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Photoemission study of a thallium induced Si(1 1 1)-($\sqrt{3} \times \sqrt{3}$) surface

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Abstract

We have investigated the surface electronic structure of the Tl induced Si(1 1 1)-($\sqrt{3} \times \sqrt{3}$) surface by using angle-resolved photoelectron spectroscopy. Three semiconducting surface states were observed in the gap of the bulk band projection. Of these three states, the one, whose binding energy is approximately 0.3 eV, hardly disperses. Regarding the two other states, we discuss their properties by comparing their dispersion behaviors with those of the surface states of the other group III metal (Al, Ga and In) induced ($\sqrt{3} \times \sqrt{3}$) reconstructions. The split observed at the $\overline{\Gamma}$ point and the smaller dispersion widths of these two states indicate that the origins of the surface states of the Tl induced ($\sqrt{3} \times \sqrt{3}$) reconstruction are not the same as those of the Al, Ga and In induced ($\sqrt{3} \times \sqrt{3}$) reconstructions. These results support the idea that the atomic structure of the Tl/Si(1 1 1)-($\sqrt{3} \times \sqrt{3}$) surface is different from that of the ($\sqrt{3} \times \sqrt{3}$) reconstructions induced by other group III metals, which was proposed in the literature.

Keywords: Angle-resolved photoemission; Surface states; Low-energy electron diffraction; Surface structure; Silicon; Thallium

1. Introduction

The interaction between the metals Al, Ga and In in group III and Si surfaces has been an object of numerous investigations. On a Si(1 1 1)-(7 × 7) surface, these three metals have been reported to form magic cluster arrays at modest temperature [1–5], and a ($\sqrt{3} \times \sqrt{3}$) reconstruction with a 1/3 monolayer (ML) coverage of metal atoms adsorbed on T_4 sites (Fig. 1) at higher temperatures [6–10]. In all cases, the Al, Ga or In group III metals behave as trivalent atoms.

Thallium (Tl), the heaviest element of this group, has a peculiar behavior in the form of the so-called *inert pair effect* that is different from the other group III metals (Al, Ga and In). This different behavior leads to the formation of a (1 × 1) phase at a coverage of 1 ML [11–16] that has not been observed by the adsorption of other group III metals. On this (1 × 1) surface, Tl has been reported to behave as a monovalent atom with the $6s^2$ electrons forming an inactive inert pair [14,16,17]. Together with the (1 × 1) surface, (3 × 1) and ($\sqrt{3} \times \sqrt{3}$) domains have been observed using scanning tunneling microscopy (STM) [13]. Taking into account that the (3 × 1) reconstruction is a typical phase formed by monovalent atoms (alkali metals or Ag) and the ($\sqrt{3} \times \sqrt{3}$) reconstruction is a typical phase formed by the other group III trivalent atoms, a variable valency for Tl on Si(1 1 1) has been proposed [13,14]. However, recently, the valence state of Tl was reported to be monovalent at coverages up to 1 ML and the atomic structure of the Tl induced ($\sqrt{3} \times \sqrt{3}$) surface has been proposed to be different from those formed by other group III metals [17]. A difference in the atomic structure and a monovalent state of Tl suggest that the Tl induced ($\sqrt{3} \times \sqrt{3}$) surface might show interesting electronic properties that differ from the Al, Ga and In induced ($\sqrt{3} \times \sqrt{3}$) surfaces. Nevertheless, the electronic structure of the Tl induced ($\sqrt{3} \times \sqrt{3}$) surface has not been studied so far. Further, there is no strong evidence pointing at any particular atomic structure of the Tl induced ($\sqrt{3} \times \sqrt{3}$) surface and the determination of the surface electronic structure is an important input to the structure determination.

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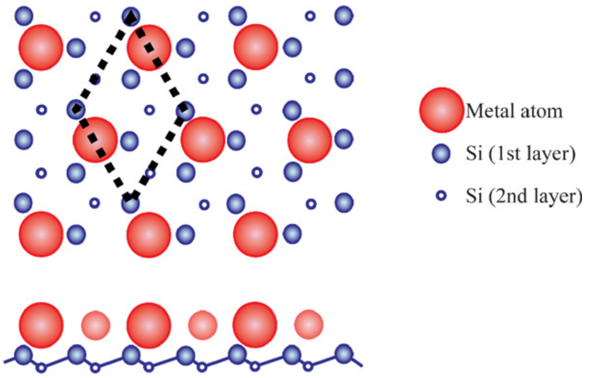

Fig. 1. Schematic illustrations of a Si(111)-($\sqrt{3}\times\sqrt{3}$) surface formed by the adsorption of 1/3 ML of the metals Al, Ga, and In in group III. Large filled circles are metal atoms, which are adsorbed on the T_4 site, and the other circles are Si atoms. The thick dashed lines indicate the $\sqrt{3}\times\sqrt{3}$ unit cell.

In this paper, we present angle-resolved photoelectron spectroscopy (ARPES) measurements of the Tl induced Si(111)-($\sqrt{3}\times\sqrt{3}$) surface. Three surface states, none of which crosses the Fermi level, were observed in the bulk band gap. We discuss the origins of these three surface states by comparing their dispersion features with those of the surface states of the Al, Ga and In induced ($\sqrt{3}\times\sqrt{3}$) reconstructions. Based on the dispersion features, we also discuss the atomic structures of the Tl induced ($\sqrt{3}\times\sqrt{3}$) surface.

2. Experimental details

The ARPES measurements and the LEED observations were performed at beamline 33 at the MAX-I synchrotron radiation facility in Lund, Sweden. Photoemission spectra were obtained using an angle-resolved photoelectron spectrometer and linearly polarized synchrotron radiation light using a photon energy of 21.2 eV. The total experimental energy resolution was ~50 meV and the angular resolution was ±2°. In order to obtain a clean surface, we annealed the sample at 1230 K by direct resistive heating in the vacuum chamber to remove the oxide layer, and at 1520 K to remove carbon contamination from the surface. After the annealing, a sharp (7 × 7) LEED pattern was observed, and neither the valence-band spectra nor the Si 2p core-level spectra showed any indication of contamination. Thallium was deposited from a Knudsen cell onto a clean Si(111)-(7 × 7) surface at a substrate temperature of 570 K. The base pressure was below 4×10^{-11} Torr during the measurements, and below 1×10^{-10} Torr during the Tl evaporation.

3. Results and discussion

The Tl/Si(111)-($\sqrt{3}\times\sqrt{3}$) surface was prepared by reducing the Tl coverage of a 1 ML Tl adsorbed Si(111)-(1 × 1) surface by annealing the sample at a temperature between 600 and 650 K. Fig. 2 shows the LEED pattern of the Tl/Si(111)-($\sqrt{3}\times\sqrt{3}$) surface obtained with a primary electron energy of 77 eV. The strong $\times\sqrt{3}$ spots observed in Fig. 2 indicate the formation of a surface covered almost entirely with ($\sqrt{3}\times\sqrt{3}$) domains, instead of small domains as reported by STM [13]. The formation of a well-defined Tl induced ($\sqrt{3}\times\sqrt{3}$) surface was also observed in recent LEED studies [14,17,18].

The ARPES spectra of the Tl/Si(111)-($\sqrt{3}\times\sqrt{3}$) surface are shown in Fig. 3, together with the Surface Brillouin zones (SBZs) of the Si(111)-(1 × 1) and ($\sqrt{3}\times\sqrt{3}$) surfaces (Fig. 3c). Figs. 3a and b are the spectra measured along the $[\bar{1}10]$ direction and along the $[11\bar{2}]$ direction using $h\nu$= 21.2 eV. All spectra are normalized to the background intensities at positions with binding energies of −0.3 eV. As indicated in Fig. 3c, the $[\bar{1}10]$ and $[11\bar{2}]$ directions correspond to the $\bar{\Gamma}$–$\bar{K}$ and $\bar{\Gamma}$–$\bar{M}$ directions of the (1 × 1) SBZ, respectively. The $[\bar{1}10]$ direction also corresponds to the $\bar{\Gamma}$–$\bar{M}(\sqrt{3})$ direction of the ($\sqrt{3}\times\sqrt{3}$) SBZ, and the $[11\bar{2}]$ direction corresponds to $\bar{\Gamma}$–$\bar{K}(\sqrt{3})$ of the ($\sqrt{3}\times\sqrt{3}$) SBZ. The symbols $\bar{M}$ and $\bar{K}$ are the symmetry points of the (1 × 1) SBZ and the symbols $\bar{M}(\sqrt{3})$ and $\bar{K}(\sqrt{3})$ are those of the ($\sqrt{3}\times\sqrt{3}$) SBZ. The angle-resolved photoelectron spectra were recorded at every 2° from an emission angle (θ_e) of −4° to 32° in the $[\bar{1}10]$ direction, and at every 2° from $\theta_e = -4°$ to 18° in the $[11\bar{2}]$ direction. A state, labeled S_1, is observed at a binding energy of approximately 0.3 eV in both directions. Since this state does not cross the Fermi level and no other state is observed at lower binding energies, we conclude that the electronic structure of the Tl/Si(111)-($\sqrt{3}\times\sqrt{3}$) surface is semiconducting. The three states labeled S_1–S_3 are surface states (see Fig. 4).

Fig. 4 displays the band dispersions of the Tl/Si(111)-($\sqrt{3}\times\sqrt{3}$) surface. The heavy dashed lines are the valence-band edge and an edge of a pocket taken from Ref. [19], and the thin dashed lines represent the symmetry points of the (1 × 1) and ($\sqrt{3}\times\sqrt{3}$) SBZs indicated at the top of the figure. The valence-band maximum (VBM) is estimated from the binding energy of the Si 2p core-level using the relation between $E_{\mathrm{B(VBM)}}$, E_{F}, and $E_{\mathrm{B(Si2p3/2)}}$ *given in Ref. [20]. The intensities of the spectral features are approximately represented by the contrast in the gray-scale of Fig. 4 which represents the second derivatives of the original ARPES spectra (bright parts in Fig. 4 corre-*

Fig. 2. LEED pattern of the Tl/Si(111)-($\sqrt{3}\times\sqrt{3}$) surface. The primary electron energy is 77 eV.