Intertwined Electronic and Structural Phase Transitions in the In/Si(111) Interface

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The structural (4×1) to (8×2) transition and the electronic metal to semimetal transition at the In/Si interface are studied with scanning tunneling microscopy and spectroscopy. Both transitions are gradual, resulting in a complex domain structure in the transition temperature regime. At these intermediate temperatures, the metallic (4×1) and semimetallic (8×2) domains coexist with each other and with new nanophases. By probing the two intertwined but distinguishable transitions at the atomic level, the interaction between different phases is visualized directly.

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Understanding the exotic behavior exhibited by highly correlated electron systems poses perhaps the deepest intellectual challenge in the physical sciences today [1]. In general, a correlated electron material is one where the potential energy is comparable to the kinetic energy. This leads to spectacular properties, which result from the competition of a multitude of low-lying excited states—the equilibrium between phases is very subtle and small perturbations can produce large responses. There is a complex interplay between the charge, lattice, and spin degrees of freedom, which produces coupled phase transitions, electronic structural, electronic magnetic, or magnetic structural [2]. Recent experiments have demonstrated that low dimensional surface systems exhibit or mimic many of the properties of bulk electron correlated materials. Quasi-two-dimensional or quasi-one-dimensional metal films on semiconductor surfaces have such narrow bandwidths that they behave like correlated electron systems, exhibiting Mott-insulating phases [3], ''glassylike'' low temperature (LT) phases [4], and very strong electron-phonon coupling [5]. The advantage of these surface systems is that the power of scanning tunneling microscopy (STM) and spectroscopy (STS) can be employed to monitor the phase transition with atomic resolution. Here, we report on the use of STM and STS to probe the details of the electronic and structural transition in the quasi-1D system indium on Si(111).

One monolayer of In on a Si(111) surface (In/Si) forms a (4×1) metallic structure at room temperature (RT) [6,7]. Photoemission spectroscopy studies [8,9] and first-principles total energy calculations [10] both confirm the metallic nature and indicate a pseudo-1D character. The In/Si interface undergoes a symmetry-lowering transition at approximately 100–130 K accompanied by an electronic transition, to a (8×2) insulating or semimetallic phase [8,11–16]. Our STM and STS studies reveal the gradual nature of the structural (4×1) to (8×2) transition as well as the electronic metal-semimetal (M-SM) transition at the interface. During the cooling process, the two transitions begin at the same onset temperature $\sim$145 K, while the completion temperature for the electronic transition ($\sim$105 K) is higher than that of the structural transition ($\sim$85 K). At intermediate temperatures, a complex domain structure is formed in which the metallic (4×1) and semimetallic (8×2) [referred to as $\times$1-M and $\times$2-SM, respectively] phases coexist with each other and with the new $\times$1-SM nanophase. It is unambiguously demonstrated that the intertwined structural and electronic transitions can be separated from each other. The interaction between different phases is observed directly in this low dimensional system.

The experiments were performed in an Omicron ultrahigh vacuum variable temperature STM system. The Si(111) substrate was cut from a *p*-type Si wafer with electrical resistivity of 0.01–0.05 Ω cm. The substrate was cleaned *in situ* following the ''flashing'' recipe until a uniform (7×7) reconstruction formed. An In overlayer was then evaporated from a tantalum-wrapped source heated by a tungsten filament. The temperature of the Si substrate was held at about 400 °C by resistive heating during the 10-min deposition, with the sample temperature and deposition time optimized to obtain a pure-phase, well-ordered (4×1) structure with minimized defects at the In/Si interface. Three types of domains in which In chains aligned along the three equivalent $[1\bar{1}0]$ directions were formed simultaneously, as checked by low-energy-electron diffraction and STM. The sample was cooled on the STM stage by using a continuous flow cryostat. Temperature at the sample surface was controlled and stabilized in the range between RT and 40 K. The bias-dependent STM imaging and STS results were repeated with different tips made by etched tungsten wires.

The structural transition at the In/Si interface is directly visualized as the change of the STM image symmetry. At RT, the STM image shows a (4×1) symmetry, as shown in Fig. 1(a). The surface reconstructs into an (8×2) symmetry at LT. The periodicities in both the parallel and transverse directions (to the In chains) are doubled, as shown in

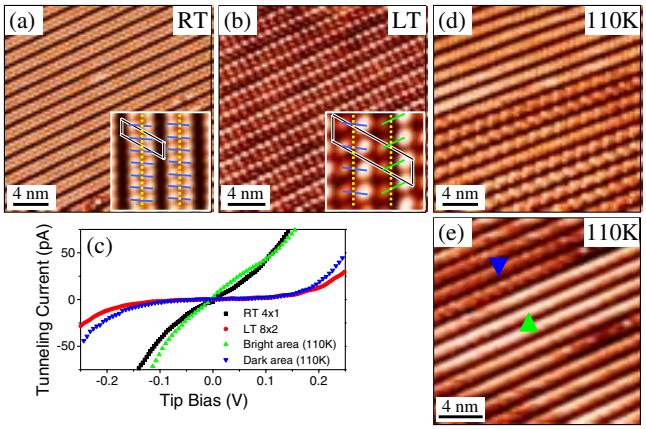

FIG. 1 (color online). The symmetry-lowering transition at the In/Si interface observed by STM topographic images at (a) RT and (b) 40 K with the tip bias voltage of -0.5 V and the feedback current of 0.1 nA. The two insets show the zoom-in features in the same scale, illustrating the change of symmetry with the (4×1) and (8×2) unit cells drawn, respectively. The In chains are sketched as yellow dashed lines and the intrachain configurations are indicated by connecting the maxima at transverse direction. The "$\times 2$" order is seen in the distance between the maxima along In chains while the "$8\times$" periodicity is presented by the alternative orientation of the lines in adjacent chains. (c) The electronic M-SM transition observed by the STS IV curves taken at RT and 40 K with the same tip conditions: tips bias at -0.5 V and feedback current at 1.0 nA. (d),(e) STM image at 115 K with the tip condition of $+1.0$ V/0.5 nA and $+0.5$ V/1.0 nA, respectively. The IV curves taken in different areas at 115 K are also plotted in (c) with the same notations as marked in (e).

Fig. 1(b). A dramatic change of the electronic characteristic is displayed in the STS IV curves [Fig. 1(c)]. The IV curves taken at 40 K are much flatter than at RT, with the differential conductivity (dI/dV) at zero bias decreased by over a factor of 10 [17]. Although small, the finite dI/dV for the LT phase demonstrates a nonzero local electron density of states (LDOS) at Fermi energy (E_F) [18], conclusively indicating a semimetallic phase, not an insulator as would have been expected in a 1D Peierls transition.

At intermediate temperatures (near 110 K), the structural and electronic RT/LT phases coexist with each other. As shown in Fig. 1(d), both the RT (4×1) (upper left part) and LT (8×2) (lower right part) symmetries appear in the same STM image. In Fig. 1(e), a lower bias is used to magnify the bright-dark nature of the M-SM phases (indicated with up-pointing and down-pointing triangles, respectively). As demonstrated more clearly in the following, the coexistence of these $\times$1-M/$\times$2-SM phases results in the domain structures with well-defined domain walls at intermediate temperatures. The structural domains and domain walls are directly visualized as the local symmetry in STM images, while the electronic domain structure is recognized by the spatial contrast in STM images since the integral LDOS determines the brightness (height). We carefully examine the relation between electronic characteristic and STM contrast by taking local STS IV curves in the domains with length scale greater than 6 nm with different tip conditions. Only two types of IV curves are observed corresponding to the M/SM domains, respectively, which coincide with the bright/dark areas [Figs. 1(c) and 1(e)] at low bias ($+/-0.5$ V). Such a relation is extrapolated to small domains (including the 1D stripes) where the bias-dependent contrast remains the same [19].

Two macroscopic order parameters are obtained to characterize the $\times$1-M to $\times$2-SM transition. The structural order parameter $P_{\times 2}$ is defined as the area percentage of the domains with "$\times 2$" symmetry averaged through numbers of large scale images [20]. As displayed in Fig. 2(a), the experimental data of $P_{\times 2}$ show a gradual change from 0 to 1 as the temperature decreases. At the onset of the structural transition, $T_1 \sim 145$ K, some 1D domains begin to appear in the (4×1) matrix. Later it will be shown that some of them are "$\times 2$" stripes (referred to as 1D-$\times 2$ in the following) that behave like the LT $\times$2-SM phase. The concentration of these 1D-$\times 2$ stripes increases upon cooling within the yellow (light gray) zone in Fig. 2. At $T < 135$ K [the light blue (medium gray) zone], 2D $(4 \times 1)/(8 \times 2)$ domains coexist at the interface. The (8×2) symmetry becomes prevalent below $\sim$105 K with some 1D-$\times 2$ chains isolated from each other [the pink (dark gray) zone]. The structural transition is completed at $T_3 \sim 85$ K when a homogeneous (8×2) structure is developed, although two degenerated lattice configurations form domain structures that keep evolving at LT [11,21].

The electronic order parameter P_{SM} is defined as the percentage of the surface that is SM, determined by the contrast in the low bias STM images. P_{SM} shows a gradual transition [Fig. 2(b)] from 0 at high temperature to 1 at LT. The electronic domains evolve from 1D-SM [within the yellow (light gray) zone] to 2D-SM [in the light blue (medium gray) zone] features, and finally unify into a semimetallic system below $T_2 \sim 105$ K.

Note that, with the same onset temperature T_1, the electronic transition appears less gradual than the structural

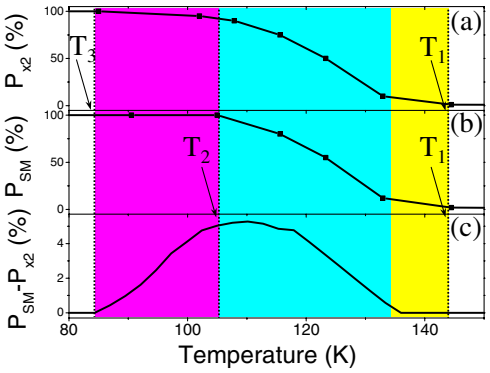

FIG. 2 (color online). Order parameters (a) $P_{\times 2}$ and (b) P_{SM} in the intermediate temperature range. (c) The difference between $P_{\times 2}$ and P_{SM}. The data in (c) are presented schematically due to the error (not shown) of the statistics of STM images.

transition with a higher completion temperature ($T_2 > T_3$). The difference between the order parameters $P_{\times 2}$ and P_{SM} is schematically shown in Fig. 2(c). The bump, although with a small amplitude of less than 5%, corresponds to a new phase—the $\times$1-SM phase. As shown in Fig. 3, the new nanophase coexists with domains of $\times$1-M and $\times$2-SM phases that appear identical to the homogeneous RT and LT phases, respectively. The line profile along *AB* shows that the three (4×1) chains on the right are at the same height as the $\times$2-SM domain (the 1D- $\times$ 2 stripe as marked by the arrow), but not as the other (4×1) chains (the left two chains) in the metallic domain. The existence of the new $\times$1-SM phase reveals the separation of the electronic transition from the structural transition. It is unambiguously distinguished from the simple picture that there is only one single transition whose order parameter induces and determines the other. The microscopic dynamics of the $\times$1-M to $\times$2-SM transition at the In/Si interface can be described as the intertwinement of the electronic and structural transitions.

The characteristic of the interface near the onset temperature T_1 [yellow (light gray) temperature zone in Fig. 2] sheds light onto the nature of the intertwined transitions. At 140 K, the interface symmetry is predominantly (4×1) but with some isolated dark stripes as marked by the green or light gray arrow in Fig. 4(a). The high-resolution STM image reveals the same behavior of the dark stripe as in the homogeneous LT $\times$2-SM phase. In Fig. 4(c), the line profiles at different bias show similar height difference versus the (4×1) area as the 2D large SM domains [see Figs. 1(c) and 1(e)]. The appearance of these 1D $\times$2-SM domains in the $\times$1-M matrix indicates the same onset temperature of the structural and electronic transitions. The arrow on the left in Fig. 4(a) points to a defect-induced $\times$2 stripe. It is still M [Fig. 4(c)], not SM as expected for the LT $\times$2-SM phase [22]. It should also be pointed out that the domain structure studied in this work is intrinsic. The STM images show that neither 1D nor 2D domains are determined by defects.

Other intrinsic stripes have disordered structure as indicated by the arrow in Fig. 4(b). Such 1D-disordered stripes are also SM, revealed by the same contrast as the 1D $\times$2 domains compared to the $\times$1-M area at various bias. These two intrinsic 1D phases ($\times$2-SM and disordered SM) coexist in a narrow temperature range around 140 K. At higher temperatures there are more disordered-SM stripes, while the 1D $\times$2-SM domains likely appear at lowered temperature, until 2D domains form with the complete (8×2) symmetry. The disordered-SM stripes are most likely the precursor of the LT $\times$2-SM phase in which the RT $\times$1-M phase becomes unstable, but the elastic coupling among adatoms along the chains that lead to $\times$2 periodicity is not stabilized. It is a gradual evolution from (4×1) to (8×2) symmetry even in microscopic scale.

The interaction between the intertwined electronic and structural transitions is now clear. When the system is cooled down to ~145 K, the electronic transition occurs first, resulting in the formation of 1D SM domains. The coupling mediated by the conducting electrons among adatoms is restrained within these 1D domains, since the LDOS at E_F decreases by an order of magnitude, which breaks the stability of the (4×1) structure. Before the LT (8×2) lattice is stabilized, the adatoms fluctuate uncorrelatedly around randomly distorted equilibrium sites, resulting in the 1D precursor (disordered-SM) phase. The structural transition occurs in some of these precursors leading to the formation of $\times$2-SM stripes. The number of these 1D domains increases upon cooling [yellow (light gray) zone in Fig. 2] until multiple chains connect below 135 K. The neighboring $\times$2 stripes form the 2D $\times$2-SM domains. Some of the disordered chains adjoin before the $\times$2 structure is stabilized. Because of the absence of the electronic domain walls, the transverse coupling between adjacent In chains is somehow enhanced, which raises the fluctuation correlation among the adatoms within the 2D SM area. Such 2D SM domains present "flat" (4×1) symmetry in the time-averaged STM image; i.e., the new $\times$1-SM phase is formed in which structural and electronic transitions are "decoupled." All these nanophases coexist until the homogeneous $\times$2-SM phase is reached below T_3. The dynamics of the transition at the In/Si interface is

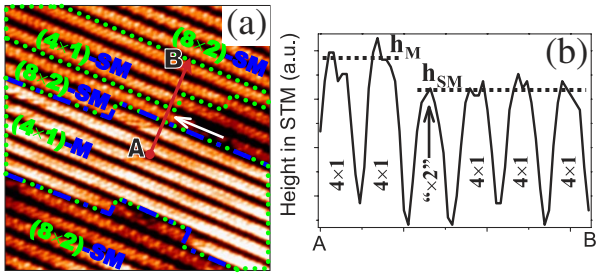

FIG. 3 (color online). (a) STM image (tip bias at +0.5 V and feedback current at 0.5 nA) of the In/Si interface at 110 K. The electronic M-SM (bright-dark) domains are separated by dashed lines. The (4×1) domains are marked with dotted lines out of the (8×2) areas. The line profile along *AB* is plotted in (b).

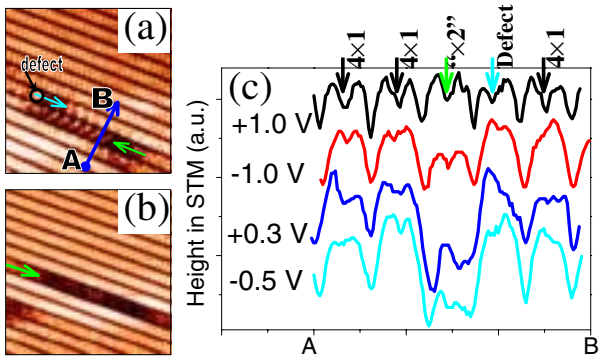

FIG. 4 (color online). (a),(b) STM image (tip bias at +0.5 V and feedback current at 0.5 nA) of the In/Si interface at 140 K. (c) The line profiles with different imaging bias across the 1D domains marked with *AB* in (a).

determined by the interaction between the structural and electronic transitions, i.e., the electronic transition induces the structural transition, while the structural transition, in turn, stabilizes the electronic order and results in the completion of electronic transition.

The structural transition also enhances the electronic transition, as witnessed by the formation of the 1D $\times 1$-SM stripes in the $\times 2$-SM matrix [in the pink (dark gray) zone in Fig. 2]. They are not simply the spatially shrunk 2D $\times 1$-SM domains, but originate from the activation of the $\times 2$ structure within certain chains. The electronic M domains begin to appear in these areas when the temperature increases. Therefore, the structural and electronic orders play equivalent roles in the $\times 1$-M to $\times 2$-SM transition.

Nussinov *et al.* [23] have used the Ginzburg-Landau theory to analyze the different phases in strongly correlated systems. This leads to inhomogeneous ground states that are more likely to be observed near the critical point. Moreover, the dynamics are slow due to the huge configurational entropy associated with these complex states. At the In/Si interface, we successfully observe all the similar behaviors of the $\times 1$-M to $\times 2$-SM transition but in microscopic details. It is indicated that this 1D system is ideal for testing the theory of correlated systems.

In summary, the $\times 1$-M to $\times 2$-SM transition at the In/Si interface is investigated by STM and STS. The transition is characterized by two order parameters. Although intertwined at intermediate temperatures, the structural and electronic orders are separable. The interaction between different phases is clearly demonstrated. Metal/semiconductor interfaces provide a platform for investigation in atomic details of the nature of phase transitions in correlated electron systems.

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[17] To eliminate the artifact introduced by the tunneling gap distance, we take IV curves with various initial tip conditions while scanning at each temperature. With a small gap distance (tip bias at $+/-0.5$ V and feedback current at 2 nA), sequent scans at the same area show no damage on the intrinsic structure, suggesting that the tip-interface interaction is moderate. The upper limit of the gap distance (with tip bias at $+/-0.75$ V and feedback current at 0.1 nA) is estimated when an artificial gap appears in the LT STS due to the sensitivity limit of the data acquisition circuit being reached. All the IV curves shown in Fig. 1(c) were taken with the same tip conditions.
[18] Within a simple tunneling model, the electron LDOS is proportional to dI/dV in the limit of small bias voltage. In real experiments, the dI/dV spectrum mimics the LDOS reasonably better if normalized by dividing it by I/V. However, such a normalization is unnecessary at small bias, whereas $(dI/dV)/(I/V)$ is identically equal to unity for ohmic systems and so carries no information.
[19] The most direct way to determine the electronic domain structure is categorizing the STS IV curves at every pixel in each STM image. It requires a long acquisition time and is not even practical because the electronic domains at the In/Si interface are mobile (discussed elsewhere).
[20] At intermediate temperatures intrinsic "$\times 2$" structure is formed in single In chains. The statistics count these 1D-$\times 2$ domains as the structural LT phase since they behave in the same way (see text).
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