Condensation of ground state from a supercooled phase in the Si(111)-(4×1) → (8×2)-indium atomic wire system

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I. INTRODUCTION

The indium induced (4×1) reconstruction on Si(111) is a prototypical atomic wire system of metal atoms on a surface and has been thoroughly investigated since it was first mentioned in 1964.1,2 During the last decade, the system has attracted attention, because the indium wires undergo a reversible phase transition from the (4×1) state. The immediate recovery of the system to the ground state is hindered by an energy barrier for the collective motion of the indium atoms along the reaction coordinate from the (4×1) to the (8×2) state. This metastable, supercooled state can only recover through nucleation of the ground state at defects like adsorbates or step edges. Subsequently, a recovery front propagates with constant velocity across the surface and the (8×2) ground state is reinstated. In a combined femtosecond electron diffraction and photoelectron emission microscopy study, we determined—based on the step morphology—a velocity of this recovery front of \( \sim 100 \text{ m/s} \).

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The HT (4×1) structure is composed of indium atoms arranged in zigzag chains [see Figs. 1(c) and 1(f)] for the low energy electron diffraction (LEED) pattern and the real space structure of the outermost surface layer. Upon cooling, the indium atoms rearrange in distorted hexagons, locally creating a (4×2) structure within the atomic wire. The nonvanishing interaction between two adjacent wires results in the observed LT (8×2) structure [see Figs. 1(a) and 1(d)] for the LEED pattern and the real space structure.\(^{11,12}\) Figure 1(b) shows that the intensity of the (00) spot decreases at 131 K upon heating and recovers at 120 K upon cooling. The existence of this hysteretic behavior during temperature cycling through the (8×2) → (4×1) phase transition proves the first order nature of the phase transition.\(^{1,17}\) The (4×1) spot exhibits the opposite behavior: its intensity increases upon transition from the LT to the HT state by a factor of two upon heating and decreases again upon cooling. The transfer of intensity from the (8×2) spots to the (4×1) spots is observed for almost all of the (4×1) spots.\(^{1,17}\) Such a rise of intensity on the expense of the (8×2) spots can be rationalized by simple kinematic scattering theory: the overall number of diffracted electrons remains constant as the position of the indium atoms during the transition from (8×2) to (4×1) structure changes by less than 0.1 Å (Ref. 15)—it is thus small compared to the interatomic distances.

The observed hysteresis is direct evidence for the existence of a significant energy barrier between the (8×2) and the (4×1) HT phase at \( T_c \).\(^{1,16}\) Such an energy barrier has also been predicted by density functional theory for low temperatures \( T < T_c \). The ground state potential energy surface (PES) shown in Fig. 1(e) exhibits three minima; two of them are the degenerate (8×2) LT-ground state \( E_{\text{gap}} = 0.1 \text{ eV} \) below the (4×1) HT state. The HT and LT states are separated by symmetric barriers of \( E_{\text{barrier}} = 40 \text{ meV} \).\(^{17}\)
When irradiated by an IR femtosecond laser pulse, the surface is photoexcited.\textsuperscript{17–21} For sufficiently high incident fluences ($\Phi_\text{in} > 2$ mJ/cm$^2$), the entire surface undergoes a photoinduced transition from the LT to the HT state.\textsuperscript{17,18} It is important to note that the structural transition occurs before an overall heating of the surface can be detected: the transient heating of the surface is delayed by 6 ps (Ref. 22) with an overall temperature rise between $\Delta T = 15–70$ K for incident fluences of $\Phi_\text{in} = 2–7$ mJ/cm$^2$, respectively. Considering the static sample temperature $T_0 = 30$ K $< T_c$, the maximum transient surface temperature $T_{\text{max}}$ (6 ps) $=(100 \pm 10)$ K at $\Phi_\text{in} = 7$ mJ/cm$^2$ remains below $T_c = 130$ K. Thus, the structural transition must be nonthermal and is driven by electronic entropy in less than one picosecond.\textsuperscript{19}

The immediate recovery of the system LT (8 x 2) ground state is prevented by the 40 meV barrier between HT and LT phases. The existence of this barrier has also been confirmed in an independent time-resolved electron spectroscopy study.\textsuperscript{17} At 30 K, i.e., with $k_B T = 2.5$ meV, the barrier cannot be overcome by thermal excitation on the observed time scale. In our previous work, we have shown that adsorbates from the residual gas act as seed for the recovery of the ground state, which is mediated by a 1D recrystallization front that propagates like a row of falling dominoes.\textsuperscript{17} Accordingly, with increasing adsorbate density, the time-constant for recovery of the ground state decreases. From a comparison of the density of adsorbates with the step morphology of the Si(111) substrate, a direct determination of the recovery front's velocity is possible which is independent of the adsorbate density.

II. EXPERIMENTAL SETUP AND SAMPLE PREPARATION

The experiments were performed under ultrahigh vacuum conditions at a base pressure of $p < 10^{-10}$ mbar. Well oriented Si(111) samples (Virginia Semiconductors, phosphor doped, 0.6–1.0 $\Omega$ cm, miscut < 0.1°) were mounted on a liquid Helium cryostat, allowing for sample cooling to a minimum temperature of 30 K. Heating of the cryostat allowed us to adjust the sample temperature between 30 K and 450 K. The sample was heated by direct current heating. Clean Si surfaces were prepared by repeated short flash-anneal cycles up to 1250°C.

One monolayer (ML, 1 ML = 7.8 x $10^{14}$ atoms cm$^{-2}$) of indium atoms was deposited \textit{in situ} from a graphite crucible at a sample temperature of 450°C. Self-assembly of the indium atoms results in the formation of the HT (4 x 1) reconstruction in three equivalent rotational domains. The integrity of the reconstruction prior to deposition, during deposition, and after each experiment was confirmed by low-energy electron diffraction (LEED) and reflection high-energy electron diffraction (RHEED). The step morphology of the samples was determined in a photoelectron emission microscope (PEEM) \textit{after in situ} step decoration through submonolayer deposition of Ag at slightly elevated temperature.

Time-resolved RHEED is employed to follow both the reversible excitation from the ground state to the HT phase and the recovery back to the ground state. We applied a pump-probe scheme in which ultrashort laser pulses excite the sample and 30 keV electron pulses probe the temporal evolution of the diffraction pattern at different time delays $\Delta t$.\textsuperscript{23,24} We used 800 nm laser pulses of 80 fs duration from a Ti:Sapphire chirped pulse amplifier with a 5 kHz repetition rate. A tilted pulse front scheme compensated the velocity mismatch at the sample between the electrons (under grazing incidence) and the laser pulses (under normal incidence).\textsuperscript{25} The temporal resolution of the entire experiment is 330 fs (full width at half maximum of the temporal instrumental response function).\textsuperscript{26}
All RHEED experiments were performed at a sample base temperature of $T_0 = 30$ K. Stationary heating of the cooled Si substrate through the incident laser irradiation was less than 4 K. The PEEM micrographs were recorded at room temperature.

III. RESULTS AND DISCUSSION

The transient intensities of the $(8 \times 2)$ and $(4 \times 1)$ spots in the RHEED diffraction pattern are analyzed to determine the relative fractions of the surface in the HT and LT phase on a femtosecond time scale. Figures 2(a) and 2(b) depict the changes of the RHEED spot intensity through the first few picoseconds of the structural transition from $(8 \times 2)$ LT to $(4 \times 1)$ HT state. The transition to the HT-phase on a subpicosecond time scale is reflected in the disappearance of all $(8 \times 2)$ spots. On the same time scale, complementing this behavior, the $(4 \times 1)$ spot intensity increases by a factor of two. Figure 2(c) shows a transient drop of $(4 \times 1)$ spot intensity with a minimum at 6 ps time delay which is caused by the Debye-Waller effect and is due to delayed heating of the surface.\(^{22}\)

The excited HT phase survives up to $(3 \pm 1)$ ns as is evident from the rather slow drop-off of the $(4 \times 1)$ spot intensity, which is shown in Fig. 2(d). We explain this slow recovery of the LT ground state through a 1D recovery front along the indium wires starting shown in Fig. 2(d). We explain this slow recovery of the LT ground state by a 1D recovery front along the indium wires starting shown in Fig. 2(d). We explain this slow recovery of the LT ground state by a 1D recovery front along the indium wires starting shown in Fig. 2(d). We explain this slow recovery of the LT ground state by a 1D recovery front along the indium wires starting shown in Fig. 2(d). We explain this slow recovery of the LT ground state by a 1D recovery front along the indium wires starting shown in Fig. 2(d). We explain this slow recovery of the LT ground state by a 1D recovery front along the indium wires starting shown in Fig. 2(d). We explain this slow recovery of the LT ground state by a 1D recovery front along the indium wires starting shown in Fig. 2(d). We explain this slow recovery of the LT ground state by a 1D recovery front along the indium wires starting shown in Fig. 2(d). We explain this slow recovery of the LT ground state by a 1D recovery front along the indium wires starting shown in Fig. 2(d).
Step bunches where the individual steps are so close to each other that they cannot be distinguished contain narrow terraces of widths $\Gamma_i < 50$ nm. These step bunches cover an area $\sim 10\%$ of the surface as estimated from image filtering with contrast enhancement. We therefore excluded these areas for the determination of the terrace width probability $p(\Gamma)$ which is defined as the probability to find a terrace of width $\Gamma$. This distribution $p(\Gamma)$ is plotted in the inset of Fig. 3 for terraces wider than $\Gamma_i > 50$ nm. The value for the narrowest terraces is flawed because of the limited resolution of the PEEM. Apart from that, the terrace width distribution can be fitted well by a power law behavior $p(\Gamma) = (C_0^2 \Gamma)^{-i} (1 - (C_0^2 \Gamma)^{-i})^{(i-1)}$, indicating a geometric terrace width distribution with a mean value $\langle \Gamma \rangle = (298 \pm 8)$ nm.

For further analysis, we assume a propagation of the recovery front with constant mean velocity $v_{\text{rec}}$ as sketched in Fig. 4(a). Based on the terrace width distribution $p(\Gamma)$, the temporal response of the system can be modeled. The time $t_i = \Gamma_i / v_{\text{rec}}$ is required for the complete recovery of a terrace of width $\Gamma_i$ to the ground state. The fraction of a terrace that already recovered the ground state can be denoted as a function of time as

$$p_r(t \leq t_i) = t \cdot v_{\text{rec}} / \Gamma_i \quad \text{and} \quad p_r(t > t_i) = 1.$$

An example for the recovery of terraces with a width $450 < \Gamma_i < 520$ nm is shown as a red shaded triangle in Fig. 4(b). The height of the triangle reflects the area of the terraces which are still in the $(4 \times 1)$ HT state as a function of time delay $\Delta t$. The linear recovery starts at $\Delta t = 0$ and ends at $\Delta t = 440$ nm/v_{\text{rec}} when the conversion of the $(4 \times 1)$ HT to the $(8 \times 2)$ LT state on these terraces is completed.

The fraction of the surface $p_{(4 \times 1)}(t)$ which has not yet recovered the $(8 \times 2)$ LT ground state is then given by

$$p_{(4 \times 1)}(t) = 1 - \int_{0}^{\Gamma_{\text{max}}} p_r(t) \cdot p(\Gamma) \cdot \Gamma \, d\Gamma,$$

with $\Gamma_{\text{max}}$ being the maximum observed terrace width.

The resulting $p_{(4 \times 1)}(t)$ is shown as a solid red line in Fig. 4(b) as a function of $\Delta t$ in units of nanometers per $v_{\text{rec}}$. It resembles an exponential decay. The slope for short time delays is indicated by the dashed red line, which yields a recovery velocity of $v_{\text{rec}} = 298$ nm. Comparing this value to the decay time constant $t_{\text{rec}} = (3 \pm 1)$ ns of the $(4 \times 1)$ intensity that we obtained from the dashed line in Fig. 2(d), we conclude a maximum velocity of the recovery front $v_{\text{rec}} = (100 \pm 40)$ m/s.

IV. CONCLUSIONS

Time resolved electron diffraction and photoelectron emission microscopy were used to study the recovery kinetics from a metastable supercooled state to the ground state in the Si(111)–(8 $\times$ 2)–In atomic wire system. This system exhibits a first order structural phase transition at $T_c = 130$ K when it is converted to a high symmetry $(4 \times 1)$ phase. This high temperature phase can also be obtained by femtosecond-laser irradiation at low temperatures $T_0 \ll T_c$. A small energy barrier along the reaction coordinate from the $(4 \times 1)$ to the $(8 \times 2)$ phase hinders the immediate recovery to the $(8 \times 2)$ ground state and for nanoseconds leaves the system in a metastable supercooled state.
The recovery of the ground state is facilitated through nucleation at pre-existing step edges of the Si substrate. The step edges act as heterogeneous seeds for the recovery front which propagates like a row of falling dominoes at a speed of $v_{\text{rec}} \sim 100$ m/s across the terraces of the slightly miscut Si(111) surface. The measured speed is by almost one order of magnitude lower than that predicted through a molecular dynamics simulation. This may be explained by the strictly one-dimensional approach in the simulation, which does not take the 2D correlation of adjacent wires into account.

Since the recovery time is found to depend on the terrace-width distribution, our study demands future experiments on Si surfaces with a higher miscut angle. It is known that misorientations of the order of $1^\circ$ relative to the (111) orientation yield narrower terrace width distributions, i.e., more ordered step-trains. Such surfaces show only one of the three rotational $(8 \times 2)$ domains and exhibit straight step edges. On these narrower terraces, the recovery time constant will be faster, i.e., of the order of a few $100$ ps—which is a regime of time delay that can be accessed more easily in our experiment. Such surfaces will thus be ideal templates to explore the influence of temperature, excitation density, or supercooling on the speed of the recovery front.

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