

## Adsorbate-Induced Pinning of a Charge-Density Wave in a Quasi-1D Metallic Chains: Na on the In/Si(111)-(4 × 1) Surface

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We find that foreign adsorbates acting as local impurities can induce a metal-insulator transition by pinning a charge-density wave (CDW) on the quasi-1D metallic In/Si(111)-(4 × 1) chain system. Our scanning tunneling microscopy image clearly reveals the presence of a new local 4 × 2 structure nucleated by Na adatoms at room temperature, which turns out to be insulating with a doubled periodicity along the chains. We directly determine a CDW gap energy  $\Delta = 105 \pm 8$  meV by identifying a characteristic loss peak in our high-resolution electron-energy-loss spectra. We thus report the first observation of a local impurity-derived Peierls-like reconstruction of a quasi-1D system.

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The intrinsic Peierls instability of a one-dimensional (1D) metal often drives the metal into an insulating phase that accompanies the formation of a charge-density wave (CDW) with a doubled periodicity [1,2]. Such a metal-insulator transition (MIT) occurs primarily as a result of the coupling between electronic states near the Fermi energy and a particular phonon mode enhanced by nested segments of the Fermi surface contours of the system. Among the limited number of 1D metallic systems (mostly based on 3D materials) reported to date, the quasi-1D metallic In chains formed on the Si(111) surface have been reported as a model system to demonstrate a Peierls-type reversible MIT upon crossing a transition temperature  $T_c = 130$  K [3,4].

In such low-dimensional systems, not only the intrinsic Peierls-like instability but also some forms of extrinsic perturbations can strongly influence their physical properties. The role of the extrinsic perturbation, mostly introduced as random local impurities in driving structural and electrical changes, has indeed been an issue for several low-dimensional interacting electron systems [5–8]. Recently two noticeable studies revealing the impurity-induced changes in electrical properties have been reported [7,8]. One is the pinning of a CDW by point defects at a temperature above  $T_c$  of the MIT for the Sn/Ge(111)-( $\sqrt{3} \times \sqrt{3}$ ) with no defects [7], and another is the MIT observed on the metallic Si(111)-(7 × 7) surface derived by adsorbate (Ba, Mg)induced disorder in site potentials [8]. Lately another interesting observation shows the intriguing nature of the role of impurities such that impurity atoms may also revert a low-temperature insulating phase to a metallic phase at room temperature [9,10].

Here we report a case where adsorbates introduced in a quasi-1D metallic system as impurity atoms can drive an MIT well above the  $T_c$  of the same system with no impurities. The system is a metallic In/Si(111)-(4 × 1)

(or 4 × 1 for short) surface at room temperature, which becomes an insulating 4 × 2 surface when Na atoms are added. A surface state composed of a nested Fermi surface contour with a nesting vector  $2k_F = 0.82 \text{ \AA}^{-1}$  is believed to drive the MIT by enhanced coupling with a lattice vibration. As observed in the temperature-induced MIT of the 4 × 1 surface [3,4], we also find the formation of a CDW with a doubled periodicity pinned by Na adatoms in our filled state image of scanning tunneling microscopy (STM). Our high-resolution electron-energy-loss spectroscopy (HREELS) data clearly reveal the opening of a CDW gap with energy  $\Delta = 105 \pm 8$  meV.

We have utilized a combination of several surface probing tools to investigate the Na-induced quasi-1D MIT. The degree of order on the surface was systematically examined using a high spatial resolution low-energy-electron diffraction (Leybold SPA-LEED) that has a nominal transfer width of  $\sim 1200 \text{ \AA}$ . The electrical property of the surface as a function of Na coverage was studied by examining characteristic loss features in HREELS data. The HREELS chamber equipped with a Leybold-Heraeus ELS-22 spectrometer of an optimum energy resolution  $\Delta E \leq 3$  meV has maintained a base pressure below  $3 \times 10^{-11}$  mbar throughout the measurements. We used a commercial SAES getter source when depositing Na on the metallic 4 × 1 surface as impurity adsorbates. The 4 × 1 surface produced by annealing the In-adsorbed surface at about 650 K as done earlier [3,4,11–14] shows the 4 × 1 LEED pattern as shown in Fig. 1A, where a unit cell is denoted by a dashed box. Note the additional fractional LEED spots from three different rotational domains on the surface. We estimated the relative coverage  $\Theta_{\text{Na}}$  of Na adatoms by measuring the work function change ( $\Delta\Phi$ ) as a function of Na exposure (not shown). We assigned  $\Theta_{\text{Na}} = 1.0$  monolayer (ML) at the minimum of the  $\Delta\Phi$  versus exposure curve [15].

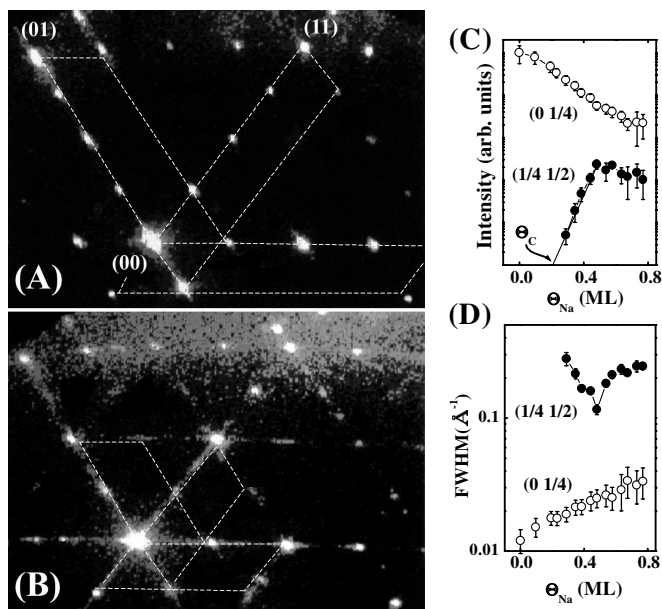


FIG. 1. LEED patterns of the metallic In/Si(111)-(4  $\times$  1) (A) and Na-induced 4  $\times$  2 (B) surfaces at room temperature. The LEED beam energy was 88 eV. Each unit cell is denoted by a dashed box although drawn three unit cells for three rotational domains. Integrated intensity and FWHM of a (0  $\frac{1}{4}$ ) spot (empty circles) and a ( $\frac{1}{4}$   $\frac{1}{2}$ ) spot (filled circles) versus Na coverage ( $\Theta_{\text{Na}}$ ) are presented in (C) and (D), respectively. Note the maximum in (C) and a minimum in (D) of the ( $\frac{1}{4}$   $\frac{1}{2}$ ) spot indicating the best development of the 4  $\times$  2 surface.

In Fig. 1B we show the 4  $\times$  2 LEED pattern from the Na-added 4  $\times$  1 (or 4  $\times$  2 hereafter) surface. The streaky fractional LEED spots along the direction perpendicular to the In chains indicate a certain disorder on the surface. This may be caused either by the reduced number of In chains or by the random phase slip between In chains of the 4  $\times$  2 structure as seen in the clean cold 4  $\times$  2 surface [3]. The gradual evolution of integrated intensity in Fig. 1C as well as the full width at half maximum (FWHM) in Fig. 1D of the (0  $\frac{1}{4}$ ) spot (from both the 4  $\times$  1 and the 4  $\times$  2 domains) and the ( $\frac{1}{4}$   $\frac{1}{2}$ ) spot (only from the 4  $\times$  2 domain) clearly indicate the growth of the 4  $\times$  2 domain at the expense of the clean 4  $\times$  1 domain. We observe that the long-range order observed in the 4  $\times$  2 LEED pattern is best developed at 0.4 ML, as indicated by the maximum intensity of the ( $\frac{1}{4}$   $\frac{1}{2}$ ) spot with a minimum in FWHM. Figure 1C shows that the minimum coverage necessary for the observation of the disordered 4  $\times$  2 domain by LEED is estimated to be  $\Theta_c = 0.2$  ML from the linear extrapolation of the decreasing trend.

The presence of the local 4  $\times$  2 short-range order induced by Na adatoms is markedly well demonstrated in our filled state STM image shown in Fig. 2 where a period doubling is apparent in the intensity profile particularly along the local 4  $\times$  2 In chains (AB line) in comparison with that of the 4  $\times$  1 In chains (CD line). The coverage of Na in Fig. 2 is estimated to be much lower

than 0.1 ML. Although we observe several local 4  $\times$  2 chains (boxed regions), the AB line exhibits the formation of the local charge-density modulation of finite length most clearly with a doubled periodicity. It is surprising to find that the structure of the Na-induced local charge-density modulation at low coverage closely resembles that of the CDW of the clean cold 4  $\times$  2 surface [3]. Note the 1D character of the Na-induced local charge-density modulation produced along only the chain direction. Apparently, the area of Na-induced charge modulation grows with increasing Na coverage. We indeed observe a fully developed Na-induced CDW at high coverages in our STM image (not shown). At high coverages where interaction between Na adatoms may significantly modify the surface band structure, the surface may transform into a 2D reconstruction rather than the 1D CDW of Peierls origin at a low coverage.

Having characterized the presence of the Na-induced 4  $\times$  2 CDW at room temperature, we now investigate concomitant changes in electrical properties of the surface. Our EELS measurements presented in Fig. 3 reveal several important features which are quite consistent with the Na-induced formation of CDW (Fig. 2). The change in the linewidth of the elastic peak in Fig. 3A unambiguously

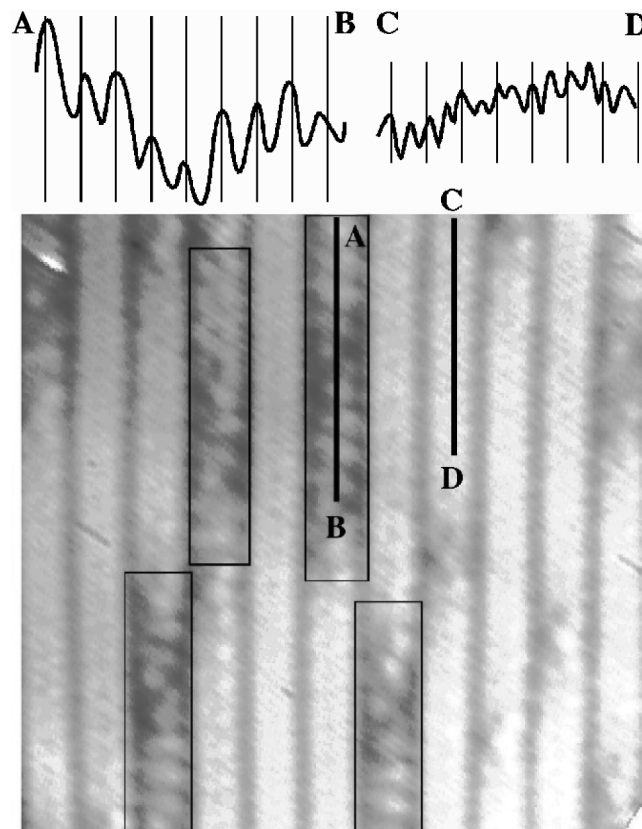


FIG. 2. A filled state STM image of the Na-added In/Si(111)-(4  $\times$  1) surface at room temperature (bottom). The intensity profiles along the line AB (of the 4  $\times$  2 domain) and the line CD (of the 4  $\times$  1 domain) are plotted to show the period doubling by Na adatoms. The bias voltage is 1 V.

reveals an MIT which appears upon Na adsorption. This is seen by the much reduced width (11.5 meV) from the  $4 \times 2$  surface compared to the wide Drude tail (33.6 meV) from the metallic  $4 \times 1$  surface. Since a long Drude tail in the elastic peak due to the continuum of interband transitions near the Fermi level represents a metallic character of a surface, its loss from the Na-induced  $4 \times 2$  surface clearly indicates the insulating nature of the surface.

In Fig. 3, loss spectra taken from the Na-induced insulating  $4 \times 2$  surface (Fig. 3B) and the clean surfaces (Figs. 3C and 3D) at different scattering geometries (different sets of incidence angle  $\theta_i$  and outgoing angle  $\theta_f$ ) are also presented. In order to find loss peaks hidden in the background and to quantify them more accurately, we have fitted the spectra assuming a Gaussian line shape for a loss peak and a polynomial background [8,16]. The loss peak  $S_P$  almost hidden in the specular geometry shows up as a discernable peak in off-specular geometry at the loss energy of 62 meV. This loss peak has been previously identified as an excitation of a flat surface phonon of the

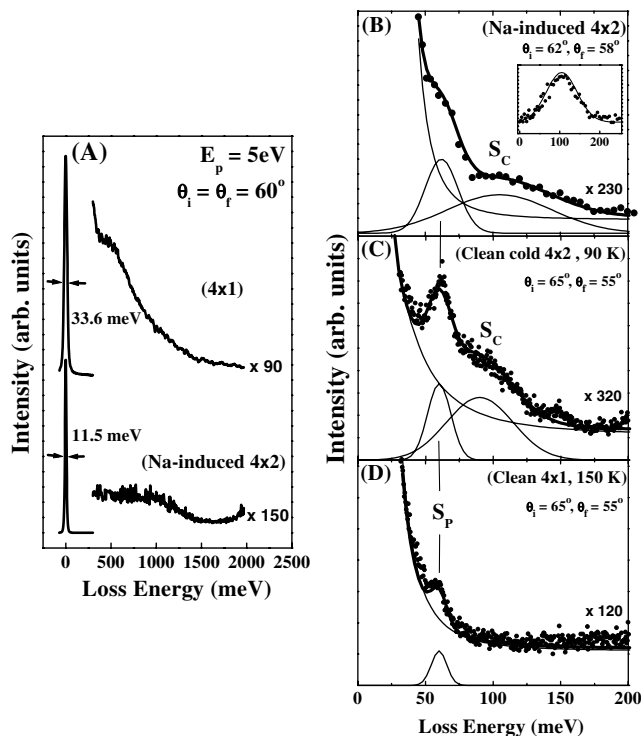


FIG. 3. Characteristic loss features in HREELS spectra revealing the electrical nature of the surfaces. In (A), the broad Drude tail indicating the metallic nature of the  $4 \times 1$  surface disappears from the  $4 \times 2$  surface demonstrating a Na-induced MIT. Off-specular HREELS spectra taken from three different surfaces, the Na-induced  $4 \times 2$  (B), the clean cold  $4 \times 2$  (C), and the clean  $4 \times 1$  (D), show their unique loss features. The spectra from the clean surface are from Ref. [4]. The solid curves are fitted peaks. Other than the loss peak  $S_P$  from surface phonon, the presence of a unique loss peak  $S_C$  (inset in B) is apparent for the two semiconducting surfaces [(B) and (C)] in sharp comparison with the absence of metallic  $4 \times 1$  surface (D). The  $S_C$  is attributed to an interband transition representing a CDW gap, as discussed in text.

clean cold  $4 \times 2$  surface [4]. An important finding here is the presence of a weak and broad loss peak  $S_C$  barely visible near the tail of the  $S_P$  for both semiconducting surfaces (Figs. 3B and 3C). Note that such a peak is clearly absent from the metallic  $4 \times 1$  surface (Fig. 3D). After subtracting the background and the phonon peak  $S_P$ , we find a well defined  $S_C$  at a loss energy of  $105 \pm 8$  meV with a linewidth of  $73 \pm 30$  meV for the Na-induced  $4 \times 2$  surface, as shown in the inset of Fig. 3B. It grows in intensity with increasing Na coverage and becomes dominant near 0.4 ML where the Na-induced  $4 \times 2$  surface is best developed. At this coverage, the peak appears to be most prominent at the off-specular geometry where  $\theta_i = 62^\circ$  and  $\theta_f = 58^\circ$ . As will be discussed below, this peak turns out to be closely related to the formation of the Na-induced CDW. In Fig. 4A, further evolution of EEL spectra with Na coverage is shown. Here we find two characteristic loss peaks  $S_1$  and  $S_2$  for the metallic  $4 \times 1$  and the insulating  $4 \times 2$  surfaces, respectively.

Now we discuss where the  $S_C$  comes from. We first exclude possibilities other than an interband transition as the origin of the loss peak, as discussed below. The significantly higher loss energy of  $S_C$  ( $E_L \sim 105$  meV) and its order of magnitude broader linewidth compared to the corresponding values of a typical metal-Si vibrational mode (for example,  $E_L \leq 25$  meV) easily rule out the vibration of atomic origin [17,18]. Also it cannot be a single-phonon peak since all the phonon peaks exist only below 100 meV [4]. The somewhat broad line width ( $\sim 73$  meV) of  $S_C$  is typical for an interband transition.

We thus believe that the  $S_C$  stems from an interband transition. A previous photoemission study reveals that there exist three In-derived surface bands  $m_1$ ,  $m_2$ , and  $m_3$  which cross Fermi energy in the third Brillouin zone for the clean metallic  $4 \times 1$  surface, as sketched in Fig. 4B (left) [3,11,14,19]. Also shown in Fig. 4B (right) is a band diagram for the insulating  $4 \times 2$  surface to explain the opening of the CDW gap with Na adsorption. Since surface bands which can be associated with this loss peak attributed to an interband transition are not found from the clean metallic  $4 \times 1$  surface [3,11], the  $S_C$  should represent a new interband transition, unique only to the  $4 \times 2$  surface where a CDW is formed. Naturally we attribute the  $S_C$  to the CDW gap energy  $\Delta$  (see Fig. 4B) as the interband transition between the split bands at the nesting vector  $2k_F = \pi/a$  ( $a = 3.84 \text{ \AA}$ )  $= 0.82 \text{ \AA}^{-1}$  [3]. This assignment explains not only the presence of the  $S_C$  itself but also the doubled periodicity of the CDW as  $1/k_F$ . We are thus led to conclude that the CDW gap energy  $\Delta = 105 \pm 8$  meV of the Na-induced  $4 \times 2$  surface manifests itself as a loss peak  $S_C$ . The value for  $\Delta$  of the Na-induced surface we thus obtained turns out to be quite close to that of the clean cold  $4 \times 2$  surface, i.e.,  $\sim 100$ – $150$  meV estimated from photoemission study [3] and  $98 \pm 3$  meV from our HREELS data in Fig. 3C. It is, however, much greater than a corresponding mean-field

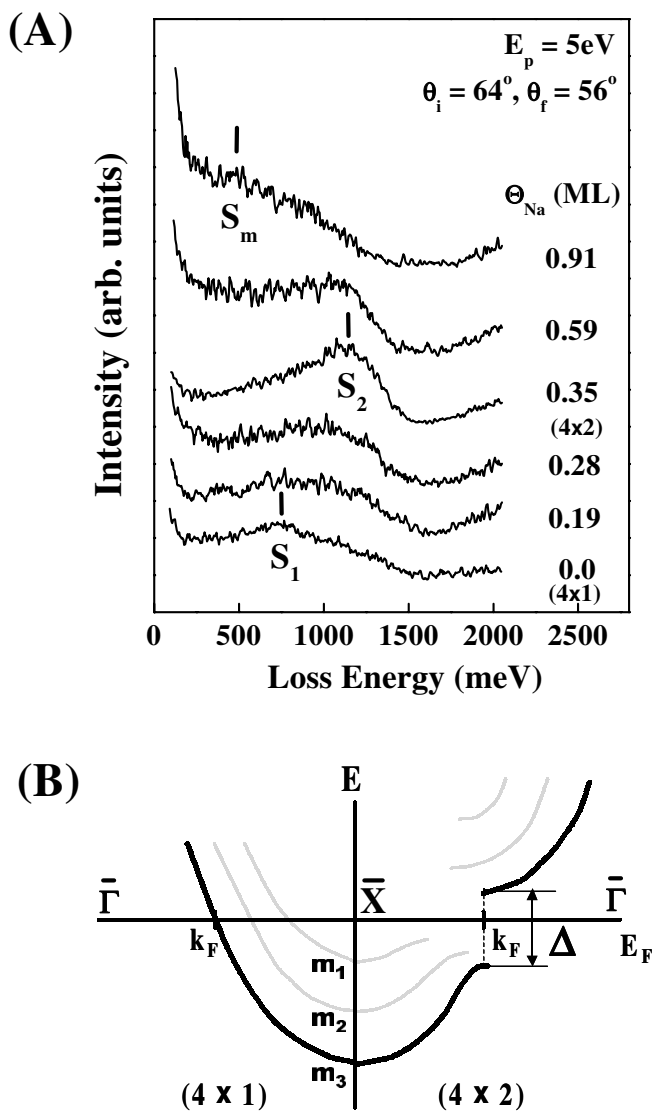


FIG. 4. (A) Spectral evolution of HREELS spectra with Na coverage at off-specular geometry. A loss peak  $S_2$  unique to the  $4 \times 2$  domain grows in intensity with increasing Na coverage at the expense of the  $S_1$  of the  $4 \times 1$  domain. Near saturation coverage, another loss peak ( $S_m$ ) indicating the overlayer metallization appears. (B) Schematic band diagrams in the third Brillouin zone for the  $4 \times 1$  (left) and the  $4 \times 2$  (right) surfaces to illustrate the opening of a CDW gap ( $\Delta$ ) with Na adsorption at  $k_F$ . The loss energy of  $S_c$  is attributed to the CDW gap energy  $\Delta$ .

value ( $E_g = 3.53kT_c$ ) of  $\sim 40$  meV calculated using  $T_c = 130$  K of the clean metallic  $4 \times 1$  surface [20]. This may imply the enhanced electron-phonon coupling in this particular quasi-1D system. The effect of Na pinning centers on  $T_c$  has not been theoretically understood even now, except for the fact that a local potential screening anomaly should play a critical role. Several such examples showing Friedel-like charge oscillations induced by local defects have been reported [21–23].

Where do the other loss peaks  $S_1$  and  $S_2$  originate? Previous studies have already identified the  $S_1$  as an interband

transition [3,11–14]. As seen in Fig. 4A the rather high loss energy and broad linewidth of  $S_2$  also indicate an interband transition as the source of  $S_2$ . We, however, cannot identify the bands associated with it at the present time due to the lack of theoretical band dispersions of the Na-induced  $4 \times 2$  surface. As seen in Fig. 4A, the surface at high Na coverage exhibits another loss peak ( $S_m$ ), which is more likely to be an interband transition between Na-derived surface bands.

In summary, we report that Na adsorbates play a decisive role as pinning centers to form a CDW when introduced on the quasi-1D metallic  $4 \times 1$  surface at room temperature. In contrast to several previous studies showing the pinning of a CDW for 2D or 3D metallic systems [1,7], we thus present the first exemplary case, to the best of our knowledge, of the impurity-induced pinning of CDW for a quasi-1D metallic system.

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