Surface Science 604 (2010) 853–856

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Interaction of Ag with the Si(1 1 1)1 × 1–H surface

J.-H. Han [a], H.-N. Hwang [b], H.-G. Jee [b], B. Kim [a,b], S. Chung [a], Y.D. Kim [c], C.-C. Hwang [b,*]

[a] Department of Physics, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea
[b] Beamline Research Division, Pohang Accelerator Laboratory (PAL), Pohang University of Science and Technology, Pohang 790-784, Republic of Korea
[c] Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Republic of Korea

ARTICLE INFO

Article history:
Received 27 August 2009
Accepted for publication 10 February 2010
Available online 14 February 2010

Keywords:
Silver atoms
Si(1 1 1)1 × 1–H surface
Ag–Si bonds
Synchrotron radiation based photoemission spectroscopy
Low energy electron diffraction

ABSTRACT

Synchrotron radiation based photoemission spectroscopy (SRPES) and low energy electron diffraction (LEED) are used to study the interaction between Ag atoms and the Si(1 1 1)1 × 1–H surface. At an Ag coverage of 0.063 monolayers (ML) on the Si(1 1 1)1 × 1–H surface, the Si 2p component corresponding to Si–H bonds decreases, and an additional Si 2p component appears which shifts to a lower binding energy by 109 meV with respect to the Si bulk peak. The new Si 2p component is also observed for 0.25 ML Ag on the Si(1 1 1)7 × 7 surface. These findings suggest that Ag atoms replace the H atoms of the Si(1 1 1)1 × 1–H surface and form direct Ag–Si bonds. Contrary to the widely accepted view that there is no chemical interaction between Ag particles and the H-passivated Si surface, these results are in good agreement with recent first-principles calculations.

1. Introduction

H-passivated Si surfaces have attracted considerable attention due to its scientific importance as a fundamental system for examining initial adsorption phenomena and its technological interest as a good template for growing epitaxial semiconducting layers in Si device fabrication [1]. Previous studies on the initial adsorption of semiconductor materials (e.g. Si and Ge) on H-passivated Si surfaces demonstrated that H atoms should play an important role as a surfactant [2–6]. However, the role of H atoms in metal adsorption on H-passivated Si surfaces is unclear.

There have been a number of experimental and theoretical studies on the initial stage of Ag adsorption on H-passivated Si surfaces using ion scattering [7,8], diverse microscopic techniques (scanning tunneling microscopy (STM), scanning electron microscopy (SEM), transmission electron microscopy (TEM)) [9–12], classical potential simulation [12] and first-principle calculations [13]. These studies suggested that Ag atoms should freely migrate over H-passivated Si surfaces without any chemical interactions with substrate [13]. Adsorbed Ag atoms on the H-passivated Si surface have a high probability of encountering other Ag atoms to aggregate into larger Ag nanoparticles [13]. This process is widely understood as general growth mechanism of Ag on H-passivated Si surfaces. However, an alternative mechanism has also been suggested for the role of H atoms. The H atoms can be partially removed from the interface by the deposited Ag atoms, which may render strong Ag–Si bonds [14,15] Recent first-principle calculations supported this mechanism [16]. However, there are no experimental reports demonstrating the existence of Ag–Si chemical bonds.

This study examined Ag adsorption on the Si(1 1 1)1 × 1–H surface using low energy electron diffraction (LEED) and synchrotron radiation based photoemission spectroscopy (SRPES) at room temperature. The existence of Ag–Si chemical bonds is evidenced by the Si 2p core level spectra. The results suggest that Ag atoms replace H atoms on the surface, resulting in the formation of direct Ag–Si bonds. Ag atoms bound to Si act as nucleation centers of three dimensional islands of Ag on the Si(1 1 1)1 × 1–H surface. These results strongly support the results of recent first-principle calculations [16].

2. Experimental details

All the experiments were performed at the 7B1 beamline in Pohang Accelerator Laboratory. A n-type Si(1 1 1) wafer was used as substrate to prepare the Si(1 1 1)1 × 1–H surface. The clean Si(1 1 1)7 × 7 surface was prepared using a direct current heating method under ultra-high vacuum (UHV) conditions with a base pressure of 2×10^{-10} torr. The Si(1 1 1) substrate was outgassed at a sample temperature of 800 °C over a one day period, and flashed up to 1250 °C. Subsequently, the sample was cooled slowly to 850 °C and annealed at 850 °C for 10 min. The sample temperature was decreased slowly to room temperature (RT). After the cleaning process, a well-developed 7 × 7 LEED pattern and well-known Si 2p spectrum were obtained.

* Corresponding author. Tel.: +82 54 279 1254; fax: +82 54 279 1599.
E-mail address: cchwang@postech.ac.kr (C.-C. Hwang).

0039-6028/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2010.02.010

Ag atoms were evaporated from a piece of high-purity Ag wire wrapped with a tungsten filament that was heated resistively. In order to prepare the Si(1 1 1)$\sqrt{3} \times \sqrt{3}$–Ag surface, Ag was deposited onto the clean Si(1 1 1)7 × 7 surface kept at 850 °C. The sample was further annealed at 800 °C for 30 s. After annealing, a sharp $\sqrt{3} \times \sqrt{3}$ LEED pattern was observed. The Si(1 1 1)$\sqrt{3} \times \sqrt{3}$–Ag surface, where Ag coverage is 1 monolayer (ML), was used to calibrate the Ag coverage on the Si(1 1 1)1 × 1–H surface from the intensity ratio of Si 2p and Ag 3d spectra. The temperature of the substrate during Ag evaporation is RT.

All the SRPES experiments were carried out at a fixed angle of 45° between the hemispherical analyzer and incident light at RT. The photoelectrons were detected at emission angles of 0° and 60° with respect to the surface normal. The intensity of each spectrum was normalized to the storage ring current. The binding energy of the photoelectrons were calibrated by the position of the Au $4f_{7/2}$ core level of an Au plate.

3. Results and discussion

The Si(1 1 1)1 × 1–H surface was obtained by exposing the clean Si(1 1 1)7 × 7 surface to an atomic hydrogen atmosphere at a sample temperature of 400 °C. Atomic hydrogen was produced by the dissociation of hydrogen gas using a hot-tungsten filament with a total molecular hydrogen exposure of 2000 L (Langmuir = 10^{-6} torr × s). The crystallographic ordering and surface quality of the prepared Si(1 1 1)1 × 1–H surface was verified by the observation of a sharp 1 × 1 LEED pattern (Fig. 1a) and two clearly separated shoulders (S1 and S2) in the Si 2p core level spectrum (Fig. 1b). The wide-scan spectrum of Fig. 1c, in which Si 2s and Si 2p core level peaks are clearly visible, show that a well-defined Si(1 1 1)1 × 1–H surface was formed without any contamination.

The Si 2p core level spectra were obtained with photon energies of 135 eV and 140 eV for the Si(1 1 1)1 × 1–H and Si(1 1 1)7 × 7 surfaces, respectively. In addition, the spectra emphasizing the Si bulk contribution were also taken with a photon energy of 108 eV (data not shown here). The binding energy of the $2p_{3/2}$ component of the Si bulk was used as a reference for determining the shift in the relative binding energy upon Ag adsorption. (The binding energy-scale of each Si 2p spectrum was adjusted with respect to the maximum intensity of the Si bulk component.) Fig. 2a shows Si 2p core level spectra obtained at an emission angle of 60° and a photon energy of 140 eV at room temperature. The closed and open circles correspond to the Si 2p spectrum of the clean Si(1 1 1)7 × 7 surface and that of the Si(1 1 1)7 × 7 surface covered with 0.25 ML of Ag, respectively. For comparison, each spectrum was normalized to its maximum intensity (Fig. 2a). The Si 2p spectrum of the clean Si(1 1 1)7 × 7 surface show a shoulder on the lower binding energy side from the bulk components, corresponding to the surface components of the Si 2p peaks [17,18]. The deposition of 0.25 ML Ag on the Si(1 1 1)7 × 7 surface causes a significant change in the Si 2p spectrum (Fig. 2a). Upon Ag deposition, the shoulder reduces in intensity, whereas new features appear at the lower binding energy side from the Si bulk peaks (denoted by arrows). The new features should be related to the formation of Ag–Si bonds.

Fig. 2b shows the Si 2p core levels of the clean and Ag–adsorbed Si(1 1 1)1 × 1–H surfaces taken at an emission angle of 60° with a photon energy of 135 eV. The closed and open circles correspond to the Si 2p spectra of the clean and Ag (0.063 ML)–covered Si(1 1 1)1 × 1–H surfaces, respectively. Similar to the results in Fig. 2a, Ag adsorption induces the appearance of additional peaks with lower binding energies than those of the Si bulk peaks. The difference spectrum in Fig. 2b clearly shows the Ag-induced changes in the Si 2p level spectrum.

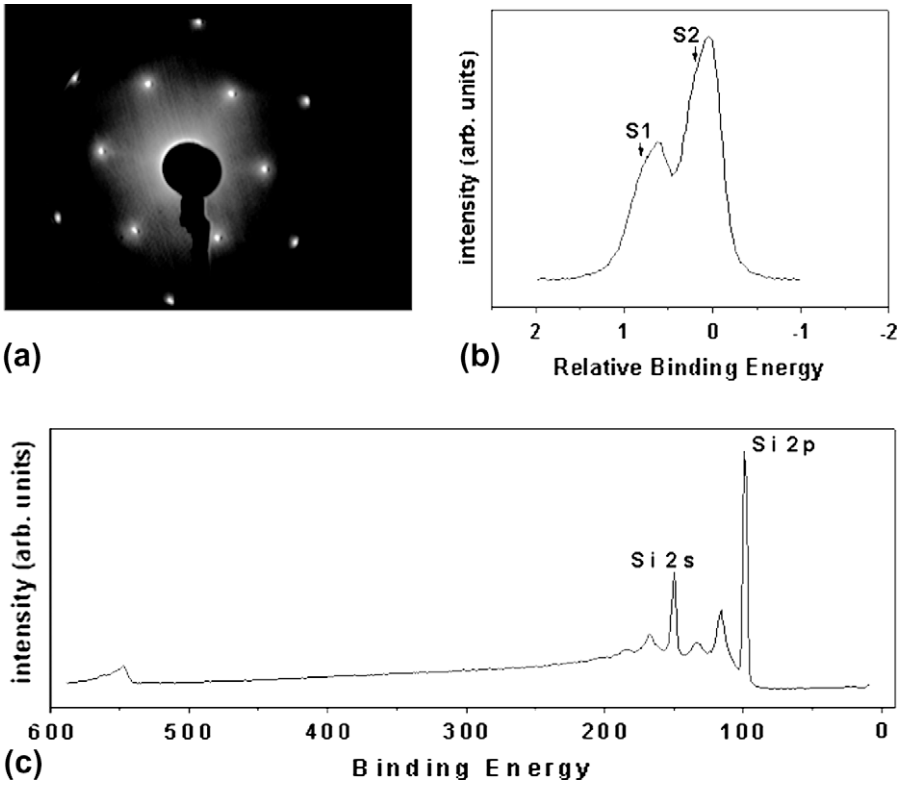

Fig. 1. (a) LEED pattern of the Si(1 1 1)1 × 1–H surface obtained at RT. (b) Si 2p core level spectrum of the Si(1 1 1)1 × 1–H; the photon energy and emission angle are 135 eV and 60°, respectively. S1 and S2 are a spin–orbit split component of the Si–H bonding [19]. (c) A wide-scan spectrum of the Si(1 1 1)1 × 1–H; the photon energy and emission angle are 630 eV and 0°, respectively.