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Atomic hydrogen induced gallium nanocluster formation on the Si(1 0 0) surface

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ABSTRACT

The influence of atomic hydrogen on the Si(1 0 0) substrate with submonolayer gallium surface phases – (2 × 3), (2 × 2) and (8 × 1) – as well as the deposition of gallium on monohydride terminated Si(1 0 0)–(2 × 1)-H surface were studied by synchrotron radiation photoelectron spectroscopy (SR-PES) and low energy electron diffraction (LEED) and compared with similar metal/Si systems. It was found that gallium deposition on the Si(1 0 0)–(2 × 1)-H surface at elevated temperature (400 °C) leads to a complete hydrogen desorption and formation of the same gallium surface phases as on the bare Si(1 0 0)–(2 × 1). Exposing the Si(1 0 0) substrate with (2 × 3)-Ga and (2 × 2)-Ga surface phases to atomic hydrogen results in the formation of gallium nanoclusters, surrounded by the Si(1 0 0)–(2 × 1)-H surface. These clusters have more than 2 monolayers in height and cover approximately 20–26% of surface, depending on the initial coverage. The results indicate that the cluster size and density may be controlled by initial Ga coverage and possibly by temperature.

1. Introduction

Gallium adsorption on Si(1 0 0) surfaces has been studied extensively in recent decades for its importance in heteroepitaxy of III–V semiconductors [1]. Gallium and its compounds may also play a significant role in various fields of nanotechnology [2,3], e.g. gallium droplets may be used as a catalyst for silica nanowire growth [4].

For coverages below half a monolayer (1 monolayer is equivalent to 6.78×10^{14} atoms cm^{-2} for an unreconstructed Si(1 0 0) surface) the deposition of gallium on the Si(1 0 0)–(2 × 1) surface leads to a formation of gallium rows oriented perpendicularly to the Si dimer rows [5,6]. These rows are constituted by gallium ad-dimers which are aligned parallel to the underlying silicon dimers [7–9]. Various sub-half monolayer reconstructions [10] are all formed by ad-dimer rows and differ from each other in the inter-row distances which are governed by repulsive interactions between these rows [7]. Rectangular arrays of gallium clusters with a spacing of $8 \times n$ with $n = 3$, 4 or 5 were observed by STM for coverages close to 0.8 ML [6,11]. As the adjacent arrays are shifted, the (8 × 1) diffraction pattern is observed [10].

The exposition of Si(1 0 0)–(2 × 1) surface to atomic hydrogen at 350–400 °C results in a formation of well-ordered monohydride Si(1 0 0)–(2 × 1)-H surface [12]. It is known that the modification of Si surface by atomic hydrogen strongly affects the nucleation and growth of metals by changing the surface free energy and/or diffusion lengths [12]. It was observed that full hydrogen termination of surfaces enhances the mobility of metal ad-atoms and thus promotes the island growth mode (Volmer–Weber) over Stranski–Krastanov one [12]. Similarly, the modification of metal/Si systems by atomic hydrogen has significant effect on the structure of metal atoms. In 1990, Oura et al. found that atomic hydrogen causes a reordering of the Si(1 1 1)–$(\sqrt{3} \times (\sqrt{3})$-Ag surface structure [13]. In the later studies, it was found that atomic hydrogen causes agglomeration of the Ag atoms into separate three-dimensional clusters. Hydrogen atoms replace Ag ones in the Si–Ag bonds. Ag atoms released in this way migrate over the remaining $(\sqrt{3} \times \sqrt{3})$-Ag surface and form clusters by mutual collisions [12]. This phenomenon is common for different metal/Si surfaces (e.g. Al/Si, In/Si, Ag/Si).

Apart from the clusters with a uniform size being formed at coverages of 0.80–0.85 ML at elevated temperatures, the droplets are formed for coverages larger than 1.5 ML. For coverages up to 0.5 ML either dimer rows or an amorphous structure is observed depending on substrate temperature. Small droplets are thus very difficult to obtain by direct deposition which limits the size range of Ga droplets available. Using atomic hydrogen after the deposition of a small amount of gallium, this limit can be surpassed. Moreover, the size of droplets may be controlled by the amount of gallium deposited on the surface.

In this paper synchrotron radiation photoelectron spectroscopy (SR-PES) was used to study the structural changes induced by atomic hydrogen in well-ordered surface phases of gallium, i.e.

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Si(100)–(2 × 3)-Ga, Si(100)–(2 × 2)-Ga, and Si(100)–(8 × 1)-Ga. In addition, the adsorption of Ga on hydrogen terminated silicon surface was examined as well. To directly observe the changes in surface structures and support interpretation of the SR-PES results, LEED was used as a complementary technique.

2. Sample preparation and analysis

The experiment was performed at the Materials Science Beamline of the Elettra Synchrotron Light Laboratory in Trieste in an UHV apparatus with base pressure below 2×10^{-8} Pa. Si samples were cut from an n-type (P-doped) silicon wafer with a resistivity of 0.0080–0.0085 Ω cm.

The samples were resistively heated and their temperature was measured by a pyrometer (wavelength 1.0 μm, the emissivity set to 0.7). The estimated error of the temperature measurement was 20 °C. Before deposition, each sample was flash-annealed several times at 1250 °C for 10–20 s while keeping the pressure under 1.5×10^{-7} Pa; after the final annealing cycle the sample was slowly cooled down to the deposition temperature in order to obtain a high quality Si(100)–(2 × 1) surface reconstruction. This was checked by LEED (Specs) which showed a good quality two-domain (2 × 1) diffraction pattern after the correct annealing process.

Gallium was deposited by a commercial e-beam effusion cell (Omicron EFM3/4) with a deposition rate of 2.0 ML h^{-1}. The deposition rate was calibrated according to the known surface structures [14]. The pressure during deposition was better than 5×10^{-8} Pa. All the analysis was carried out at room temperature.

Atomic hydrogen beam was produced by a home made thermal dissociation source. In the source a high purity (99.999%) hydrogen gas was flown through a tungsten capillary heated by electron bombardment to ~2000 °C. The dissociation ratio determined by a mass spectrometer (Balzers) was higher than 95%. In accordance with literature, additional experiments confirmed that molecular hydrogen has no effect on surface structure since its sticking coefficient on silicon surfaces is extremely low [15].

The photoelectron spectroscopy analysis was carried out using a hemispherical analyzer (Specs Phoibos 150). The spectrometer was operated in the Fixed-Analyzer-Transmission mode with a pass energy of 2 eV. The spectra were acquired in 0.1 eV energy steps and the beamline and monochromator slits were set to achieve a resolving power of 2000 (the total instrumental energy resolution was better than 0.1 eV). The diameter of an analyzed area was smaller than 100 μm. All the measured spectra were normalized to the intensity of p-polarized incident radiation which was decreasing in time due to a continuous decrease of electron current in the storage ring (down to the half of initial intensity). The incident radiation energy was determined by measuring the Fermi edge of a gold foil mounted on a sample holder. The radiation with energy of 145.7 eV was used for all experiments. Two different emission angles were used: 0° (normal emission) and 60° with respect to the surface normal. In both cases the angle between the detected photoelectrons and incoming photons was 60°.

3. Results and discussion

3.1. Atomic hydrogen interaction with Si(100)–(2 × 1)

The Si 2p spectrum taken from a clean silicon sample with the (2 × 1) reconstruction together with its deconvolution to the peak components is shown in Fig. 1. The peak parameters and their assignment according to [16] are summarized in Table 1 and discussed in our previous paper [14].

After exposure of the Si(100)–(2 × 1) surface to atomic hydrogen (300 L dosage) at 400 °C the well-ordered monohydride Si(100)–(2 × 1)-H surface [12] was formed. This was checked by LEED which showed a sharp two-domain (2 × 1) diffraction pattern. During the hydrogen adsorption apparent changes in the photoelectron spectra were observed. In the Si 2p spectrum (Fig. 2) the peaks related to Si dimers disappeared, the intensity of Si–S3 peak (second layer atoms) increased and intensity of Si–S4 and Si–S4′ peaks (third layer atoms) significantly decreased probably due to symmetrization of Si dimers, and a new component (marked as Si–H) with the SCLS + 0.36 eV and the Gaussian width 0.5 eV was observed. This new component can be attributed to the Si atom comprised in the symmetric monohydride terminated Si dimer since its position is very close to the value 0.35 eV for the Si–H bond observed during water adsorption on the Si(100)–(2 × 1) surface [14].

The valence band spectra of the Si(100)–(2 × 1) and Si(100)–(2 × 1)-H surfaces are shown in Fig. 3. Upon hydrogen adsorption the electronic states associated with asymmetric Si dimer dangling bonds (Si-D) at ~0.8 eV [17,18] completely disappeared and new states corresponding to Si–H bonds (s-SiH, SiH-1 and SiH-2) emerged. The s-SiH peak at ~8 eV is related to a s-type Si–H bond and two states SiH-1 and SiH-2 at 5.7 and 4.8 eV, respectively, may be assigned to the interaction between two adjacent Si–H sp hybrids within a dimer, with Si–H band splitting into to SiH-1 and SiH-2 subbands [17,18]. A shift of the whole spectrum by 0.2 eV to higher BE due to a band bending change was also observed after the saturation hydrogen coverage was reached.

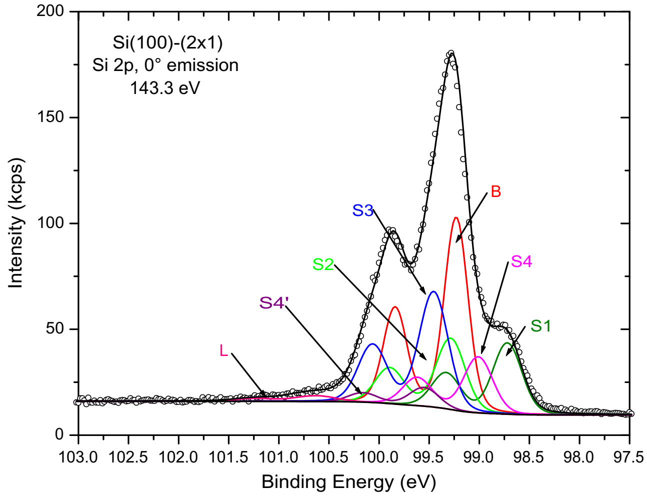

Fig. 1. Si 2p spectrum taken from Si(100)–(2 × 1) surface. For the components positions and assignment, see Table 1.

Table 1
Surface-core level shifts (SCLSs), Gaussian widths (GWs) and assignment of Si $2p_{3/2}$ peak components

Component	SCLS (eV)	GW (eV)	Peak assignment
Bulk (B)	0.00	0.25	Bulk silicon
S1	−0.510	0.31	Up dimer
S2	+0.055	0.31	Down dimer
S3	+0.225	0.31	Second layer
S4	−0.220	0.31	Half of third layer
S4′	+0.320	0.31	Second half of third layer
L	+1.4	0.45	Surface loss structure
Si–H	+0.36	0.5	Si–H, water adsorption
Si–OH	+0.95	0.5	Si–OH, water adsorption
Si–Ga1	−0.02	0.38	Si–Ga, Ga dimer
Si–Ga2	−0.16	0.38	Si–Ga, Ga cluster

The spin-orbit splitting 0.610 eV, branching ratio 0.5 and Lorentzian width 0.05 eV were common for all components.