Highly-stable passivation of a Si(111) surface using bilayer-GaSe

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Abstract

As a stable and 'epitaxial' passivation of a Si surface, we propose the bilayer-GaSe termination of a Si(111) surface. This surface is fabricated by depositing one monolayer of Ga on a clean Si(111) surface and subsequent annealing in a Se flux at around 520°C, which results in unreconstructed 1×1 termination of the Si(111) surface by bilayer-GaSe. We found by scanning tunneling microscopy observation that slow cooling of the clean Si(111) surface from 850°C to 520°C with simultaneous deposition of a Ga flux results in better termination of the Si(111) surface. It was also found that this surface is stable against heating around 400°C in O_2 atmosphere of 3×10^{-3} Pa. By utilizing these properties of the bilayer-GaSe terminated surface, we have succeeded in fabricating ZnO quantum dots on this substrate.

Keywords:

Surface passivation, Si, GaSe, bilayer-GaSe, dangling bond termination, ZnO, quantum dot

1. Introduction

The passivation of a Si surface is a key issue to utilize this material for many kinds of electronic devices. The formation of SiO_2/Si interface is the best passivation method to obtain the lowest defect density. However, the SiO_2 layer is not a single crystal so that it is difficult to fabricate a heteroepitaxial film of another compound on it, which may realize a novel Si-based hybrid device. As a single-crystalline, 'epitaxial' passivation of a Si surface, monohydride termination of a Si(111) surface is one of the effective methods, in which each active dangling bond is regularly terminated and an unreconstructed 1×1 surface is provided [1, 2]. On this surface it is possible to fabricate epitaxial films of organic molecules [3, 4], or of compound semiconductors with a layered structure [4, 5] by molecular beam epitaxy (MBE). In ultrahigh vacuum (UHV) the H-terminated Si(111) surface is stable up to around 270°C [6-8], so that deposited materials are able to migrate freely and form epitaxial layers without reacting with the Si surface. However, at higher temperature hydrogen atoms begin to desorb and the surface becomes reactive. In addition, the H-terminated surface is not stable against the oxidation in humid ambient [9], which will restrict the application of the terminated substrate in air.

As a more stable 'epitaxial' passivation of a Si surface, a bilayer-GaSe termination of a Si(111) surface has been recently proposed [10-14]. This surface (hereafter abbreviated to

'BGS' surface) can be fabricated by depositing one monolayer (ML) Ga on a clean Si(111) surface and successive annealing in a Se flux at 500 ~ 600°C [10, 11, 14], or by evaporating bulk GaSe onto the clean Si(111) surface at 550°C [12, 13]. The surface structure of the BGS surface is reported as shown in Fig. 1(a) [11, 12]. In this structure half of a unit layer of bulk GaSe (Fig. 1(b)) [15] is just located on the ideal Si(111) surface, although 2.2% mismatch exists between the lateral Si-Si interval (0.384 nm) and the lattice constant of a GaSe crystal (0.376 nm). Thus, it was expected that the BGS surface is as inactive as the cleaved surface of bulk GaSe free of active dangling bond. It was already reported that an epitaxial film of GaSe could be grown on the BGS substrate by MBE [16-18] in the manner of van der Waals epitaxy [19, 20], and we have also succeeded in fabricating GaAs quantum dots (QDs) [14] using the droplet epitaxy technique [21, 22] on the BGS substrate. It was also reported the BGS surface was not oxidized during the exposure to air for 30 days [13].

In this paper we will report on the first observation of the BGS surface by scanning tunneling microscope (STM), and propose an effective process to obtain a flat BGS surface. Then we will indicate the stability of the BGS surface against the heating in O_2 atmosphere. Finally, we will show results about the fabrication of ZnO QDs on this especially stable substrate against the oxidation.

2. Formation and Characterization of BGS surfaces

The BGS surface was formed in an UHV-MBE chamber with the base pressure of 3 $\times 10^{-8}$ Pa. Boron-doped *p*-type Si(111) wafers (1 ~ 10 Ωcm resistivity) were used as the substrate. A clean Si(111) surface was obtained by the direct current heating process; heating at 600°C for 12 h, repeated flash heating from 850°C to 1250°C, fast cooling to 850°C. Then the sample was cooled down to 520°C at various cooling rates. Some samples were irradiated with a Ga flux during the cooling from 850°C to 520°C, while onto other samples Ga atoms were deposited after the cooling to 520°C. Intensity of the Ga flux measured by a nude ion gauge type monitor was 8×10^{-7} Pa, corresponding to the deposition rate of about 0.25 ML/min (1 ML $\approx 7.8 \times 10^{14}$ atoms/cm^2).

Fig. 2 indicates the change of reflection high energy electron diffraction (RHEED) patterns observed along two directions during the deposition of Ga atoms onto the clean Si(111)-7×7 surface (Fig. 2(a, b)) at 520°C. When 1/3 ML Ga atoms were deposited, the 7×7 reconstruction diminished away, and $\sqrt{3}\times\sqrt{3}R30°$ reconstruction [24] patterns were observed as shown in Fig. 2(c, d). During the deposition of additional Ga atoms, streaks of the $\sqrt{3}\times\sqrt{3}R30°$ reconstruction faded away, and streaks originating from a 6.3×6.3 reconstruction [25] appeared in RHEED patterns. After the deposition of about 1ML Ga

atoms, RHEED patterns fully changed to those of the 6.3×6.3 reconstruction as shown in Fig. 2(e, f). In these patterns additional streaks can be seen just inside the 1×1 streaks of the Si(111) surface. When the surface was irradiated with the Ga flux during the cooling, the $\sqrt{3}\times\sqrt{3}R30°$ reconstruction began to appear at the substrate temperature about 650°C, and the 6.3×6.3 reconstruction began to appear at about 600°C.

Every 6.3×6.3 reconstruction surface where 1 ML Ga had been deposited was irradiated with a Se flux at the substrate temperature of 520°C. Typical intensity of the Se flux was 2×10^{-4} Pa. Just after the start of irradiation, additional streaks of the 6.3×6.3 reconstruction rapidly diminished, and only clear streaks coming from the BGS surface remained as shown in Fig. 2(g, h). The streak interval of RHEED patterns of the BGS surface was the same as that of the Si(111)-1×1 surface within the error. Therefore it is suggested that the lattice constant of the BGS surface is larger than that of bulk-GaSe.

Fig. 3 indicates scanning tunneling microscope (STM) images of the BGS surfaces fabricated by different processes. When a clean Si(111)-1×1 surface was cooled at the rate of 4°C/min without the Ga flux, the final BGS surface had some large smooth terraces as wide as 100 nm, although there were a large number of small holes and islands as shown in Fig. 3(a). When the Si surface was irradiated with the Ga flux during the cooling at the rate of

4°C/min, the surface structure drastically changed as shown in Fig. 3(b). Large islands were distributed on step terraces, and the surface of islands and terraces seems to be smooth. As observed in the STM image, the height of these islands is just the same as that of step edges. This indicates that these islands consist of bilayer-Si and terminating bilayer-GaSe, because each isolated step edge on the Si(111) surface has the bilayer height. From this result it is suggested that the irradiation of the Si surface with the Ga flux during the cooling is effective to obtain a more flat and uniform BGS surface. Finally, Fig. 3(c) shows an STM image of the BGS surface when the sample was cooled at the rate of 1°C/min with the Ga flux. In this case the flat area is wider than that in the previous cases, although there are holes instead of islands on step terraces. Thus, it is concluded that the slower cooling of the clean Si(111) surface together with the irradiation with a Ga flux is effective for fabricating a more smoothly terminated BGS surface.

The mechanism of the flattening of the BGS surface can be explained as follows: Through the fabrication process of the BGS surface, Si atoms near the surface and deposited Ga atoms must change their positions according to the change of surface structures; 1×1 (850°C) $\rightarrow$ 7×7 $\rightarrow$ $\sqrt{3}\times\sqrt{3}$ $\rightarrow$ 6.3×6.3 $\rightarrow$ BGS. When Ga atoms are deposited at one time onto the Si(111)-7×7 surface at the substrate temperature of 520°C, diffusion of those atoms

may be insufficient. In contrast, the diffusion of these atoms can be promoted when the sample is slowly cooled and the deposition of Ga atoms starts at higher substrate temperature than 520°C. When cooling rate is the slowest, excess Si atoms on the terrace produced by the change of reconstructions can migrate into step edges, so that holes mainly exist on the terrace instead of isolated islands.

In order to check the stability of the BGS surface, we annealed the sample at 400°C for 30 min in O_2 atmosphere of 3×10^{-3} Pa. In the case of the H-termination of a Si(111) surface, di- and trihydrides at step edges begin to desorb at around 270°C and the surface becomes reactive, although monohydrides on flat terraces are stable up to 450°C [6-8]. In Fig. 4, (a) and (b) represent Auger electron (AE) spectra measured before and after the annealing, respectively. The primary electron energy for the AE measurement was 5000 eV. Neither the appearance of oxygen peak nor the change of the composition of the BGS surface was observed in the AE spectrum after the annealing, which proves stability of the BGS surface against oxidation.

The higher stability of the BGS surface than the H-terminated Si(111) surface can be explained as follows. In the case of H-termination, each hydrogen atom makes a chemical bond only with one Si atom, and no direct bond exists between hydrogen atoms. In

contrast, there is intra-layer chemical bonding in the bilayer-GaSe, as shown in Fig. 1(a), in addition to the termination of each dangling bond of Si by the Si-Ga covalent bond. This additional chemical bond network is thought to stabilize the termination of the Si(111) surface more effectively than the H-termination.

3. Fabrication of ZnO QDs on a BGS surface

By utilizing the stability of the BGS surface against oxidation, we tried to fabricate ZnO QDs on it. Zn atoms were evaporated from a Knudsen cell, and its flux intensity was 3.0×10^{-4} Pa. First Zn atoms were deposited onto the BGS surface at room temperature under O_2 atmosphere of 3×10^{-3} Pa for 50 sec, then the sample was annealed under the same O_2 pressure at the substrate temperature of 400°C for 50 min. In Fig. 4, (c) indicates an AE spectrum of this sample, and (d) indicates that of ZnO powder for comparison. The peak intensity ratio of Zn:O of the grown sample is similar with that of the ZnO powder, which suggests the growth of stoichiometric ZnO through the present process. In addition, peaks of Ga and Se still remain in the AE spectrum of the grown sample with little decrease of the intensity. This indicates that the BGS surface is not fully covered by deposited ZnO.

Fig. 5 indicates an atomic force microscopy (AFM) image of this sample taken in

ambient air, which clearly proves the growth of ZnO QDs on the BGS substrate. It was found by the AFM observation that the mean diameter of QDs is 14 nm with the standard deviation of 4 nm, and the dot density is 1.6×10^{11} cm^{-2}. Now we are inspecting electronic and optical prpperties of these ZnO QDs using X-ray photoelectron spectroscopy, photo-luminescence and cathodeluminescence spectroscopy [26].

4. Summary

As a stable and 'epitaxial' passivation of a Si surface, we examined the bilayer-GaSe termination of a Si(111) surface. We found by STM observation that slow cooling of the clean Si(111)-1×1 surface from 850°C to 520°C together with simultaneous deposition of Ga atoms results in better termination of the Si(111) surface by bilayer-GaSe. It was also found that this surface is stable against the heating around 400°C in O_2 atmosphere of 3×10^{-3} Pa. By utilizing these advantages, we have succeeded in fabricating high-density ZnO quantum dots on this substrate.

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Figure captions

Fig. 1 Schematic views of a Si(111) surface terminated by bilayer-GaSe (a), and a unit layer of bulk GaSe (b).

Fig. 2 Evolution of RHEED images during the fabrication of a BGS surface. Ga atoms were deposited onto a clean Si(111)-7×7 surface at 520°C. Incident electron beam was set parallel to the $[10\bar{1}]$ direction in (a,c,e,g) and to the $[11\bar{2}]$ direction in (b, d, f, h). (a, b) a clean Si(111)-7×7 surface, (c, d) a $\sqrt{3}\times\sqrt{3}R30°$ reconstruction surface after the deposition of about 1/3 ML Ga, (e, f) 6.3×6.3 reconstruction surface after the deposition of about 1 ML Ga, (g, h) a BGS surface after the annealing in a Se flux.

Fig. 3 STM images of BGS surfaces fabricated by different processes. (a) cooled at the rate of 4°C/min without the Ga flux, (b) cooled at the rate of 4°C/min with the Ga flux, (c) cooled at the rate of 1°C/min with the Ga flux. Sample bias voltage was 3.0 V and tunnel current was 0.1 nA for every image.

Fig. 4 Auger electron spectra of (a) a clean BGS surface, (b) a BGS surface annealed at 400°C in O_2 atmosphere, (c) a BGS surface irradiated with a Zn flux in the O_2 atmosphere at RT and annealed in the O_2 atmosphere at 400°C, (d) powder of ZnO for the comparison.

Fig. 5 An AFM image of ZnO QDs fabricated on a BGS surface.

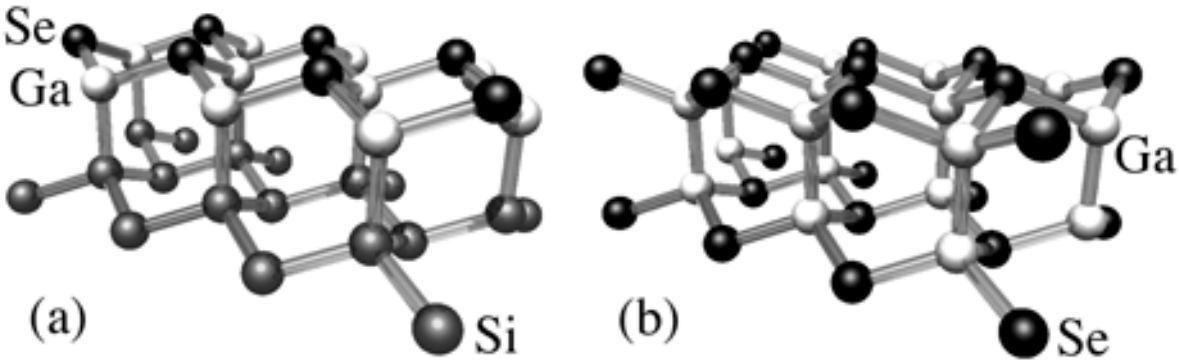

Fig. 1 K. Ueno et al.

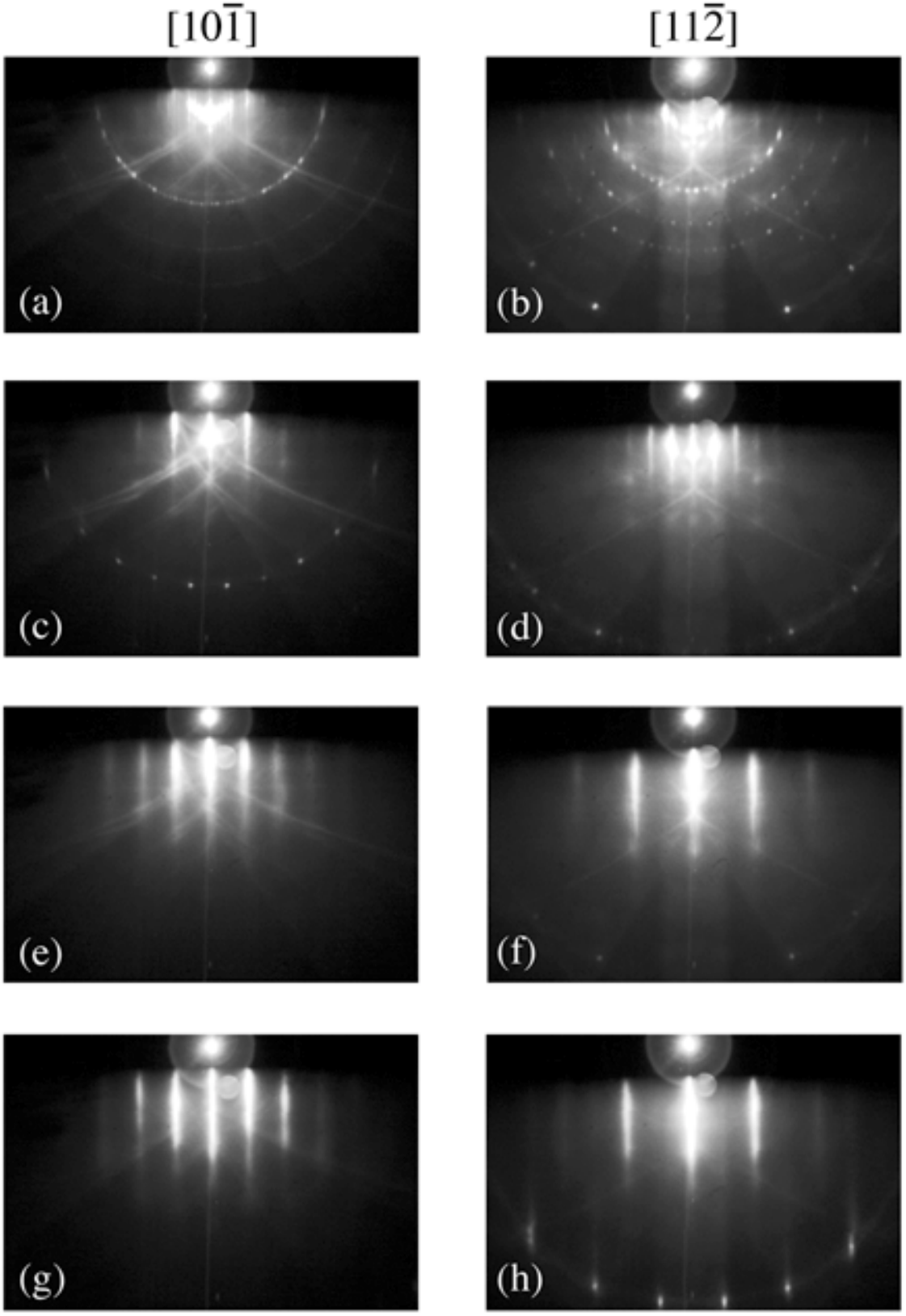

Fig. 2 K. Ueno et al.

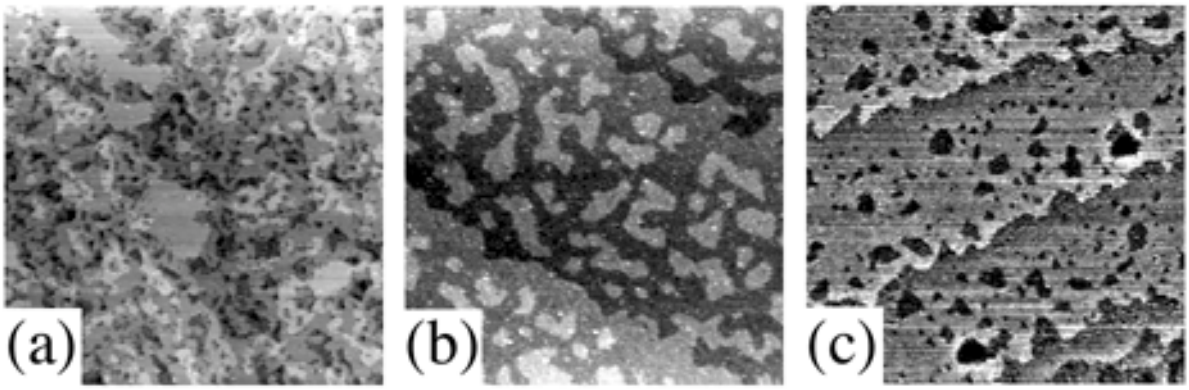

Fig. 3 K. Ueno et al.

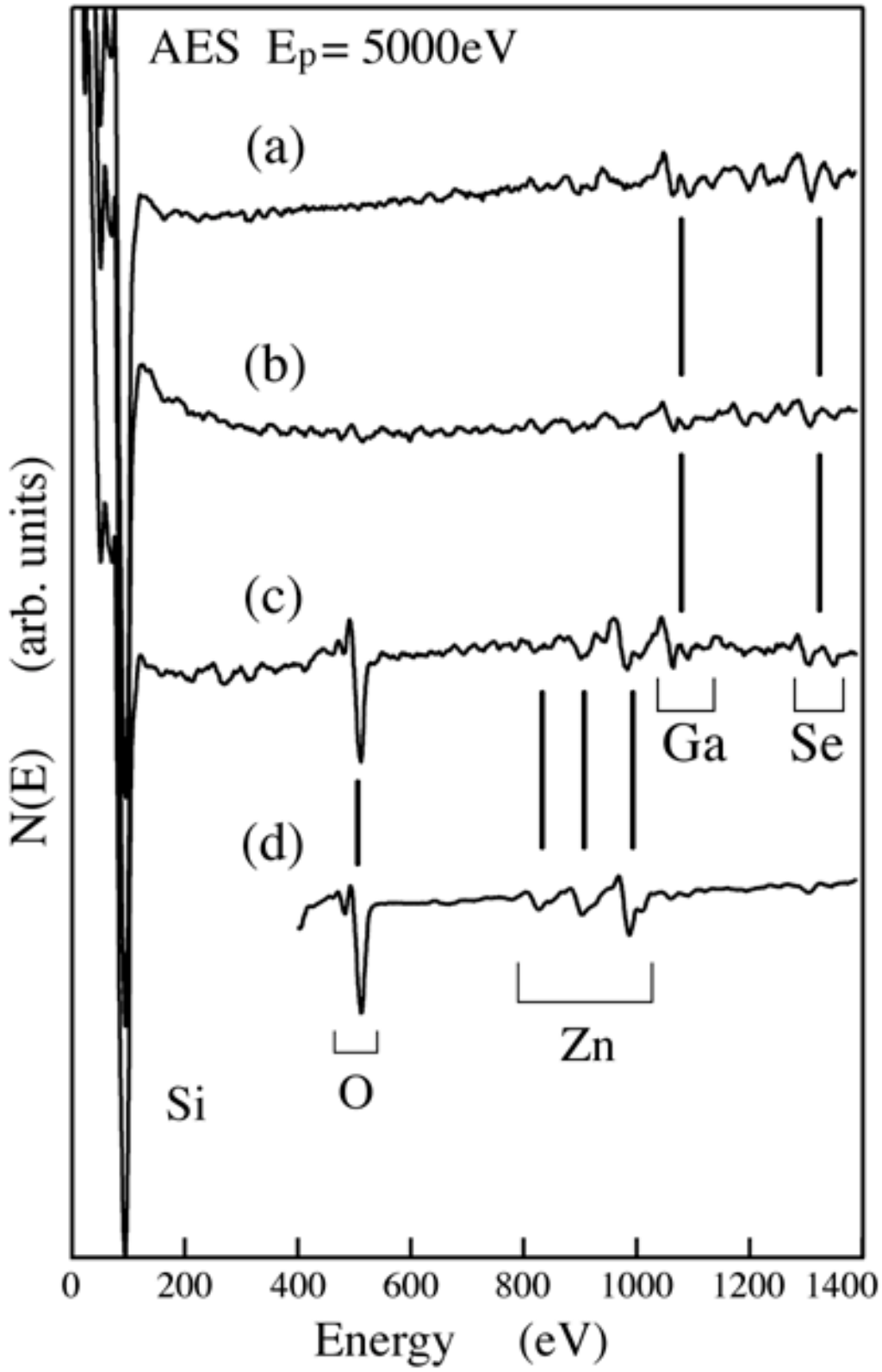

Fig. 4 K. Ueno et al.

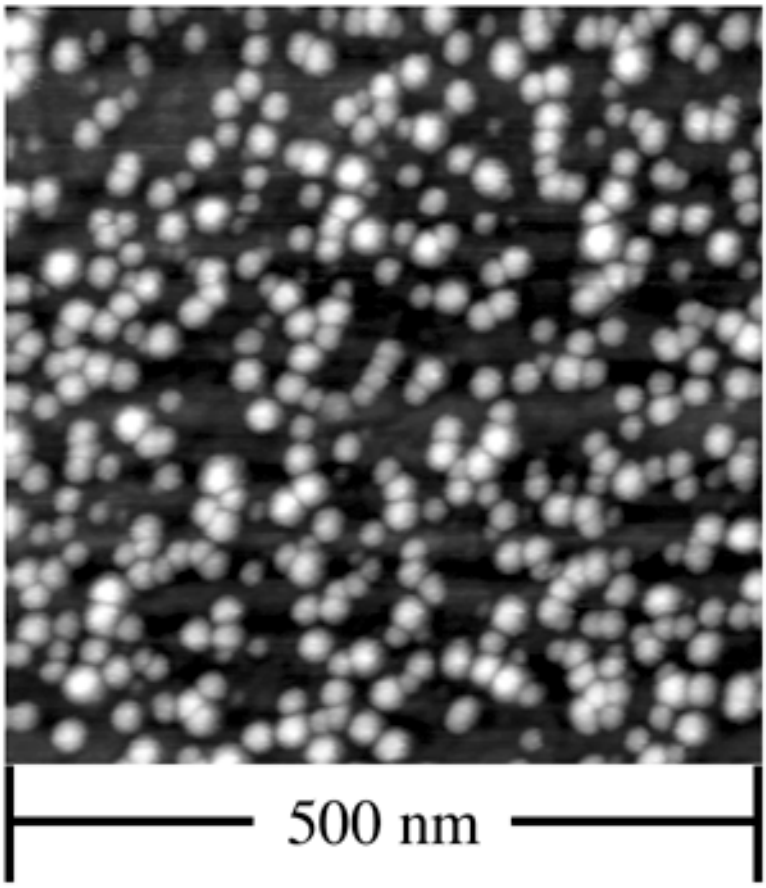

Fig. 5 K. Ueno et al.