STM Study on Initial Te Adsorption on Si(111) 7 × 7 Surface

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(Received 12 November 2005; Accepted 15 February 2006; Published 19 April 2006)

The initial adsorption process of Te on Si(111) 7 × 7 surface at elevated temperatures was observed using STM. Te atoms form clusters. However the adsorption site changes with the substrate temperature. The adatom cluster sits in between the faulted and unfaulted halves at around 300°C, and the preferential adsorption at center adatoms is observed. The triangular clusters form on three adatoms in either the faulted or unfaulted halves without remarkable preference at around 500°C. [DOI:10.1380/ejssnt.2006.406]

Keywords: Scanning Tunneling Microscopy; Te; Si(111)

I. INTRODUCTION

It is known that Te atoms can terminate surface dangling bonds of Si surfaces, which are chemically active. Te saturated Si surface is frequently used to form a hetero interface with Ge film on it. That is, Te acts as a surfactant of Ge growth on Si surface [1―4]. And Te terminated Si surface is also available as a template of following Te-based compound semiconductor growth, such as CdTe [5], which is quite important material for radiation detector, optoelectronic devices and so on. Most of studies which have been done up to now, however, are in use of Si(100) surface as the substrate. Since Te is a hexavalent element, the adsorption on the bridge site should be stable on Si(100) surface [6―11]. The similar adsorption on the bridge site on Si(100) surface has been established for the adsorption of S [12] and Se [13―15], which are in the same group VI element as Te.

Si(111) surface shows a three-fold symmetry and the well-known 7 × 7 reconstruction takes place. Then it is interesting to observe how Te atoms adsorb in the initial stage on Si(111) 7 × 7 surface. There are a few studies on adsorption of Te atoms on Si(111) 7 × 7 surface [16―18]. The obtained adsorption site of Te atoms is the bridge site. Dev, et al. have reported on the adsorption site of Te on chemically cleaned and cleaved Si(111) surface using X-ray standing wave method [19]. They showed that Te atom also bridges between two adjacent Si atoms in the first layer of the ideal 1 × 1 surface. According to the similarity of the adsorption site seen in the case of Si(100) substrate in the group VI element, it is expected that Te atoms adsorb on the bridge site as well. However, the distance between adatoms on Si(111) 7 × 7 surface is rather large. Therefore the behavior of Te adsorption might become much more complicated. And the chemical nature of adatoms would not be unique within the 7 × 7 unit cell because there are the faulted and unfaulted halves and also the corner and center adatoms in each half. For example, the preferential adsorption on the corner adatoms has been frequently observed in the initial growth of metals on Si(111) 7 × 7 surface [20].

In the present paper, we will show the initial adsorption process of Te on Si(111) 7 × 7 surface at elevated temperatures observed with STM. Below half monolayer Te atoms form cluster, but the adsorption site of clusters varies with substrate temperature. The change of the surface morphology with Te coverage is also discussed.

II. EXPERIMENTAL

Specimen used was a B-doped p-type Si(111) surface, whose resistivity was 1-100 Ω cm. The off-set angle was within ±0.1°. The cleaning of the specimen was carried out by direct current heating up to about 1200°C and slowly cooling down to room temperature. After the cleaning procedure, the Si(111) 7 × 7 surface showed a few atomic defects which was confirmed with STM. Deposition of Te (purity: 6N) was done using a heated Mo crucible, and the deposition rate was estimated by a quartz oscillator in which the sticking probability on the Si(111) 7 × 7 surface is assumed to be the same as that on the quartz surface. The estimated deposition rate was about 0.2 ML/min, where 1 ML was defined as the atomic density of the Si(111) surface. The substrate temperature during the Te deposition was calibrated using an optical pyrometer and an infrared pyrometer through the heating current.

Observation of the initial growth of Te on Si(111) 7 × 7 surface was carried out with a commercially available STM in an ultra high vacuum chamber (UHV) connected to a sample-preparation and load-lock chamber. A chemically etched W tip was used. The constant current topographies were recorded at room temperature. The base pressure in the UHV chamber was 4 × 10⁻⁹ Pa and the working pressure during the deposition was kept below 1 × 10⁻⁸ Pa.

III. RESULTS AND DISCUSSION

Figure 1 shows STM images of Te/Si(111) surface, whose coverage is 0.36 ML, prepared at about 300°C and 500°C. The size of the images is 60 nm × 60 nm. The sample bias was 1.5 V and the tunneling current was 0.3 nA.

*This paper was presented at 5th International Symposium on Atomic Level Characterizations for New Materials and Devices (ALC05), Hawaii, USA, 4-9 December, 2005.
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Adsorbed Te atoms form small clusters, which appear as white protrusions in the images, in both cases. It seems that the number of Te clusters at about 500°C is larger than that at about 300°C, and the size of Te clusters is not so different in both temperatures. The reason of this can not be understood at present. The deposition rate might not be so stable, then the true coverage of Te might be different. The preferential adsorption at step edges and/or domain boundaries has not been observed. This might indicates that the adsorption of Te clusters is not governed by the interaction with surface defects but by that between the substrate Si(111) 7 × 7 surface with Te atoms.

The substrate Si(111) 7 × 7 template can be still seen in between Te clusters in both STM images. It is considered that impinged Te atoms migrate on the Si(111) 7 × 7 template without any disturbance to the atomic arrangement of Si atoms, and get together at a certain adsorption site to form clusters. As seen in the inset in Fig. 1(a), most of Te clusters sit between one adatom in the faulted half and that in the unfaulted half like a bridge between the faulted and unfaulted halves. Then the shape of Te clusters appears as oval. On the other hand, the shape of Te clusters seen in the inset in Fig. 1(b) is mostly triangle. Such triangular clusters form on three adatoms in either faulted or unfaulted half. Figure 2 shows a schematic drawing of the adsorption sites on the Si(111) 7 × 7 template. A yellow oval shows Te cluster formed at about 300°C, and a green triangle that formed at about 500°C. In this figure only one cluster for each substrate temperature is illustrated. However, there are two equivalent sites for the yellow oval, which bridges two corner adatoms, and one oval which bridges two center adatoms. Similarly there exist three equivalent green triangles in the faulted and unfaulted halves, respectively.

The preference of such two types of adsorption geometry, oval and triangular clusters, was examined at about
300°C and 500°C. Top drawing in Fig. 3 shows a schema of four adsorption sites: triangular cluster in the faulted half (TFH), oval cluster on the center adatoms (OCT), that on the corner adatoms (OCN) and triangular cluster in the unfaulted half (TUH). Figures 3(a) and (b) show the distribution of Te clusters at about 300°C and 500°C, respectively. As mentioned above, the preference on OCT and OCN is seen at about 300°C, and that on TFH and TUH at about 500°C. At about 300°C, the number of oval cluster on OCT is about 1.5 times greater than that on OCN. Although the number of cluster on OCT and OCN is not large at about 500°C, the preference on OCT can also be seen. For the triangular clusters the difference between on TFH and TUH at about 300°C and 500°C is not so prominent.

Figure 4 shows STM images of different Te coverage prepared at about 500°C. The coverage is 0.18 ML, 0.36 ML and 1.0 ML, respectively. The size of images is 30 nm×30 nm. The white lines in the inset in (a) is the frame of Si(111) 7 × 7 unit cell for eye guide. Although the number of Te clusters at 0.18 ML is much less than that at 0.36 ML, most of Te clusters is on TFH and TUH in Fig. 3. Instead a lot of ring-like protrusions can be seen in Fig. 4(a). The inset shows the magnified STM image of this surface. The ring-like protrusions have three maxima on the center adatoms in either the faulted or unfaulted halves. There is no remarkable preference of either halves. The protrusion of the ring-like cluster is slightly elongated. Therefore it would be plausible that Te atoms adsorb preferentially on center adatoms in the initial stage of the growth. At this substrate temperature, Te atoms coalesce with each other with increasing coverage and the triangular clusters form on one corner and two center adatoms as schematically shown in Fig. 2. With increasing the coverage up to around 1 ML, the regular shaped Te clusters can not recognized any more as shown in Fig. 4(c). The Si(111) 7 × 7 template can not be well distinguished as well. The clear Te adsorbed structure is not resolved but non-uniform contrast is seen. Then it is expected that the continuous Te film starts to form at around 1 ML, but the film is not so uniform. The STM image for Te/Si(111) surface prepared at about 300°C also showed the formation of the continuous Te film at around 1 ML.

As described above, the adsorption behavior of Te on Si(111) 7 × 7 surface is quite different between at the substrate temperature of about 300°C and about 500°C. The hexavalent Te atoms would prefer to adsorb the bridge site between adatoms. SEXAFS study showed that the average distance between Si and Te atoms on Si(111) 7 × 7 surface is 2.75 Å [16]. The results of the first principle calculation showed that the bond length between Si and Te atoms on Si(100) 1 × 1 surface is 2.53 Å [11], which is very close to experimental value of 2.52 Å [8]. The distance between adatoms on Si(111) 7 × 7 surface, however, is about 7.68 Å, which is too large to bridge adjacent two adatoms with a single Te atom. Then the oval cluster should contain at least two Te atoms, but the exact estimation of the number of Te atoms in a single Te cluster was impossible in the present study. In the case of the triangular cluster, several Te atoms would consist in a single cluster. The bond length between Si and Te atoms obtained by SEXAFS study assumed that Te atoms bridge two Si atoms whose arrangement is almost ideal 1 × 1 structure [16–18]. However, the present STM observation clearly shows that Te clusters sit on Si(111) 7 × 7 template. Then the distance obtained by SEXAFS study might be that between
two Te atoms in the cluster.

Several reconstructions by Te adsorption has been observed by LEED [18]. At the substrate temperature of 400°C, the $\sqrt{3} \times \sqrt{3}$ LEED pattern was observed at 0.25 ML and the mixture of $2 \times 2$ and $3 \times 1$ structure at 0.5 ML. The weak super spots from $7 \times 7$ structure was also observed up to 1 ML. As shown in Fig. 4, $7 \times 7$ framework can be observed up to around 1 ML so that it can be understood that the origin of the weak $7 \times 7$ spots observed in LEED pattern is the remaining $7 \times 7$ framework. The clear evidence of the other reconstructions observed at low coverage region has not been confirmed in the present STM study.

The most interesting feature observed in the present study is the change of the adsorption site of Te clusters by substrate temperature. The reason why the adsorption site changes is not clear at present. Since Si(111) $7 \times 7$ surface consists in dimers, adatoms and stacking fault, the activation barrier to interact and destroy such complicated reconstructed surface to form the continuous film on it would be different site by site. The further investigations including the theoretical work are required to fully understand such interesting phenomena.

IV. CONCLUSIONS

The initial adsorption process of Te atoms on Si(111) $7 \times 7$ surface at elevated temperatures was observed using STM. Te atoms form clusters. However the adsorption site changes with the substrate temperature. Because Te atom is a hexavalent element, it prefers to bridge the substrate Si atoms. The atomic distance of adatoms on Si(111) $7 \times 7$ surface, however, is too large to bridge directly. Such situation would induce clustering of Te atoms. Although the details of the growth kinetics of Te on Si(111) $7 \times 7$ surface has not been fully understood, the present results show the interesting behavior of Te atoms on it.

Acknowledgments

A part of the present work was supported by a Grant-in-Aid for Creative Scientific Research (No. 13GS0022) from Japan Society for the Promotion of Science.

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