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Metal-adsorbate-induced Si(111)-(1×3) reconstruction

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The (1×3) phases generated by the adsorption of silver and alkali-metal atoms on the Si(111)-(7×7) surface are confirmed as a substrate reconstruction through the measurements of low-energy electron diffraction *I-V* curves for the (1×3) structures. The metal adsorbates which induce the (1×3) reconstruction are all at coverages below $\frac{1}{3}$ and have no long-range order.

I. INTRODUCTION

The Si(111) surface has been used in a variety of studies of the metal-semiconductor interface.[1-3] A number of ordered structures of the interface have been observed at submonolayer metal coverages.[1-4] Among those ordered phases is a (1×3) phase which has been observed for Ag (Refs. 2 and 3) and all alkali-metal[4] adsorption. The exact atomic structures of the (1×3) phases, however, are not available and all proposed models for them are of ordered overlayers of (1×3)-row adatoms.[2-5]

Recently, a (1×3) phase has also been observed for alkali metals adsorbed on the Ge(1110-*c*(2×8) surface.[6] In that case, low-energy electron diffraction (LEED) measurements have shown almost identical *I-V* curves for the different adsorbates. Those identical LEED *I-V* curves for the (1×3) structures clearly indicate that the adsorbates have no long-range order on the surface and that the (1×3) structure is due to reconstruction of the Ge(111) surface.

Since the (111) surfaces of diamond structure crystals have certain general properties such as the $(\sqrt{3}\times\sqrt{3})R30^\circ$ reconstruction,[7] it is worthwhile to examine the LEED *I-V* curves for the (1×3) structures of silver and alkali-metals adsorbed Si(111) surface. The results of LEED and Auger-electron spectroscopy (AES) studies to be reported here are contradictory to the current overlayer model for the (1×3) structure, and suggest an adatom-induced reconstruction of Si(111) consistent with the recent LEED results of the Ge(111) surface.[6]

II. EXPERIMENTAL

The experiments were performed in an ultra high-vacuum (UHV) chamber with a four-grid LEED optics, which was also used as a retarding field analyzer for AES. The LEED *I-V* curves were measured from the LEED optics with a video camera interfaced to a computer. In the experiments, two different Si(111) samples were used. The first one was cut from an undoped silicon single crystal block and aligned with x-ray diffraction to expose the (111) surface to better than 0.2°. The surface was mechanically polished in air to yield a smooth flat surface and then cleaned in UHV by Ar (1-keV) ion bombardment and annealed at 1100 °C. The second one was a piece of a *p*-type doped Si(111) wafer with a resistivity of 60 Ω cm. The second sample was treated in air with nitric acid and hydrochloric acid to reduce the thickness of the surface oxide layer and the metal impurities in the surface region, and the surface was cleaned by annealing at 1200 °C in UHV.

The alkali-metal deposition sources were the thermal cells from SAES Getters Inc. and the silver source was a tungsten wire source. The deposition sources were mounted about 12 cm away from the sample. The deposition rates of the sources were calibrated by a quartz microbalance attached next to the sample. The vacuum in the chamber was better than 3×10^{-10} Torr during the experiments.

The samples after cleaning showed clear (7×7) LEED patterns before adsorption of Li, Na, and Ag. The mechanically polished sample was first used in the exposure to the vapors of Li, Na, and Ag. For the alkali-metal deposition, ordered structures were searched within the exposure range of between 0.05 and 1 monolayer (ML), and an anneal temperature range of up to 1100 °C at which the (7×7) structure was restored. At low alkali exposures (≈0.2 ML), a (1×3) structure was observed for both Li and Na after an anneal at about

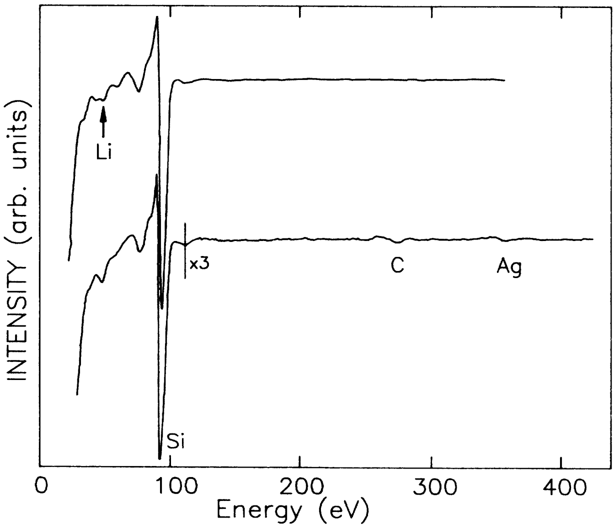

FIG. 1. The AES spectra of Li and Ag Si(111)-(1×3) structures.

800 °C for several minutes. At higher exposures (>0.3 ML), the (1×3) phase was still observed after an anneal, however for the Li deposition (>0.3 ML), a $(\sqrt{3}\times\sqrt{3})R30$ phase was first observed after an anneal at 600 °C for a few minutes. This $(\sqrt{3}\times\sqrt{3})$ phase gradually disappeared while annealing at 800 °C and was replaced by the (1×3) phase.

For the silver deposition (>0.3 ML) on the Ar^+ sputter cleaned sample, a mixture of a (1×3) and weak (1×6) phase appeared after an anneal at about 900 °C for 1 min. This mixed phase, which results from other residual metal impurities on and/or in the surface, has been also observed by other groups.[2,5] However, the anneal of the acid-treated sample exposed to silver (>0.3 ML) first resulted in a clear $(\sqrt{3}\times\sqrt{3})$ phase and then a clear (1×3) phase at a temperature of about 900 °C. There

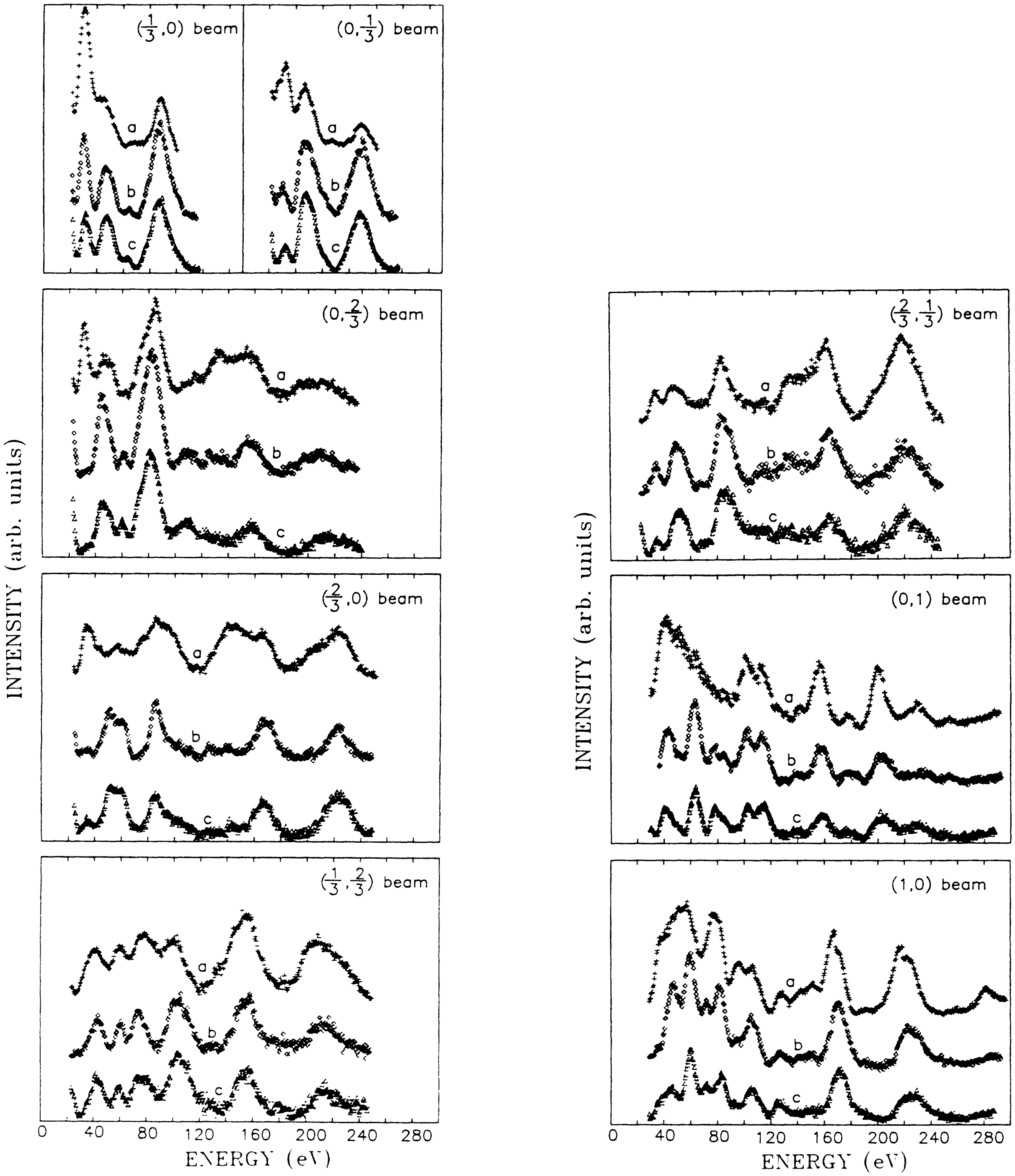

FIG. 2. The measured LEED I-V curves of the (1×3) structures of (a) Ag-, (b) Li-, and (c) Na- exposed Si(111) surface.

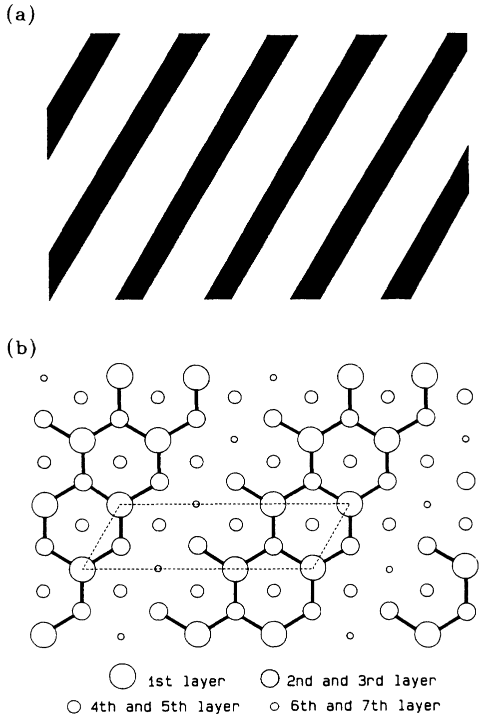

FIG. 3. (a) The sketch of the STM image (Ref. 5) of the Ag-(1×3) structure. (b) A proposed missing-row model of the (1×3) reconstruction of the Si(111) surface induced by Ag and alkali-metal adsorption.

was no trace of the (1×6) phase observed in the (1×3) LEED pattern.

III. DISCUSSIONS

The concentrations of the Ag and the alkali metals in the Si(111) surface were examined by AES. As shown in Fig. 1, the AES signals for Li and Ag for the (1×3) structures are extremely small, approximately one-fifth of the AES signals observed for the $(\sqrt{3}\times\sqrt{3})$ structures. The Ag and alkali-metal concentrations estimated from the AES data are about 0.01. The low values are a result of the diffusion and desorption of the adatoms during annealing at high temperature. It is improbable, therefore, that the (1×3) structures observed after adsorption and annealing due to the previously proposed metal atom overlayer structure.[2,4,5]

LEED *I-V* curves for the (1×3) structures of Ag, Li, and Na on the Si(111) surface were measured as shown in Fig. 2. The *I-V* curves of each individual beam for Li and Na are almost identical in spite of the dramatic difference in atomic size and scattering factor of Li and Na. The equivalence of the LEED *I-V* spectra clearly indicates the existence of an identical atomic structure of the Li and Na (1×3) phases. As a result, the (1×3) structure could not be due to ordered adlayer of Li and Na. Therefore, the (1×3) phase of alkali-metal adsorption is a result of the Si(111) substrate reconstruction. This result is consistent with the recently reported (1×3) reconstruction of alkali-metal exposed Ge(111) surface.[6]

The LEED *I-V* curves of most individual beams for the Ag-(1×3) phase are almost identical or very similar to those for alkali-metal (1×3) phase in Fig. 2. The notable differences between the *I-V* curves of the Ag (1×3) phase and those of the Li and Na (1×3) phases are mainly at lower-energy range (< 100 eV). These are probably a response to the changes in the surface potential barrier due to the different adsorbates. The other differences in the *I-V* curves at energy > 100 eV may result from a combination of several possibilities, such as some subtleties of the reconstructed structure.

The basis for the metal-induced reconstruction is probably a charge transfer between adatoms and substrate atoms in the Si(111) surface region. As a result of the adsorption, the surface electronic band structure of the substrate is altered significantly.[8–10] The change in the electronic band structure of substrate surface could result in an instability of the surface-phonon structure, which would drive the surface reconstruction at high temperature for a lower total surface energy.

The determination of the exact atomic structure of the (1×3) reconstruction requires further studies through LEED dynamical calculations. However, some speculations can be made as to the (1×3) surface structure, especially in light of recent scanning tunneling spectroscopy (STM) studies.[5] Based on the present combined LEED and AES work and the STM images in Ref. 5, the atomic structure of the (1×3) reconstruction would be a "missing-row" structure [Fig. 3(b)]. This suggestion stems from the narrow dark bands and broad bright bands seen in the STM image interpreted as a missing single row of silicon atoms and protruding double rows of silicon atoms. This interpretation is strongly affected by STM parameters (bias voltage and polarity and tip condition) and hence the exact structure could be more complicated than stated. As noted, this is currently being determined through full dynamical calculations.

IV. CONCLUSIONS

A (1×3) reconstruction of the metal adsorbed Si(111) surface has been identified through the comparison of LEED *I-V* curves from Ag, Li, and Na adsorbed surfaces. Both LEED and AES results clearly indicate that the adsorbates do not participate in any long-range-ordered structure and serve only to induce the surface reconstruction.

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