT phase by defects as random disorders destroying the long-range ordering. In contrast, T_c was raised for the O-exposed surface suggesting the assisting role of the O-induced defects in the transition. Correlated arrangement of the O-induced defects or a hole-doping effect by oxygen adsorption is speculatively proposed to account for the O-induced increase in T_c.

II. EXPERIMENTS

Experiments were carried out in an ultrahigh-vacuum chamber equipped with LEED and STM. The base pressure was maintained below 1.2×10^{-10} Torr. The Si(111) sample was cut from a P-doped (n-type) Si wafer with an electrical resistivity of $5-10$ Ω cm and a miscut angle less than 0.5°. The In/Si(111)-4×1 surface was prepared by deposition of 1 ML of In from a Ta-wrapped In source on the Si(111) surface heated at about 400 °C.[28] Dosing of H_2 and O_2 gases onto the surface was done at RT through a guided tube in front of the sample directing the gas flow toward the sample surface. At the end of the tube, a W filament was heated to effectively dissociate the gas molecules into atoms. Since the

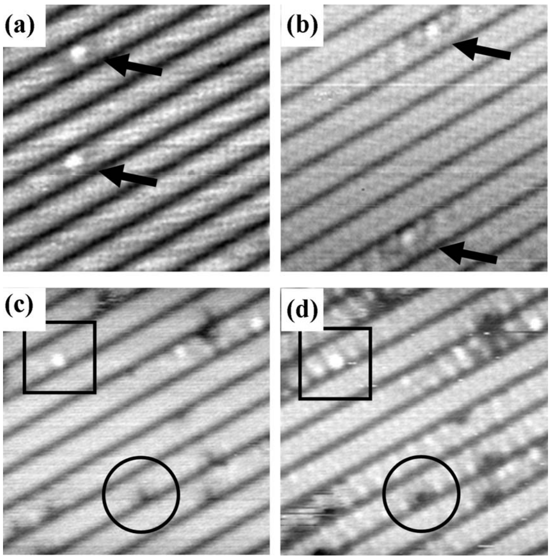

FIG. 1. Representative STM images from H-adsorbed (indicated as arrows) [(a) $V_s=-1.0$ V and (b) $V_s=-0.2$ V] and O-adsorbed (indicated as a circle and a square) [(c) $V_s=-0.8$ V and (d) $V_s=-0.2$ V] surfaces, respectively. On the O-adsorbed surface, the dark features dominantly appear while the bright features are minor.

amounts of the adsorbed H and O were unknown, the dosage is given by the gas exposure in units of L ($1\ \text{L}=1\times10^{-6}$ Torr sec). After dosing each gas with different amounts on the surface at RT, LEED pictures were taken with a charge-coupled device camera at different sample temperatures while cooling with liquid nitrogen.

III. RESULTS

Figure 1 shows representative STM images of the In/Si(111)4×1 surface monitored at RT after the surface was exposed to hydrogen and oxygen, respectively. Bright features are present in the images of the hydrogen-dosed surface [indicated with arrows in Figs. 1(a) and 1(b)]. In the images of the oxygen-dosed surface [Figs. 1(c) and 1(d)], dark features appear predominantly while bright features (these are different from bright H features) are also induced as a minority. The bright H features in Figs. 1(a) and 1(b) were previously identified as atomic hydrogen (H) adsorbed at the surface since they only appear when the filament before the tube was heated.[18] The O-features in Figs. 1(c) and 1(d) are not identified with regard to whether they are dissociatively adsorbed oxygen atoms (O) or molecularly adsorbed oxygen (O_2). Whether the filament was heated or not, the same O features were found. Regardless of their identities, the H and O features manifest similar characteristics in the images. At high bias voltages [Figs. 1(a) and 1(c)], they appear as just localized disturbances. The adsorption features, however, induce extended perturbations around the localized disturbances in the chain direction, as evident in the images taken at low bias voltages [Figs. 1(b) and 1(d)]. The extended perturbations induced by both adsorbates commonly have a double (×2) periodicity in the chain direction compared with that of the clean defect-free 4×1 surface. The H-induced extended perturbation was found to remain metallic and thus be distinct from the insulating (or poorly metallic) 8×2-LT structure.[18] Its origin is electronic rather than structural in that the perturbation is bias-voltage dependent and appears prominently at low bias voltages, i.e., near the Fermi level. The O-induced feature, though not thoroughly examined, also seems to be similar in origin.

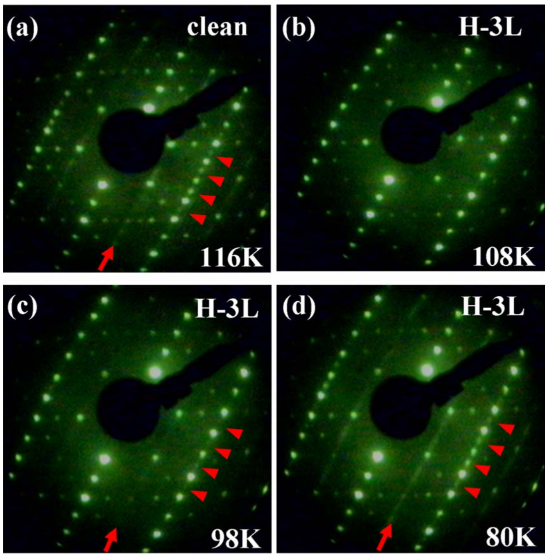

FIG. 2. (Color online) LEED pictures taken from (a) the clean surface (116 K), and the H-exposed (3 L) surface at different temperatures (b) 108 K (c) 98 K, and (d) 80 K. Both 8× spots and ×2 streaks are indicated with arrowheads and arrows, respectively.

Figure 2 shows representative LEED pictures of the clean and the H-exposed In/Si(111) surfaces taken at various temperatures. The LEED picture of the clean surface taken at 116 K, which is below the T_c (~126 K, which will be determined later) of the clean surface, showed an 8×2 pattern [Fig. 2(a)]. In contrast, the surface exposed to H with 3 L still remained in the 4×1-RT phase even at a lower temperature (108 K) [Fig. 2(b)]. Upon further cooling to a lower temperature (98K), the LEED pattern of the H-exposed surface just started to reveal both the 8× spots and ×2 streaks [Fig. 2(c)]. It is obvious that appearance of the 8× spots and ×2 streaks in the LEED pattern upon sample cooling is delayed for the H-exposed surface compared with the clean surface. At 80 K, the 8×2 LEED pattern developed strong, suggesting sufficient progress in the transformation into the 8×2-LT phase.

With the surface exposed to oxygen, a different trend was observed. Representative LEED pictures of the In/Si(111) surface exposed to different amounts of oxygen are shown in Fig. 3. While the clean surface showed a 4×1 LEED pattern at 129 K [Fig. 3(a)], all the O-exposed surfaces show 8×2 LEED patterns at the same or higher temperatures; 129 K with 2 L [Fig. 3(b)], 149 K with 4 L [Fig. 3(c)], and 172 K with 10 L [Fig. 3(d)], respectively. Overall, both the 8× spots and the ×2 streaks in the 8×2 LEED from the O-exposed surfaces become weakened and broadened as the oxygen exposure increases. However, their visibility at temperatures where the clean surface remains in the 4×1-RT phase clearly indicates that the O-covered surfaces undergo

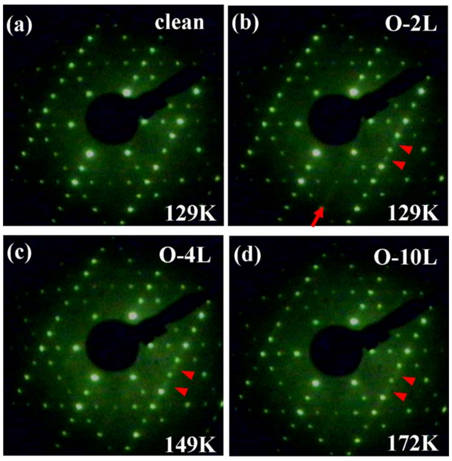

FIG. 3. (Color online) Representative LEED pictures taken from (a) the clean surface (129 K) and [(b)–(d)] the O-exposed surfaces with different exposures (b) 2 L (129 K), (c) 4 L (149 K), and (d) 10 L (172 K). Note that while the clean surface shows 4 × 1 LEED, all the O-exposed surfaces show the 8 × 2 LEED patterns.

the phase transition at higher temperatures than the clean surface.

For more accurate determination of T_c, the LEED intensities of the 8× spots in the LEED pictures taken at different temperatures were measured. Figures 4(a) and 4(b) show the measured intensities plotted as a function of temperature for several exposure levels of H and O, respectively. Clearly, the LEED spot intensity decreases with increased exposure to both H and O. T_c for each case was determined as the onset temperature where the intensity starts to rise up. In the case of the clean surface, T_c is determined to be ~126 K. The values of T_c's determined in this way are plotted as a function of H and O doses in Fig. 4(c).

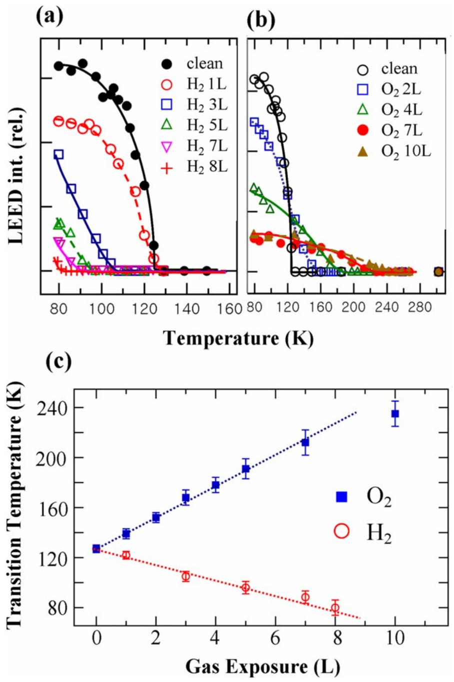

FIG. 4. (Color online) [(a)–(b)] Intensities of the eighth-order superstructure spots as a function of the sample temperature for H- and O-adsorbed surfaces with different exposures, respectively. (c) T_c vs gas exposures (in L). T_c for each case was determined as the onset temperature of the rise of the LEED intensity. The lines are guides to eyes.

Through the quantitative analysis of the temperature-dependent LEED intensity of the 8× diffraction spots inherent to the LT phase, we found the followings: (i) Hydrogen-induced defects lower T_c of the $4\times1\rightarrow8\times2$ phase transition. (ii) On the other hand, oxygen-induced defects raise T_c. (iii) The shifts in T_c increase monotonically with the dosing amounts of both hydrogen and oxygen gases. The T_c change is nearly linear with the dosing amounts, at least at the initial stages. (iv) The intensity-temperature curves near the transition become rounded for both cases compared with a rather sharp rise in the case of the clean surface.

IV. DISCUSSION

The decrease in T_c with the H dose indicates the effects of H-induced defects suppressing the $4\times1\rightarrow8\times2$ phase transition. This is expected rather than unusual, considering that the adsorbed H atoms are randomly distributed as shown in the STM image at RT [see Fig. 1(a)].[29] A random distribution of defects has destructive effects in two aspects, impurity scattering of electrons and local pinning of the CDW. The former breaks a coherent electron-hole pair with a total momentum of $2k_F$ and thus lowers the T_c of the CDW transition. As for the latter, defects can locally pin the fluctuating 1D-CDWs, as observed in the previous STM studies.[21–23] Although the pinning of the fluctuating 1D-CDWs induces local 4 × 2-LT structures even well above T_c,[21,27] it does not result in the condensation into the true 8 × 2-LT phase. Since randomly distributed defects fix the phases of their own pinned 1D-CDWs, the correlation between them is weakened. Even if the sample is cooled below the T_c of the pristine surface, the condensation into the LT phase may not occur. When the sample is cold enough, the energy gain in forming the 8 × 2-LT phase through the interchain coupling of the CDWs can overwhelm the energy gain through the defect-pinning CDWs without long-range ordering. Then the 8 × 2-LT phase is eventually formed at a temperature lower than the pristine T_c.

General influences of defects in the phase transition have been theoretically studied with different random-field models of statistical physics. It has been shown that the presence of random frozen dilute defects makes the transition occur at a lower temperature than in a pure system.[30–32] The sharp transition in the pure system may be rounded due to the presence of the defects. These theoretical conclusions were commonly derived for both first-order[31,32] and second-order[30] transitions. Indeed, Monte Carlo simulations applied to a real system, the $2\times1\rightarrow c(4\times2)$ phase transition of a Si(100) surface, also concluded that the transition region becomes broad and shifted to lower temperature due to the presence of defects.[33,34] The broadening and the shift to lower temperature of the transition under the influence of defects have been reported in other systems undergoing CDW (Refs. 35 and 36) or non-CDW (Ref. 37) phase transitions. The influence of H-induced defects on the phase transition of the In/Si(111) surface is also in good accordance with these general expectations.

In the context of the above discussion, the rounding of the $4\times1\rightarrow8\times2$ phase transition of the In/Si(111) surface with O-induced defects is expected, as also in the case of H-defects. However, the O-induced increase in T_c is quite exceptional. It indicates that the O-induced defects help condensation of the 8×2 phase during the sample cooling. This may be possible if the O-induced defects were spatially correlated instead of being randomly distributed. The 1D-CDWs pinned by the spatially correlated O-induced defects could interfere constructively both in longitudinal and in transverse directions. Then the long-range order of the 8×2-LT phase would be established at a temperature higher than the pristine T_c. However, like in the case of hydrogen adsorption, STM images show that the O-induced defects on the 4×1 surface are randomly distributed without long-range ordering at RT [see Fig. 1(b)].[18,38] In order to have spatially correlated distribution of the O defects at least near the transition, the O defects need to become mobile and rearrange themselves during cooling of the sample. The rearrangement of the defects is then expected to be due to the defect-defect interaction mediated by the formation of the CDW. Mobile defects assisting the formation of long-range ordering of the broken-symmetry structures have been theoretically discussed[39] and proposed to explain the nonrandom distribution of the defects observed for several surface systems.[3,9,10]

Another possible cause for the O-induced increase in T_c is the alteration of the Fermi level of the surface by hole doping. The 4×1-RT surface has three metallic surface-state bands, namely, the m_1, m_2, and m_3 bands.[40] The m_3 band crossing the Fermi level with about a half filling is known to be responsible for the CDW transition with a double periodicity in the chain direction.[2] Using angle-resolved ultraviolet photoemission spectroscopy (ARUPS), a value of $k_F \approx 0.5(G/2)$ of the m_3 band was measured for the clean surface. However, the theoretically calculated value of k_F is $0.48(G/2)$,[41] which is slightly smaller than the perfect commensurate condition, $2k_F = G/2$ (G and k_F stand for a reciprocal-lattice vector and the Fermi wavevector, respectively). Is it possible to relate the explanation of the raise of the transition temperature in terms of hole? If the theoretical value is correct, O-defects depriving electrons of the surface (in other words, hole doping by O-defects) will reduce the filling of the m_3 band (as well as of the m_1 and m_2 bands) and thus lower the Fermi level. The O-induced lowering of the Fermi level will in turn increase k_F to bring $2k_F$ closer to $G/2$. This approach toward the perfect Fermi-surface nesting condition for the commensurate CDW would make the condensation of the commensurate CDW easier and raise the T_c of the transition. A similar doping argument has recently been used to explain the conversion of the 4×1 phase into the 8×2 phase by illuminating the surface with intense light.[42] The optical pumping using external photoexcitation supplies holes to the surface. We also observed the decrease in T_c by the introduction of Na impurities and attributed it to the similar but opposite doping effect (electron doping).[43] This scenario needs to be checked by investigating the electronic structures using ARUPS.

In conclusion, we have investigated the changes in T_c of the structural phase transition of the q-1D In/Si(111) surface exposed to different gasses, namely, hydrogen and oxygen. T_c was found to be lowered for the hydrogen case but raised for the oxygen case. These changes in T_c indicate opposite influences of the H-induced and O-induced defects on the 4×1-RT$\rightarrow8\times2$-LT phase transition, suppression by the former and enhancement by the latter driving the transition. The H-induced decrease in T_c was explained by the general view that the defects acting as random disorders inhibit or delay the long-range ordering. However, the unexpected O-induced increase in T_c is proposed to be either due to mobile defects or due to the hole-doping effect by oxygen adsorption changing the Fermi level and thus the Fermi-nesting condition for the formation of the commensurate CDW. Further experiments, including low- or variable-temperature STM measurement as well as photoemission spectroscopy measurement are called for in order to distinguish between the possible scenarios.

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