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Hysteresis in phase transitions at clean and Au-covered Si(111) surfaces

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By measuring the temperature dependence of the superlattice-spot intensity in reflection high-energy electron diffraction from a clean Si(111) surface during the phase transition between 7×7 and 1×1 structures, a hysteresis was found with a temperature difference of 5 °C between heating and cooling processes. We conclude that a first-order phase transition is present. Hysteresis was barely observed for the (5×2 or $\sqrt{3}\times\sqrt{3}$)-1×1 phase transitions of Au-induced superstructures.

Dynamic processes such as epitaxial growth on surfaces have been extensively studied with various sophisticated techniques.[1] Phase transitions of surface structures are one of the main subjects of these studies, partly because the reduced dimensionality of the system allows for a wider variety of phase transitions compared to three-dimensional (3D) systems and thus provide a testing ground for theoretical models.[2]

Since the report by Lander[3] of a reversible transformation at ~850 °C between 7×7 and 1×1 structures on a clean Si(111) surface, a number of groups have investigated the transition experimentally as well as theoretically. However, any understanding of this transition appears to be very limited. Even the order of the phase transition is still controversial. The nature of the transition inevitably depends on the structure of the 1×1 high-temperature phase as well as the 7×7 dimer-adatom stacking-fault (DAS) structure[4] at low temperature. Ino[5] observed a gradual disappearance of the 7×7-superlattice spots at the transition, without broadening, in reflection high-energy electron diffraction (RHEED), which was quantitatively confirmed in a recent report by Chevrier, Vinh, and Cruz.[6] Ino also found diffuse spots of a $\sqrt{3}\times\sqrt{3}(R\,30^\circ)$ periodicity in the 1×1 phase, which were also observed in low-energy electron diffraction (LEED).[7] This indicates that the 1×1 high-temperature phase is not a simple truncated (111) face of a bulk crystal. From the striking observations of reflection electron microscopy[8,9] (REM) and low-energy electron reflection microscopy,[10] the transition was concluded to be of first order by taking into account the fact that the 7×7- and 1×1-phase domains separately coexist during the transition. No appreciable hysteresis could be observed. Helium-atom diffraction experiments[11] led to the conclusion that a first-order transition of an order-disorder type occurs. On the basis of rocking-curve measurements in RHEED, Kohmoto and Ichimiya[12] also inferred the same type of transition, but not a simple order-disorder process, and proposed a structural model for the 1×1 phase with adatoms randomly adsorbed over a relaxed bulklike surface. A similar model had been discussed in Ref. 7. The presence of adatoms on a 1×1 substrate was also inferred by observing the shift of monatomic steps in REM images during the transition.[9] The first REM observation[8] and a recent high-temperature scanning-tunneling-microscopy[13] (STM) study also revealed that atomic step edges play an important role in the transition. Symmetry considerations led to the conclusion that the 1×1-7×7 transition cannot proceed via a continuous phase transition.[14,15] On the contrary, in LEED observations,[16,17] the continuous and gradual changes in spot intensities during the phase transition led to the conclusion that a second-order transition and an order-disorder transition occur, resulting in excess diffuse scattering appearing in place of the 7×7 spots. MacRae and Malic[18] confirmed this conclusion from a detailed analysis of LEED spot profiles. Tanishiro, Takayanagi, and Yagi examined the contrast of the 7×7 domain in REM images,[19] and reversed the earlier conclusion,[8] suggesting a second-order transition.

In addition to the controversy over the order of the phase transition, there is another interesting question, namely, whether or not there exists a transient structure such as a 7×7 reconstruction, without the adatoms of the DAS model, during the phase transition.[20,21] The problems regarding this phase transition are considered to be closely related to homoepitaxy of Si on the Si(111) surface, in which the 7×7 structure on the substrate must be converted into a 1×1 structure in order to grow, and the surface of the Si epilayer reconstructs in turn into the 7×7 structure from a 1×1 structure.

In this paper we again measured the intensity changes of the 7×7-superlattice spots in RHEED during the phase transition with precise temperature control. A hysteresis with a temperature difference of about 5 °C was observed in the intensity changes between in heating and cooling processes across the transition temperature. The phase transition is concluded to be of first order. For comparison, furthermore, similar measurements for reversible structural transitions at Au-deposited Si(111) surfaces were carried out. In the case of the transitions between Au-induced superstructures [Si(111)-5×2-Au and

β-$\sqrt{3}\times\sqrt{3}$-Au (Ref. 22)] and 1×1-Au phases appreciable hysteresis could not be observed with our experimental precision.

The experiments were performed with a conventional ultrahigh vacuum chamber with a RHEED system of 15-kV acceleration[5] and metal-evaporation sources of alumina-coated W baskets. A p-type Si(111) wafer of 8–18 mΩ cm resistivity and $25\times4\times0.4$ mm^3 size was used. The surface was cleaned by several flash heatings up to 1200 °C with dc current of 9.0 A fed through the wafer, and by cooling down. On cooling, a temporary annealing for about 30 sec at a temperature just below the 1×1-7×7 transition was carried out to make the structural conversion complete on the whole surface,[17,19,23] resulting in a clear 7×7 RHEED pattern at room temperature (RT).

The sample temperature was controlled by a dc heating current supplied with a stabilized power supply in constant-current mode. The temperature was measured with an optical pyrometer, with an estimated accuracy of ±20 °C. Since the temperature (T) is empirically related to the heating current (I) through $\log T \propto \log I$,[24] a calibration curve can be made to convert the current reading into temperature. The precise control of the relative change in temperature was then easily achieved with good reproducibility by accurate control of the heating current and sufficient waiting time for temperature stabilization, although absolute values of temperature were not accurately determined in the present study. In fact, the critical temperature of the 7×7-1×1 transition in this paper (800 °C) seems slightly lower than the literature values (830–870 °C). A temperature change of 1 °C corresponded to a current change of about 10 mA at the transition around 800 °C with a heating current of 2 A. Starting from 760 °C in the 7×7 phase (after being maintained for about 10 min at this temperature for stabilization), we heated up the sample stepwise with about a 1 °C increment up to 805 °C to convert the surface into the 1×1 phase. 30 sec or 1 min was allowed at each temperature step to let the system equilibrate. At each temperature, a picture of the RHEED pattern was successively taken with a television camera in a $512\times480\times8$ bit format through an average of 32 frames, and stored in a magneto-optical disk. Symmetrically the same measurements were followed in the cooling process, starting from 805 °C in the 1×1 phase to 760 °C to return to the 7×7 one. After successive measurements both in the heating and cooling processes across the transition, which took 45 or 90 min in total, integrated intensities of individual superlattice spots were analyzed from the stored image data.

Figure 1 shows the changes in the integrated spot intensity [without a correction of the Debye-Waller (DW) factor] of the $(\frac{1}{7},\frac{3}{7})$ superlattice reflection from a clean Si surface. Hysteretic changes with a temperature difference of about 5 °C is noticed during steep changes in intensity in the interval of 785–800 °C, while the relatively slow temperature dependences over the region below 785 °C coincide with each other. There were no indications of peak broadening during the transition. The same hysteretic changes were also observed with other nonequivalent 7×7-superlattice reflections. The results were independent of the waiting time of each temperature step in the heating-cooling processes, 30 sec or 1 min. We also carried out two successive series of heating-cooling processes, i.e., heating, cooling, heating, cooling across the transition to confirm the reproducibility. From the reason mentioned below, the sample temperature was believed to be equilibrated within at least 1 °C precision at each temperature step both in the heating and cooling processes. At each negative or positive temperature increment over the temperature range presented, the voltage drop between a pair of voltage pickup contacts of the four-probe-resistance-measurement sample holder[25] during the flowing heating current, swiftly stabilized within $\frac{1}{1000}$ of its value with a few seconds. The voltage drop divided by the current follows a temperature dependence of $\exp(-E_g/2kT)$ at elevated temperatures, where E_g is the band-gap energy of Si. This is the same as that of the resistance of an intrinsic semiconductor, which is very sensitive to the temperature. Therefore, the temperature stabilization will be confirmed with this voltage drop.

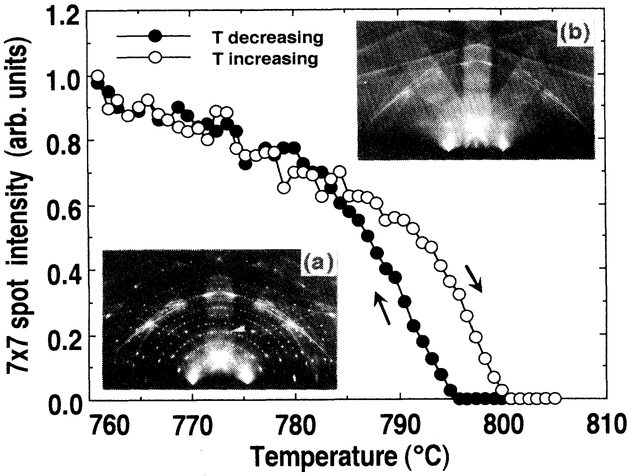

FIG. 1. Integrated intensity of the $(\frac{1}{7},\frac{3}{7})$ superlattice RHEED spot from a clean Si(111)-7×7 surface as a function of temperature. $[11\bar{2}]$ incidence. The RHEED patterns of a 7×7 phase at RT (a) and a 1×1 phase at 805 °C (b) are inserted.

Although a similar temperature difference of about 3 °C between the warming and cooling curves across the transition was reported in a LEED experiment by Bennett and Webb,[17] they did not conclude the existence of hysteresis, attributing that the intensity on the cooling curve had not reached a steady value because of a slow equilibration rate. According to them, the 7×7-superlattice spot intensity slowly equilibrates with a $t^{-1/2}$-diffusive tail after an initial period of exponential relaxation in the case of a 1×1-7×7 transition by a negative temperature increment (t is time). We carried out similar experiments as theirs, in which the temperature was suddenly dropped across the transition and the time evolution of the superlattice spot intensity was monitored. Although we also observed a similar "critical slowing down" phenomenon as they did (Fig. 17 in Ref. 17), the spot intensity reached its final value at most within 20 sec, shorter than their results. So we can safely say that, in our observations, the spot intensity as well as temperatures were equilibrated at each temperature step with 30-sec intervals. The hysteretic change confirmed in this way is now an unequivocal signature of a first-order transition. As discussed later, some reasons such as strain field[6,15,19] may raise the apparent broadening of the transition.

Figure 2(a) shows a similar change in the integrated spot intensity of the $(0,\frac{1}{5})$ superlattice reflection from the 5×2 structure with about 0.5 ML Au coverage[22,26] without the correction of a DW factor. In contrast to Fig. 1 we could not conclude the existence of hysteresis with well-grounded reasons, although a temperature difference of about 1 °C between the heating and cooling curve is seen. Any peak broadening was not observed at this transition. For the case of the β-$\sqrt{3}\times\sqrt{3}$-Au (about 1 ML Au coverage) to the 1×1-Au transition[22,27] as shown in Fig. 2(b), the intensity of the $(\frac{1}{3},\frac{1}{3})$ superlattice spot gradually changed in a wider temperature range compared with the curves in Figs. 1 and 2(a). Any hysteresis was again barely perceptible. The peak appeared to become streaky during the transition in this case, suggesting a continuous transition. In this way, negligible hystereses at these transitions on Au-covered surfaces may justify our experimental precision of temperature control.

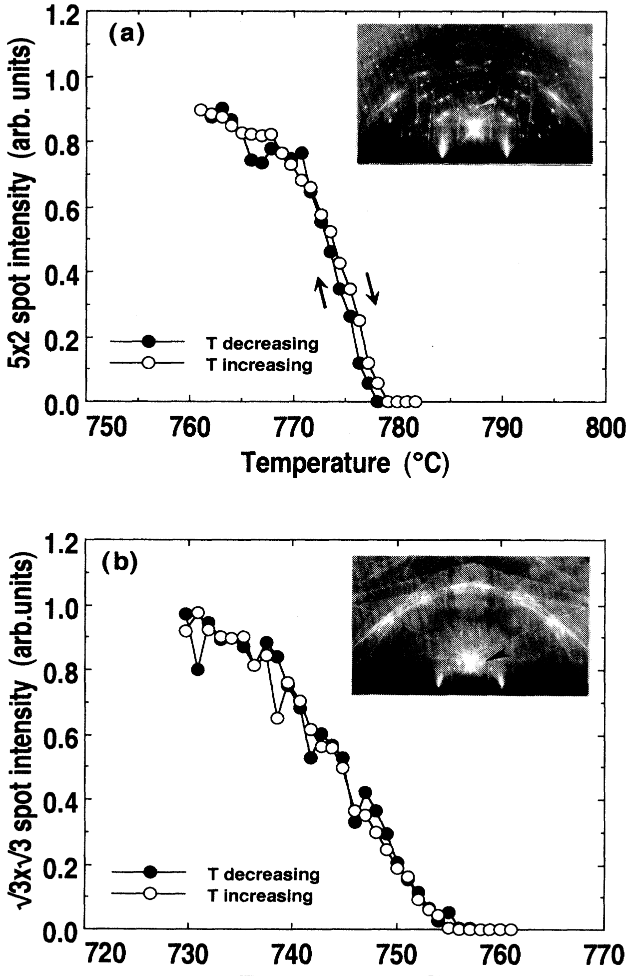

FIG. 2. (a) Integrated intensity of the $(0,\frac{1}{5})$ superlattice RHEED spot from the Si(111)-5×2-Au surface (inserted RHEED pattern), and (b) that of the $(\frac{1}{3},\frac{1}{3})$ spot from the Si(111)-β-$\sqrt{3}\times\sqrt{3}$-Au surface (inserted RHEED pattern) as a function of temperature, respectively.

In addition to the changes in intensity of superlattice spots reported here, the measurements of their profiles, relative intensity distribution, and time dependence of spot intensity with temperature changes are now in progress and will be soon reported elsewhere.

Although we cannot conclude at present whether the transitions of 5×2-Au and β-$\sqrt{3}\times\sqrt{3}$-Au to 1×1-Au are of first order or continuous (Świech, Bauer, and Mundschau concluded the transition of 5×2-1×1 to be first order[28]), negligible hysteresis during these transitions are distinctly different from the appreciable hysteresis for the 7×7-1×1 case. If we adopt structural models for Au-induced superstructures, such as often inferred ones[26,27] in that Au atoms arrange over a bulklike Si(111) substrate, the negligible hystereses are attributable to order-disorder processes involving only the Au adsorbates (1 ML or less) without the rearrangement of Si atoms in the substrate, while the appreciable hysteresis for the 7×7-1×1 case originates from the rearrangement of Si atoms in at least a DAS layer (2 ML or more). In this sense, the 7×7-1×1 transition could be said to be more 3D-bulklike.

The fractional-order spots of $(\frac{3}{7},0)$, $(\frac{4}{7},0)$, $(\frac{3}{7},\frac{1}{7})$, $(\frac{4}{7},-\frac{1}{7})$, and equivalent ones in the 7×7 RHEED pattern from a clean Si(111) surface are known to be stronger than other superlattice reflections, due to the interference of waves scattered from adatom arrays of 2×2 periodicity in the DAS unit.[29] This feature was observed to remain during the 7×7-1×1 transition, implying that the structural conversion is not triggered by randomizing the adatom arrangement, but that the dimer-stacking fault layers are dissolved at the same time with the topmost adatom layer. Reversibly, the conversion of 1×1-7×7 also seemed to proceed by simultaneous construction of each "component" in the DAS unit. In other words, there seems no transient structure such as a "δ 7×7" structure[30] during the transition, which seems consistent with a STM observation,[13] while some reports suggest a transient structure of a 7×7 periodicity without adatoms near the transition.[20,21]

As observed by REM (Refs. 8, 9, and 19) and STM (Ref. 13), the atomic step configuration on the surface varies and 2D sublimation islands appear on the terrace due to the redistribution of Si atoms during the 7×7-1×1 transition. Such a displacive transition is considered to be strongly influenced by impurities, defects, and strains on the surface. Bauer (p. 157 in Ref. 2) suggests that in the carbon-contaminated region the transition temperature is reduced due to the 1×1 stabilizing and step-pinning effects of the carbon. This is the reason why the apparent continuous transition occurred over a wide temperature range of about 50 °C in the previous diffraction experiments,[2,16,17] while the transition temperature range observed in the microscopy studies[8,10] is only around 10 °C. Looking at the steep decrease of the 7×7 spot intensity in the ranges of 785–795 °C in the temperature-decreasing process and 790–800 °C in the temperature-increasing process in Fig. 1, the transition in our experiment seems to take place in a temperature range as narrow as the previous microscopy observations (compare Fig. 1 in the present study with Fig. 5 in Ref. 8). From this consideration, we believe that trace carbon negligibly affects our results.

In addition to subsurface carbon, a high density of irregular steps and other kinds of defects will seed the phase transition due to strain fields on the surface. These make it difficult to observe hysteresis with a metastable surface in a truly thermodynamical sense of an ideal system. So there is a possibility that the hysteretic changes reported here depend upon the step density on the surface. Similar measurements, then, may be needed with step-bunched or -antibunched surfaces, or vicinal surfaces.

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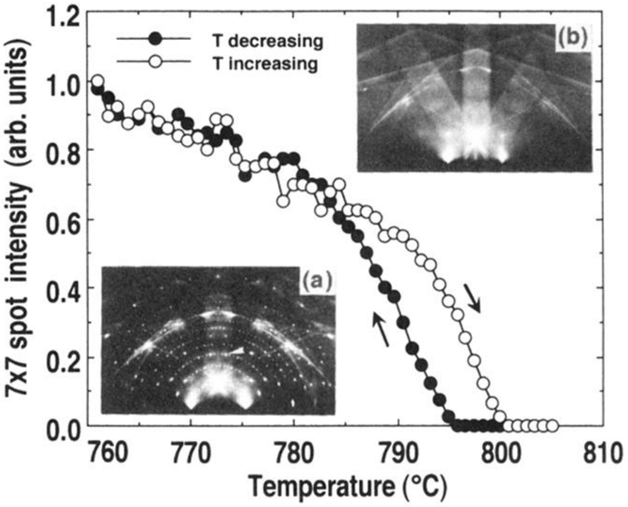

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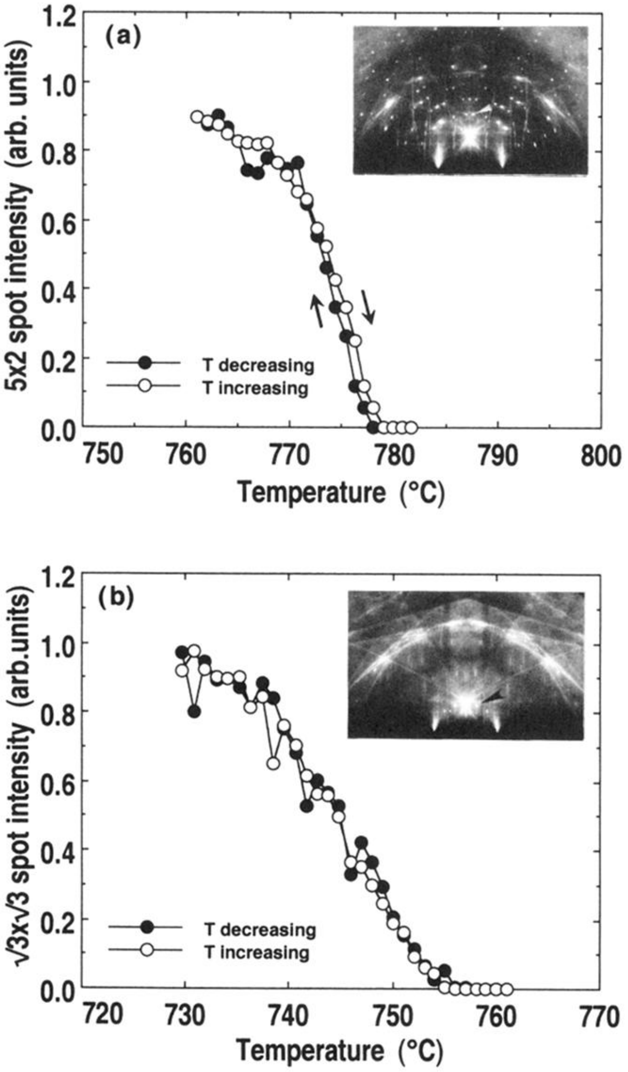

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