RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 49, NUMBER 23 15 JUNE 1994-I

Structural model for the metal-induced Si(111)3 × 1 reconstruction

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(Received 2 August 1993)

We present a structural model for the metal-induced Si(111)3×1 reconstruction. Fivefold Si rings form one-dimensional π-bonded chains along $\langle 1\bar{1}0\rangle$. These chains are separated by empty channels that can accommodate $\frac{1}{3}$ monolayer of metal atoms. We propose that π-bonded chains undergo a strong disturbance resulting in the formation of alternating dimers consistent with published scanning tunneling microscope images [K.J. Wan *et al.*, Phys. Rev. B **46**, 13 635 (1992)]. Unlike previous models, this model accounts for most experimental observations, including a large band gap and chemical passivation.

The cleaved Si(111) surface exhibits a surface reconstruction with a doubling of the surface unit cell along the $\langle\bar{2}11\rangle$ direction.[1] This π-bonded chain reconstruction is metastable and transforms into the more complex (7×7) reconstruction[2] upon annealing. The driving force for these reconstructions is the reduction of the number of unsaturated surface dangling bonds which are energetically unfavorable and highly reactive. When monovalent metals, such as alkali metals or Ag, are deposited onto Si(111) at substrate temperatures in the desorption regime, the surface undergoes a (3×1) reconstruction.[3–10] Although alkali metals are highly reactive and typically enhance the surface oxidation rate, the alkali-metal-induced (3×1) reconstruction appears to be *chemically passivated*,[7] suggesting that the dangling-bond surface states are completely filled or absent. Recent scanning tunneling spectroscopy experiments[8] revealed an energy gap of ∼ 1 eV. In that study, it was suggested that the gap was due to electron correlation. Undoubtedly, the metal-induced Si(111)3×1 reconstruction exhibits unique chemical and physical phenomena that should be explored further. A prerequisite for further analysis is the resolution of both the metal-atom coverage and atomic structure.

Previously proposed (3×1) structures fail to explain the majority of observations. Fan and Ignatiev (FI) have characterized the (3×1) surface as an impurity-stabilized *substrate* reconstruction because their low-energy electron diffraction (LEED) *I-V* data were weakly metal specific and only small metal Auger electron spectroscopy (AES) signals were observed.[6] From scanning tunneling microscopy (STM) images of the Si(111)3×1-Na interface, Jeon *et al.* proposed a Na *overlayer* structure with an absolute coverage (Θ) of $\Theta_{\mathrm{Na}}=\frac{2}{3}$ ML, assuming that the Na atoms form the image at the applied tunneling bias.[8] Wan, Lin, and Nogami interpreted their STM data of Li and Ag differently, proposing a missing top-layer (MTL) model with $\Theta_{\mathrm{Ag,Li}}=\frac{2}{3}$ ML (Ref. 9) although they recognized that their model would make LEED *I-V* data[6] metal specific. Since STM does not reveal the chemical identity or the actual position of surface atoms, the atomic structure remains unresolved. In this paper, we propose the structural model depicted in Fig. 1. In this MTL model, fivefold Si rings form one-dimensional (1D) π-bonded chains along the $\langle 1\bar{1}0\rangle$ direction, separated by empty channels that can accommodate $\frac{1}{3}$ ML

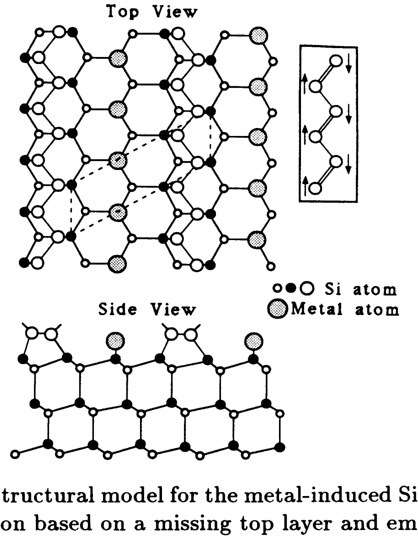

FIG. 1. Structural model for the metal-induced Si(111)3×1 reconstruction based on a missing top layer and empty channels which can accommodate $\frac{1}{3}$ ML of metal atoms. Inset: Peierls-like distortion of π-bonded Si chain resulting in the modulation of Si–Si bond lengths (alternating dimers).

0163-1829/94/49(23)/16837(4)/$06.00

of metal atoms. Our analysis is based on thorough characterization of the Si(111)3 × 1 reconstruction induced by Na, K, or Ag with LEED, AES, electron energy loss spectroscopy (EELS), and work-function change ($\Delta\Phi$) measurements. First, we show that $\Theta \leq \frac{1}{3}$ ML, thus ruling out models where $\Theta = \frac{2}{3}$ ML.[8,9] Second, we find that the Si(111)($\sqrt{3} \times \sqrt{3}$)$R30°$-Ag reconstruction proceeds from the saturated (3 × 1) surface *at room temperature* (RT). With this knowledge, we reinterpret the STM data[8,9] by introducing a model that, unlike alternative models, qualitatively accounts for most experimental observations including chemical passivation; a nonmetallic ground state; STM observations of channels, or "missing rows"; and, possibly, the similarity of LEED *I-V* data for different metals.

LEED, AES, and $\Delta\Phi$ measurements were performed in a UHV system ($p \approx 4 \times 10^{-11}$ mbar). EELS experiments were performed in another system ($p \approx 5 \times 10^{-11}$ mbar) housing LEED and a Leybold-Hereaus ELS-22 spectrometer. $\Delta\Phi$ was measured by the retarding field method using the LEED guns. Thus EELS data could be cross-referenced with *relative* coverages determined by AES. Alkali metals were deposited using thoroughly degassed chromate dispensers; Ag was deposited from a Knudsen cell. Si(111) wafers ($\rho = 1\ \Omega$ cm) were cleaned by the Shiraki method and heated to ~ 850 °C in UHV to obtain the (7 × 7) structure. The (3 × 1) structures were grown at substrate temperatures in the desorption regime (~ 400 °C for Na and K; ~ 600 °C for Ag). Special care was taken to thermally quench the substrate as soon as deposition was terminated. Otherwise, thermal desorption of metal atoms led to the coexistence of metal-induced (3 × 1) and bare (7 × 7) domains.[9] After cooling to RT, LEED revealed *only* three-domain (3 × 1) patterns. The coverage regime was extended by further deposition of alkali-metal atoms at RT, and $\Delta\Phi$ and AES data were acquired simultaneously. Ag was deposited on top of Si(111)3 × 1-Ag and Si(111)7 × 7 both at RT and 500 °C (below the Ag desorption temperature). At $T_s \approx 500$ °C, the (7 × 7) surface initially converts into a (3 × 1); at higher coverages, giant Si(111)($\sqrt{3} \times \sqrt{3}$)$R30°$-Ag domains are formed.[10] In the generally accepted honeycomb-chained-trimer model, $\Theta_{\mathrm{Ag}} = 1.0$ ML for the Si(111)($\sqrt{3} \times \sqrt{3}$)$R30°$-Ag domains.[10–12]

In Fig. 2 we show the AES intensity ratio $\mathfrak{R}$ of the Ag(MNN) and Si(LVV) AES signals as a function of deposition time ($T_s = 500$ °C). A clear kink marks the completion of the Si(111)($\sqrt{3} \times \sqrt{3}$)$R30°$-Ag interface corresponding to $\Theta_{\mathrm{Ag}} = 1.0$ ML.[10–12] Beyond the monolayer break, $\mathfrak{R}$ is nearly constant due to Ag clustering.[3] For the initial (3 × 1) interface, $\mathfrak{R}$ varied from sample to sample, ranging from ~ 0.05 to ~ 0.11; this distribution peaked at $\mathfrak{R} \approx 0.09$. For (3 × 1) interfaces having an initial $\mathfrak{R} \lesssim 0.08$, RT deposition resulted in diffuse LEED patterns. *For samples with an initial* $\mathfrak{R} \gtrsim 0.08$, *the (3×1) surface transformed into a Si(111)(*$\sqrt{3} \times \sqrt{3}$*)R30°-Ag structure upon subsequent RT deposition.* Typically, the formation of the Si(111)($\sqrt{3} \times \sqrt{3}$)$R30°$-Ag interface starting from (7 × 7) requires ~ 400 °C. Apparently, the major activation barrier is the removal of the (7 × 7) stacking fault. It is likely that (3 × 1) interfaces with $\mathfrak{R} \approx 0.08$ have *excess* Ag present in small Si(111)($\sqrt{3} \times \sqrt{3}$)$R30°$-Ag nuclei from which larger domains grow upon further deposition at RT. Although very small (7 × 7) domains possibly coexist, $\mathfrak{R} \approx 0.08$ for the pure (3 × 1) interface; *this corresponds to* $\Theta_{\mathrm{Ag}} \approx \frac{1}{3}$ *ML* (Fig. 2).

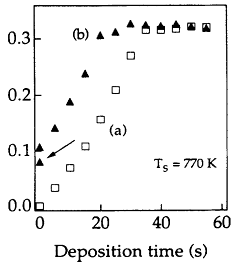

FIG. 2. $\mathfrak{R}$ of Ag*(MNN)* and Si*(LVV)* AES intensities as a function of deposition time, staring with (a) clean Si(111)7 × 7 surface or (b) Si(111)3 × 1-Ag interface. Arrow marks $\mathfrak{R}$ for the nearly stoichiometric Si(111)3 × 1-Ag interface.

AES uptake curves for RT Na deposition onto the clean Si(111)7 × 7 surface and Si(111)3 × 1-Na interface are shown in Fig. 3. Both curves exhibit a nearly linear uptake after which $\mathfrak{R}$ saturates. This behavior indicates growth to a single monolayer. $\Delta\Phi$ is consistent with this interpretation. The vertical offset in Fig. 3 (arrows) is equal to $\mathfrak{R}$ for the initial (3×1) interface and corresponds to a difference in Θ of ~ 25% of the RT-saturation coverage of the (7×7) interface. Although Θ for the saturated (7 × 7) interface has yet to be determined, a reasonable assumption is that the atomic density of a monatomic Na layer on Si(111)7 × 7 does not exceed that of bulk Na which corresponds to $\Theta \approx 1.1$ ML. Then, for the initial 3 × 1 interface, $\Theta_{\mathrm{Na}} \leq 0.3$ ML. We also measured the ratio of the K(LMM) and Si(LVV) Auger intensities for the Si(111)3×1-K and RT-saturated Si(111)7×7-K interface (0.10 and 0.36, respectively). Similar analysis leads to the conclusion that $\Theta_{\mathrm{K}} \leq 0.2$ ML for Si(111)3×1-K.[13]

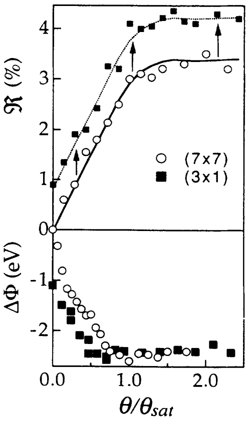

FIG. 3. $\mathfrak{R}$ of Na(KLL) and Si(LVV) AES intensities (top) and $\Delta\Phi$ (bottom) as a function of *relative* coverage θ with respect to RT saturation, starting with either the clean Si(111)7 × 7 surface or the Si(111)3 × 1-Na interface. Φ_{min} occurs at $\theta = 1$ ML for the (7 × 7) interface; Φ_{min} occurs at $\theta \approx 0.67$ ML for the (3 × 1).

Based on our data, we conclude that the coverage for the metal-induced (3×1) reconstruction is $\Theta \leq \frac{1}{3}$ ML. This is consistent with the small $\Delta\Phi$ of the initial Si(111)3×1-Na and Si(111)3×1-K interfaces with respect to the clean (7×7) surface (-1.0 and -1.4 eV, respectively). These observations are *absolutely incompatible* with previously proposed overlayer models requiring $\Theta = \frac{2}{3}$ ML. This strongly suggests that the features imaged by STM (Refs. 8 and 9) are not metal atoms but rather *displaced Si atoms*. Furthermore, the fact that the (3×1)-Ag interface can be transformed in a Si(111)($\sqrt{3} \times \sqrt{3}$)$R30°$-Ag interface at RT indicates that both reconstructions are closely related, suggesting that the (3×1) interface is also a MTL reconstruction. Wan, Lin, and Nogami reached the same conclusion based on the observation that the apparent height of the Si(111)($\sqrt{3} \times \sqrt{3}$)$R30°$-Ag and (3×1) phases is similar in STM.[9] Therefore, the key ingredients of our structural model are a *missing-row–missing top-layer reconstruction with* $\Theta = \frac{1}{3}$ *ML.*

In Figs. 4(a)–4(d), we show previously proposed models of the (3×1) reconstruction. The LeLay model[3] consists of adsorbate rows along $\langle 1\bar{1}0 \rangle$ separated by two empty rows [$\Theta = \frac{1}{3}$ ML, Fig. 4(a)]. The model of Jeon *et al.*[8] has two adsorbate rows leaving one row of dangling bonds exposed [$\Theta = \frac{2}{3}$ ML, Fig. 4(b)]; the observed nonmetallic behavior is viewed in terms of a Mott-Hubbard insulator. The model of Wan, Lin, and Nogami[9] consists of a missing-row arrangement of Si atoms along $\langle 1\bar{1}0 \rangle$ [$\Theta = \frac{2}{3}$ ML, Fig 4(c)]. In this MTL model, the metal atoms are bonded to the dangling bonds along the Si chains. However, half-filled dangling bonds still exist in the empty channels. The FI model[6] consists of a missing-row arrangement of Si atoms, but the metal atom positions were not considered since the reconstruction was thought to be impurity induced [Fig. 4(d)]. None of these models accounts for chemical passivation because unsaturated dangling bonds remain at the surface.

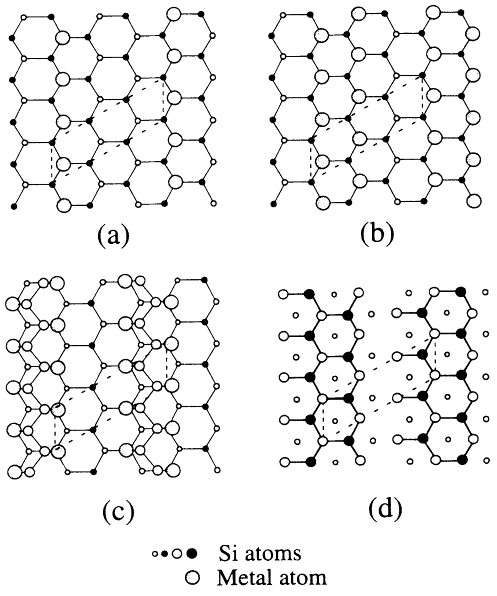

FIG. 4. Structural models for the metal-induced Si(111)3×1 surface reconstruction according to (a) LeLay (Ref. 3); (b) Jeon *et al.* (Ref. 8); (c) Wan, Lin, and Nogami (Ref. 9); (d) Fan and Ignatiev (Ref. 6).

Our (3×1) surface model (Fig. 1) incorporates a MTL reconstruction and missing rows similar to the structure of Ref. 9; specifically, $\frac{2}{3}$ ML of Si atoms form chains along $\langle 1\bar{1}0 \rangle$ atop an ideally truncated Si(111) surface. The Si chains consist of fivefold rings, reminiscent of the Si(111)2×1 structure.[1] Placing the metal atoms in the troughs, bonding to and *saturating* the *second-layer* dangling bonds, gives $\Theta = \frac{1}{3}$ ML. The remaining Si atoms in the chains possess half-filled dangling bonds that are tilted with respect to the $\langle 111 \rangle$ direction. Rather than satisfying these dangling bonds with metal atoms,[9] in our model, these hybrid states delocalize along the chain, forming a quasi-1D half-filled π band. As previously noted,[14] such a bonding scheme is chemically reasonable. If the chains were truly 1D, they should be unstable with respect to a Peierls distortion with modulation wave vector $2k_F$, where k_F represents the Fermi wave vector. Consequently, the Si–Si bond length would be modulated with a period of $2\pi/2k_F$, resulting in a conjugated chain with alternating Si=Si "double bonds," or dimers, similar to conjugated polymers like polyacetylene.[15] In fact, this scenario is consistent with the STM images of Wan, Lin, and Nogami.[9] The filled-state image reveals parallel 1D chains composed of alternating units which clearly *break the mirror-plane symmetry.* The empty-state image reveals a narrow band along the π-bonded chains.

The inequivalence of the neighboring chain atoms within the (3×1) unit cells opens a small gap (on the order of tens of meV) near the surface Brillouin-zone boundaries,[16] similar to Si(111)2×1,[1] and, strictly speaking, lifts the Peierls condition. However, to account for the large band gap of 1 eV, a strong lattice distortion is required. A Peierls-like distortion, or dimerization, of the *symmetric* chains would reduce the bandwidths of the occupied and unoccupied π bands, thereby increasing the gap. As noted previously,[17] the magnitude of the gap in conjugated chains scales with the asymmetry, suggesting that dimerization could indeed be energetically favorable. The magnitude of the observed surface band gap, $E_g \approx 1$ eV, is significantly larger than that of the *symmetric* π-bonded chain reconstruction of Si(111)2×1 ($E_g \approx 0.4$ eV).[18] For Si(111)3×1, the sharp onset of the interband excitation (Fig. 5) is indicative of a high surface density of states due to a $\pi \rightarrow \pi^*$ transition. It is not clear what sort of interchain interaction occurs to reverse the sense of dimerization between the chains, as seen with STM.[9] The channels appear dark because the metal-Si bonding-antibonding states probably reside well in the bulk bands. We also note that the relatively large gap may be difficult to explain based on the structural relaxation alone. It is possible that correlation effects act to enhance the size of the observed gap as they do for the conjugated polymers.

This model is consistent with the weak dependence on the metal species in LEED studies. The (3×1) interfaces have a wide homogeneity range[3,19] suggesting that most samples are nonstoichiometric. Certainly, this is

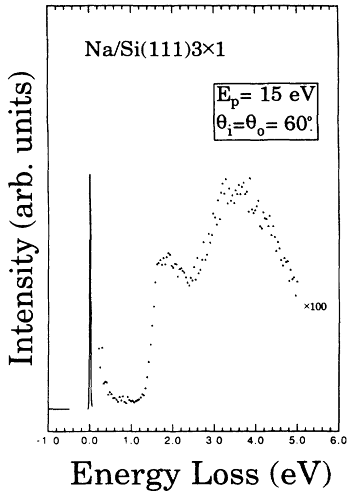

FIG. 5. EELS spectrum of the Si(111)3 × 1-Na interface acquired in the specular geometry. The steep onset at $\sim$ 1.2 eV is likely due to the $\pi \rightarrow \pi^*$ transition in the distorted π-bonded Si chains along $\langle 1\bar{1}0 \rangle$.

true for the K-induced reconstruction ($\Theta \leq 0.2$ ML). The AES data of FI indicated that $\Theta \ll \frac{1}{3}$ ML.[6] Deviations from ideal stoichiometry may reflect the experimental difficulty in quenching the sample temperature fast enough to inhibit metal desorption, probably resulting in a random occupancy disorder in the troughs consistent with streaking along $\langle 1\bar{1}0 \rangle$ in LEED.[9]

In conclusion, we have presented a model for the metal-induced Si(111)3 × 1 reconstruction consistent with most experimental observations. The saturation coverage for the metal species is $\Theta \leq \frac{1}{3}$ ML. We have also demonstrated that the Si(111)($\sqrt{3} \times \sqrt{3}$)$R30°$-Ag surface forms on the Ag-induced (3 × 1) surface at room temperature. The nonmetallic behavior of the (3 × 1) interface is likely due to a Peierls-like distortion of the quasi-1D Si chains. This represents an example of a surface reconstruction incorporating Si=Si double bonds. Such dimerization may lead to fascinating physical phenomena similar to what is observed in doped conjugated polymers.[15] In this regard, it would certainly be interesting to study the elementary excitations at this interface in more detail.

We thank S. C. Erwin, E. W. Plummer, and R. P. Messmer for stimulating discussions. Financial support was provided by the NSF-MRL program under Grants Nos. DMR 91-20668 and NSF-DMR 91-20398. E.J.M. acknowledges financial support from DOE under Grant No. 91ER45118. R.P.S. acknowledges financial support from the NIH-MBRS program under Grant No. 5506GM08267-05.

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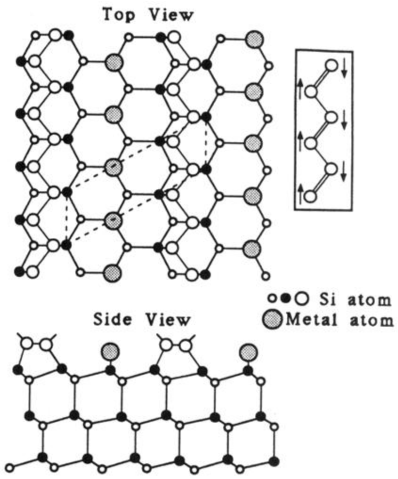

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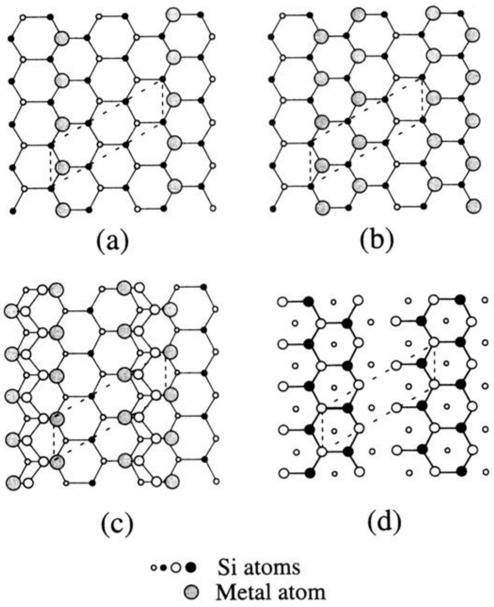

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