PHYSICAL REVIEW B **89**, 121107(R) (2014)

Hysteresis proves that the In/Si(111) (8×2) to (4×1) phase transition is first-order

F. Klasing,[*] T. Frigge,[†] B. Hafke, B. Krenzer, S. Wall,[‡] A. Hanisch-Blicharski, and M. Horn-von Hoegen
Department of Physics and Center for Nanointegration (CENIDE), University of Duisburg-Essen, Lotharstrasse 1, 47048 Duisburg, Germany
(Received 22 December 2013; revised manuscript received 18 February 2014; published 14 March 2014)

Indium on silicon (111) exhibits a Peierls-like phase transition from a (4×1) reconstructed high-temperature phase to a (8×2) reconstructed ground state. A controversial debate is going on what kind of phase transition it is: first- or second-order. We employed high-resolution low-energy electron diffraction under slow thermal heating and cooling cycles to follow the phase transition. A robust hysteresis of diffraction spot intensities with a width of 8.6 K has been observed, which is independent of the heating and cooling rate. This hysteresis directly proves the existence of an energy barrier at the phase transition temperature and thus the first-order behavior of this phase transition.

DOI: 10.1103/PhysRevB.89.121107 PACS number(s): 61.05.jh, 68.35.Rh, 73.20.Mf, 64.60.A−

I. INTRODUCTION

One-dimensional metallic systems have attracted much attention due to their exotic electronic phenomena such as charge density wave formation induced by a Peierls instability [1,2], metal-insulator transition, and non-Fermi liquid behavior of the electrons [3,4].

The In-induced (4×1) reconstruction on Si(111) is a prototype for an atomic wire-type arrangement of metal atoms on a surface and has been subject to intense studies since it was first mentioned in 1964 [5,6]. It has attracted much attention during the last decade because the In wires undergo a reversible phase transition at the critical temperature ∼130 K from the (4×1) high-temperature phase to the (8×2) reconstructed ground state at low temperatures. This stuctural phase transition is accompanied by a metal-insulator transition [7–13]. However, the nature of the driving force for the phase transition has been controversial. As a driving force for the phase transition it is postulated to be either the formation of a charge density wave (CDW) or an order-disorder transtion. In the first scenario the quasi-one-dimensional chains, consisting of zig-zag distributed In atoms, form a (4×1) structure. Upon cooling the In atoms rearrange in an (8×2) structure stabilized by a redistribution of the charge density. The vast majority of experimental work supports this scenario [7–10,13–17]. However, it is commonly agreed that the phase transition does not follow a simple Peierls-type mechanism because more than one electronic band is involved in the CDW formation [7,8,10,13]. Furthermore, it was found that the phase transition is of first-order on the atomic scale [14]. Theoretical studies that are in accordance with the experimental findings found that in the low-temperature structure the In atoms form a distorted hexagon creating a (4×2) structure within the atomic wire [18,19]. The nonvanishing interaction between two wires results in the observed (8×2) structure. A recent density functional theory (DFT) calculation including van der Waals forces found also an (8×2) ground state [20]. The authors, however, found that the energy lowering is simply achieved through the lattice distortion accompanying the hexagon formation on the surface. This in contrast to the Peierls mechanism supported by the previous DFT calculations [18–20].

The presence of defects, i.e., missing atoms or adatoms, are the origin of domains where either the (4×1) structure exists below the phase transition temperature or (8×2)/(4×2) structures above the phase transition temperature [12,14]. It was concluded that these domains show different critical temperatures for the phase transition with a complicated interplay between domain boundaries [14]. Macroscopically this leads to an apparent second-order transition or pseudo-first-order transition [16]. The coexistence of the two phases, i.e., (4×1) and (8×2)/(4×2), even at 20 K led some authors to the conclusion that the phase transition is an order-disorder transition, and thus a second-order phase transition [12,21]. Theoretical studies supported this scenario [22,23]. They also found that the building blocks of the reconstruction are hexagons arranging in a (4×2) structure within the atomic wire. With increasing temperature the hexagons start to fluctuate between four energetically degenerate (4×2) arrangements, thus creating an apparent (4×1) structure [22]. It is concluded that the phase transition is driven by a shear phonon mode rather than nesting of surface electronic bands [23]. From the above discussion the origin of the controversy between the two scenarios, i.e., surface nesting and order-disorder transition, can be deduced. Even if the transition on a nanoscale is of first-order, the influence of defects changes this to an apparent second-order transition on the macroscale.

Recently we have observed the electronic excitation of the (8×2) to (4×1) phase transition at temperatures well below T_C [24,25]. We found an undercooled excited (4×1) phase that survives for almost a nanosecond due to the presence of an energy barrier hindering the immediate recovery of the ground state [24,25]. While this is evidence in favor of a first-order transition it still does not prove the existence of a barrier at the critical temperature T_C as supposed for a first-order transition [26].

Here we present high-resolution low-energy electron diffraction (LEED) studies on the In/Si(111)$(8 \times 2) \leftrightarrow (4 \times 1)$ phase transition. The diffraction spot intensity is monitored for increasing sample temperatures and compared to decreasing sample temperatures. For finite heating and cooling rates one would expect metastable phases of (8×2) and (4×1) above and below the phase transition temperature, respectively [27–29].

[*]Present address: VS Sensorik GmbH, Edisonstrasse 19, 33689 Bielefeld, Germany.
[†]Author to whom correspondence should be addressed: tim.frigge@uni-due.de
[‡]Present address: IMS Fraunhofer, Finkenstrasse 61, 47057 Duisburg, Germany.

The observation of a hysteretic behavior of the phase transition would therefore prove the existence of an energy barrier at the phase transition temperature. Following Landau [26], the phase transition is then be classified as first-order. In the past the existence of a hysteresis has been mentioned [8] but no data were shown. Here we present experimental data showing such a hysteresis.

II. EXPERIMENTAL SETUP

The experiments were performed in an ultra-high-vacuum (UHV) chamber at a base pressure of 2×10^{-10} mbar. The surface structure and morphology was investigated by spot profile analysis low-energy electron diffraction (SPA-LEED) [30,31]. Precision-orientated ($\pm 0.1^{\circ}$) Si(111) samples (phosphorus doped, 0.8 Ωcm) were mounted on a liquid nitrogen-cooled cryostat. The native oxide was removed by direct current heating via short flash-anneal cycles close to the melting point. The substrate quality was verified by the presence of a clear (7×7) LEED pattern at room temperature. Prior to the In deposition the sample temperature was increased to 700 K via direct current. About one monolayer (1 ML = 7.83×10^{14} cm^{-2}) of In was deposited from an electron beam-heated graphite crucible [32]. Subsequently the sample was rapidly cooled to liquid nitrogen temperatures, and the experiments were performed. The surface structure was verified by SPA-LEED. During the experiment the sample temperature was adjusted using a liquid nitrogen cryostat with an integrated ohmic heater. Simultaneously to the SPA-LEED measurements the sample temperature was measured by an ohmic sensor (Pt100), which is directly coupled to the sample via a molybdenum clamp. The Pt100 was calibrated at liquid nitrogen temperature to ensure an accurate temperature determination. Heating and cooling rates dT/dt between 0.05 and 0.35 K/s were applied. The initial temperature for all experiments was set by the liquid nitrogen-cooled cryostat and was always below 80 K.

III. ANALYSIS AND RESULTS

The SPA-LEED pattern of an In induced (8×2) reconstruction at 80 K is shown in Fig. 1 (upper panel). Clear, sharp (8×2) spots and narrow twofold streaks reflect the typical features of the (8×2) reconstruction. Upon heating, the LEED pattern changes around 135 K into a (4×1) reconstruction as shown in Fig. 1 (lower panel). Cooling of the sample leads to a transition back to the (8×2) reconstruction around 125 K.

In order to quantitatively follow the phase transition we recorded intensities of representative LEED spots as function of temperature. The analyzed (8×2) spot and the twofold streak are marked in the LEED pattern of Fig. 1. Figure 2 depicts the resulting LEED intensities (rectangle) of the eighth-order spot (top) and the twofold streak (bottom) versus the sample temperature. Upon heating at a rate of $dT/dt = 0.3$ K s^{-1} the initial LEED spot intensity I_0 of the eighth-order spot and the twofold streak decrease due to the Debye-Waller effect. During the course of the phase transition between 130 and 140 K the spot intensities vanish and drop to background intensity. Cooling with the same rate leads to an intensity rise between 130 and 120 K. Upon further cooling the spot

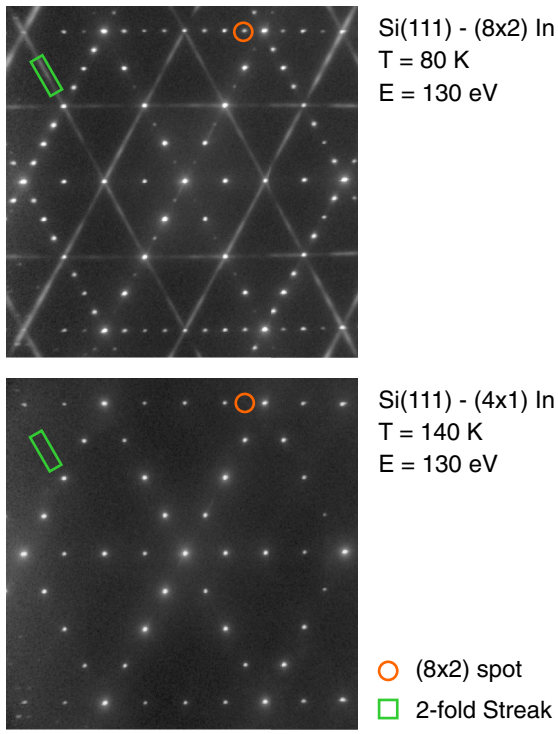

FIG. 1. (Color online) LEED pattern of the low-temperature Si(111) (8×2) phase (upper panel) and the high-temperature Si(111) (4×1) phase (lower panel). The analyzed intensities of representativ LEED spots displayed in Fig. 2 of the (8×2) spot and the twofold streak are indicated by an orange circle and a green rectangle, respectively.

intensity increases again due to the Debye-Waller effect. The analyzed peak intensities of the diffraction spots, however, do not recover completely. This is attributed to the adsorption from residual gas, which results in a change of (8×2) domain morphology during the course of each heating-cooling cycle [24,25,33]. This causes slight spot broadening of the (8×2) spots as shown in the insets of Fig. 2: while the total intensity has to be conserved, the peak intensity must decrease. The twofold streaks can not show such a behavior because they cannot broaden any further.

At the phase transition the (4×1) spots show a slight increase upon heating and decrease upon cooling in intensity in the same temperature regime, reflecting the structural change accompanied with the phase transition (not shown here). The temperature range where the phase transition is observed for the heating and for the cooling cycle differs significantly by about 10 K, evidencing the presence of a hysteresis. The difference of the temperature range for heating and cooling where the phase change is observed is independent of the number of cycles.

In order to extract the width of the hysteresis we describe the LEED intensities of the (8×2) spots and the streaks by

$$I_{\pm}(T) = I_{\text{back}} + I_0 \cdot \exp(-\alpha \cdot T) \cdot \Gamma_{\pm}(T, T^{\pm}, \delta). \quad (1)$$

I_{back} is the diffuse background intensity, which is taken constant, and I_0 is the initial intensity of each spot. Any spot is affected by the Debye-Waller effect, which causes an exponential decay of spot intensity with increasing temperatures due to larger vibrational amplitudes of the surface atoms. Thus

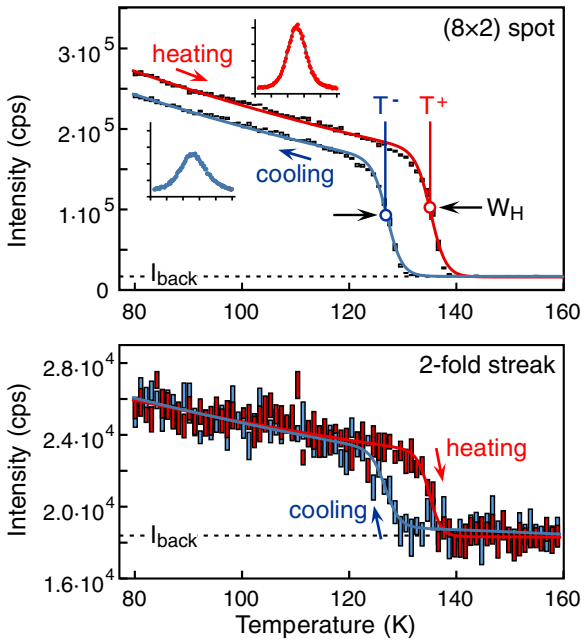

FIG. 2. (Color online) LEED intensity of the (8×2) spot (upper panel) and the twofold streak (lower panel) as function of temperature. The statistical error of the data points is represented by the vertical dimension of the rectangles. Upon heating with a rate of $dT/dt = 0.3$ Ks^{-1} the LEED (8×2) spot intensity decreases due to the Debye-Waller effect. Above the phase transition the intensity of both the (8×2) spot and the twofold streak drop to the background. Cooling with the same rate leads to the transition back into the (8×2) reconstruction. The insets in the upper panel show identically scaled spot profiles of the (8×2) spot prior and after the heating cycle. The nomenclature used in this figure is explained in the text.

any spot intensity has to be multiplied by $\exp(-\alpha \cdot T)$ with the fitting parameter α.

The transitions shape is qualitatively described by a sigmoid function:

$$\Gamma_{\pm}(T,T^{\pm},\delta) = \left[1 + \exp\left(\frac{T - T^{\pm}}{\delta}\right)\right]^{-1}, \qquad (2)$$

where $T^{\pm}$ are the points of inflection of $\Gamma_{\pm}$. The parameter δ describes the abruptness of the transition. The fit of Eq. (1) to the experimental data is plotted as solid red (heating) or blue (cooling) lines (see Fig. 2). The temperatures $T^{\pm}$ are indicated in Fig. 2 as well. This fitting procedure allows a robust and precise determination of the hysteresis width W_H

$$W_H = T^{+} - T^{-}. \qquad (3)$$

This analysis unambiguously shows the existence of a hysteresis. The width as defined by Eq. (3) is the same for the (8×2) spot and twofold streak and determined to be 8.6 K (cf. Fig. 2).

To ensure that the observed hysteresis is not an artifact caused by the experimental setup, the phase transition was cycled at various heating and cooling rates in the range from 0.05 to 0.35 K s^{-1}. If the hysteresis would originate from a different thermal coupling of the temperature sensor and the sample, then changes of the heating and cooling rates should lead to a systematic variation of the width W_H of

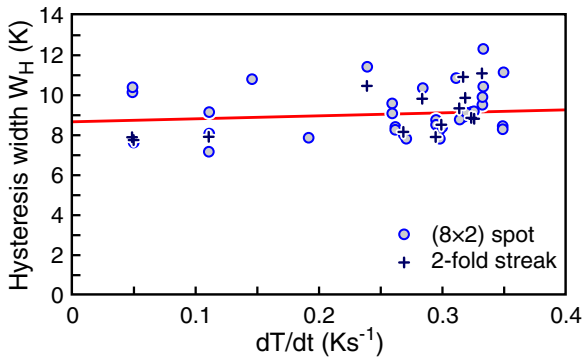

FIG. 3. (Color online) Dependency of the width of the hysteresis W_H on the rate of the temperature change is depicted. Results obtained from (8×2) spots and twofold streaks are indicated by blue circles and crosses, respectively. The heating and cooling rate dT/dt was varied between 0.05 and 0.35 K s^{-1}. A linear interpolation results in an intercept with the y axis at $W_H = 8.6$ K.

the hysteresis. In such a case a linear extrapolation of W_H as function of heating/cooling rate dT/dt would point to a vanishing hysteresis width $W_H \to 0$ K for infinitesimal small heating/cooling rates.

In Fig. 3 the dependency of the width of the hysteresis W_H on the rate of temperature change dT/dt is plotted. An intercept with the temperature axis of $W_H = 8.6$ K of the linear extrapolation to $dT/dt = 0$ validates the existence of a hysteresis beyond doubt.

IV. CONCLUSIONS

We observed the existence of a robust hysteresis loop upon slow increase and decrease of the sample temperature at the $(8 \times 2) \leftrightarrow (4 \times 1)$ phase transition of In on Si(111). The width of the hysteresis loop of $W_H \approx 10$ K is almost independent of the heating and cooling rate. This is direct evidence for the existence of a significant energy barrier between the (8×2) ground state and the (4×1) excited state. However, the detailed analysis of the hysteresis and the extraction of an energy barrier has to be further elucidated. It is important to note that the above study examines the surface macroscopically. The previously observed first-order type transition on the nanoscale [14] is thus confirmed on a macroscopic scale. This rules out the order-disorder scenario for the phase transition [26]. The transition from the (8×2) structure at low temperatures to the (4×1) structure at elevated temperatures is connected to a change in the surface atomic arrangement and not to a fluctuation between degenerate ground-state structures. A detailed analysis of the hysteresis loop in the future might shed light on the question if the phase transition is solely driven by energy lowering due to the lattice distortion or by a Peierls-type mechanism.

ACKNOWLEDGMENTS

We are grateful for G. Lee, H. Pfnür, J. Schäfer, C. Tegenkamp, and W. G. Schmidt for stimulating and fruitful discussions. Financial support through the collaborative research center SFB616 "Energy Dissipation at Surfaces" is gratefully acknowledged.

[1] R. Peierls, *Quantum Theory of Solids*, International Series of Monographs on Physics (Clarendon Press, Oxford, 1955).
[2] G. Grüner, *Density Waves in Solids* (Addison-Wesley, Reading, MA, 1994).
[3] S. Tomonaga, Prog. Theor. Phys. **5**, 544 (1950).
[4] J. M. Luttinger, J. Math. Phys. **4**, 1154 (1963).
[5] J. J. Lander and J. Morrison, Surf. Sci. **2**, 553 (1964).
[6] P. C. Snijders and F. F. Weitering, Rev. Mod. Phys. **82**, 307 (2010).
[7] H. W. Yeom, S. Takeda, E. Rotenberg, I. Matsuda, K. Horikoshi, J. Schaefer, C. M. Lee, S. D. Kevan, T. Ohta, T. Nagao *et al.*, Phys. Rev. Lett. **82**, 4898 (1999).
[8] O. Gallus, T. Pillo, M. Hengsberger, P. Segovia, and Y. Baer, Eur. Phys. J. B **20**, 313 (2001).
[9] S. J. Park, H. W. Yeom, S. H. Min, D. H. Park, and I.-W. Lyo, Phys. Rev. Lett. **93**, 106402 (2004).
[10] J. R. Ahn, J. H. Byun, H. Koh, E. Rotenberg, S. D. Kevan, and H. W. Yeom, Phys. Rev. Lett. **93**, 106401 (2004).
[11] G. Lee, J. Guo, and E. W. Plummer, Phys. Rev. Lett. **95**, 116103 (2005).
[12] J. Guo, G. Lee, and E. W. Plummer, Phys. Rev. Lett. **95**, 046102 (2005).
[13] Y. J. Sun, S. Agario, S. Souma, K. Sugawara, Y. Tago, T. Sato, and T. Takahashi, Phys. Rev. B **77**, 125115 (2008).
[14] S. J. Park, H. W. Yeom, J. R. Ahn, and I.-W. Lyo, Phys. Rev. Lett. **95**, 126102 (2005).
[15] E. Speiser, S. Chandola, K. Hinrichs, M. Gensch, C. Cobet, S. Wippermann, W. G. Schmidt, F. Bechstedt, W. Richter, K. Fleischer *et al.*, Phys. Status Solidi (b) **247**, 2033 (2010).
[16] S. Hatta, Y. Ohtsubo, T. Aruga, S. Miyamoto, H. Okuyama, H. Tajiri, and O. Sakata, Phys. Rev. B **84**, 245321 (2011).
[17] K. Fleischer, S. Chandola, N. Esser, W. Richter, and J. F. McGilp, Phys. Rev. B **76**, 205406 (2007).
[18] S. Wippermann and W. G. Schmidt, Phys. Rev. Lett. **105**, 126102 (2010).
[19] W. G. Schmidt, S. Wippermann, S. Sanna, M. Babilon, N. J. Vollmers, and U. Gerstmann, Phys. Status Solidi (b) **249**, 343 (2012).
[20] H.-J. Kim and J.-H. Cho, Phys. Rev. Lett. **110**, 116801 (2013).
[21] C. Kumpf, O. Bunk, J. H. Zeysing, Y. Su, M. Nielsen, R. L. Johnson, R. Feidenhans'l, and K. Bechgaard, Phys. Rev. Lett. **85**, 4916 (2000).
[22] C. González, F. Flores, and J. Ortega, Phys. Rev. Lett. **96**, 136101 (2006).
[23] C. González, J. Guo, J. Ortega, F. Flores, and H. H. Weitering, Phys. Rev. Lett. **102**, 115501 (2009).
[24] S. Wall, B. Krenzer, S. Wippermann, S. Sanna, F. Klasing, A. Hanisch-Blicharski, M. Kammler, W. G. Schmidt, and M. Horn-von Hoegen, Phys. Rev. Lett. **109**, 186101 (2012).
[25] T. Frigge, S. Wall, B. Krenzer, S. Wippermann, S. Sanna, F. Klasing, A. Hanisch-Blicharski, M. Kammler, W. Schmidt, and M. Horn-von Hoegen, Phys. Rev. Lett. **111**, 149602 (2013).
[26] L. Landau and E. Lifschitz, *Statistical Physics* (Pergamon Press, New York, 1951).
[27] K. Binder, Rep. Prog. Phys. **50**, 783 (1987).
[28] G. P. Zheng and J. X. Zhang, J. Phys. Condens. Matter **10**, 275 (1998).
[29] L. I. Klushin and A. M. Skvortsov, J. Phys. A **44**, 473001 (2011).
[30] K. Gronwald and M. Henzler, Surf. Sci. **117**, 180 (1982).
[31] M. Horn-von Hoegen, Z. Kristallogr. **214**, 591 (1999).
[32] P. Kury, R. Hild, D. Thien, H.-L. Günter, F.-J. Meyer zu Heringdorf, and M. Horn-von Hoegen, Rev. Sci. Instrum. **76**, 083906 (2005).
[33] H. Shim, J. Yeo, G. Lee, and H. Kim, Phys. Rev. Lett **111**, 149601 (2013).