Cross-sectional transmission electron microscope observation of Si clathrate thin films grown on Si (111) substrates

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Abstract

By means of high-resolution transmission electron microscopy (HR-TEM) observations, and energy dispersive X-ray analyses performed with a scanning TEM (STEM-EDX), we evaluated the residual Na contents and the induced crystal strains in type-II Si clathrate films grown on a Si substrate and treated with iodine for Na elimination. Cross-sectional TEM and STEM-EDX observations verified the formation of the type-II Si clathrate thin film on the Si substrate. The guest-free (without any Na inclusion) clathrate crystal was obtained by iodine (I₂) treatment for more than 3 cycles. The resulting films were polycrystalline. No buffer layer was observed at the boundary of the Si clathrate crystal film and the substrate, suggesting a chemical bonding between them. The crystalline strains defined here by the deviation of the d value were within 3.5%. These findings might allow us to fabricate epitaxial Si clathrate films on Si substrates.

Keywords: Si clathrate film, NaSi film, Iodine treatment, TEM, STEM-EDX.

1. Introduction

Si clathrates [1-3] are composed of Si polyhedral cages (Si_{20} , Si_{24} , and Si_{28}) encapsulating alkali metals, such as sodium (Na), as guest atoms. Each polyhedron shares its faces with the neighboring polyhedrons. The crystal structures of the Na doped Si clathrates are classified by the combination of the Si polyhedral cage structures into: (i) type-I ($\text{Na}_8\text{Si}_{46}$), and (ii) type-II ($\text{Na}_x\text{Si}_{136}$: $x = 0-24$). The presence of Na induces metallic properties in the clathrates, owing to the free electrons provided by the positively ionized Na atoms [4]. However, the clathrates without guest atoms, better known as guest-free clathrates, exhibit semiconducting properties [5-12]. The guest-free type-I Si clathrate shows an indirect band structure with a gap of about 1.8 eV [13]. On the other hand, the guest-free type-II Si clathrate exhibits a direct band structure with a gap of 1.9 eV, almost twice the corresponding value for diamond-structured silicon [14]. In addition, the guest-free type-II alloyed clathrates having the Si-Ge mixture framework ($\text{Si}_x\text{Ge}_{136-x}$) are theoretically expected to have a direct band gap ranging from 1.2 to 2.0 eV as a depending on the Ge mole fraction [13]. Hence, the guest-free type-II Si and/or Ge clathrates are promising candidates for applications in optoelectronic semiconductor devices. However, the fabrication of the type-II clathrate in the form of a thin film, which is useful for photovoltaic applications, is difficult to achieve, because the crystal growth mechanism of the type-II clathrate film is still unclear.

Recently, we have synthesized type-I and type-II Si clathrate thin films ($\text{Na}_8\text{Si}_{46}$ and $\text{Na}_x\text{Si}_{136}$) on single-crystalline Si substrates [14-16]. The Si clathrate films were obtained from a well-controlled thermal annealing of the NaSi films under vacuum. These films were evaluated by X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HR-TEM) and were found to be polycrystalline [16]. However, it has not been assessed yet whether the Si clathrate can be epitaxially grown on the Si substrate. In the case of Ge clathrate $\text{Na}_x\text{Ge}_{136}$, the epitaxial growth on the Ge substrate was strongly suggested from the

pole figure measurements with XRD [17]. Therefore, we expected the epitaxial growth of the Si clathrate (111) plane on the Si (111) substrate. Concerning the NaSi film, which is a precursor of the Si clathrate, the epitaxial growth on the Si (111) surface was strongly suggested by previous works [14, 15]. Furthermore, the type-I and -II Si clathrate thin films were selectively formed on the Si (100) and Si (111) substrates, respectively [15]. A feasible explanation of this result lies in the fact that the nucleation of the clathrate structure occurs at the interface between the NaSi and Si surfaces, under the influence of an atomic arrangement of the Si substrate surface. In order to gain insight into the growth mechanism of the Si clathrate on the Si substrate, the direct observation of the boundary is required. Clarification of the crystal growth will lead to the production of a high quality film of Si clathrate usable as a solar cell.

In this study, we studied the lattice at the interface with the Si substrate by HR-TEM observations, in order to understand how the Si clathrate crystal grew up at the interface with the Si substrate. We investigated the relationship between the growth directions and the induced strains of the Si clathrate crystals at the interface with the Si substrate, in order to find an appropriate crystalline orientation of the Si clathrate for their epitaxial growth on the Si (111) substrate. Furthermore, performing the iodine (I_2) treatment to remove sodium atoms from the Si clathrates, is the most important process in order to obtain a semiconducting Si clathrate. The usefulness of I_2 -treatment for the preparation of guest-free Si clathrate has been reported [11]. We also investigated the influence of the I_2 -treatment on the crystal strains of the Si clathrates by comparing the strains in the samples subjected to different I_2 -treatment conditions. The sodium contents in the Si clathrate thin films grown under different I_2 -treatment conditions were investigated by energy dispersive X-ray analyses using a scanning TEM (STEM-EDX), in order to find the most suitable I_2 -treatment condition.

2. Experimental

The Si clathrate films were prepared on single-crystalline Si (111) substrates. The Si clathrate crystal was transformed from the sodium silicide (NaSi) film obtained by the reaction of Si with Na. The Si substrate with (111) surface orientation was horizontally placed in the Ta crucible, at 10 mm above the sodium slice and under Ar atmosphere. The crucible was then sealed in a stainless container and heated at a temperature of 580 °C for 48 h (first annealing). The Si substrate, which reacted with the Na vapor to form NaSi on its surface, was taken out from the container and then annealed at 400 °C for 3 h under a vacuum below 10^{-3} Pa (second annealing). The type-II Si clathrate thin films ($\text{Na}_x\text{Si}_{136}$) were obtained by this second annealing. The Na content (x) in the $\text{Na}_x\text{Si}_{136}$ films prepared under the same conditions was estimated to be about 10 [16]. In order to remove the Na atoms, an additional I_2 -treatment was necessary and it was carried out according to the following process. First, the obtained film was rinsed by an ethanol (99.5%) solution to remove the residual sodium and sodium oxide from the prepared film. Second, the film was sealed in a glass tube together with solid iodine (Wako: 99.8%) under vacuum (around 10^{-3} Pa), and then annealed at 460 °C for 5 h, in order to reduce the Na atoms in the cages. Finally, the sample was rinsed by a 10 minutes sonication using super dehydrated acetonitrile (99.5%) and ethanol (99.5%), so that iodine and its composites were removed from the film surface. In order to discuss the effect of the I_2 -treatment on the physical properties, three types of samples subjected to different I_2 -treatment cycles (1, 3, and 6) were prepared in this study. The residual Na contents and the induced strains of the Si clathrate crystals in these three samples, were characterized by HR-TEM observations (accelerating voltage of 200 kV) and STEM-EDX elemental mapping measurements (JEOL, JEM-2010 MX), respectively.

3. Results and discussion

Figure 1 (a) - (c) show the results of the cross-sectional STEM observations on the Si clathrate films after performing the I_2 -treatment for 1, 3, and 6 cycles, respectively. The left column in Fig. 1 shows the cross-sectional STEM images, while the central and the right columns present the cross-sectional elemental maps of carbon and sodium, respectively. The red and yellow regions indicate the high concentration of each element. A comparison of the STEM images and the carbon maps revealed the presence of carbon in the bright areas of the STEM images. This unexpected carbon inclusion was likely to arise from the kerosene in which the sodium ingredient has been stored. We assumed that the carbon in the kerosene solution evaporated and was then included in the film during the first annealing process. Further HR-TEM observations revealed the amorphous phase of these carbon-rich areas.

On the other hand, Na was obviously detected in the film after 1 cycle of the I_2 -treatment. However, the Na signals for the other samples after I_2 -treatment (3 and 6 cycles) could not be distinguished from the background signals. The Na content in these films decreased under the detection limit of ~ 1 at.%. This result indicates that a type-II Si clathrate thin film without any inclusion of Na, can be obtained by the I_2 -treatment for more than 3 cycles.

In order to analyze the crystal structure of the Si clathrate films, we performed HR-TEM observations on the three samples. The lattice was not visible in the I_2 -treated sample for 1 cycle. This effect is likely to be due to the non-homogeneity of the obtained samples, characterized by the presence of crystalline-rich regions and amorphous-rich regions even in the same sample. Unfortunately, we observed the amorphous-rich region, although we have checked the sample by Raman measurements prior to preparing it for cross-sectional TEM observations.

On the other hand, we observed the lattice images of the Si clathrate thin films after the I_2 -treatment for 3 and 6 cycles. Figure 2 shows the typical HR-TEM lattice image of the Si clathrate at the interface with the Si substrate, after 3 cycles of the I_2 -treatment. This lattice

image is one of the several observed in different regions of the Si clathrate thin film. The obtained film was polycrystalline and the crystal grain size was about 20-50 nm. From the TEM observations of Si clathrate films, the size of the clathrate grains did not change by the number of I₂-treatment cycles. It can be noted that the boundary between the Si clathrate film and the substrate is clearly recognizable. In addition, a regrown Si layer appeared at the boundary in some areas, as shown in Fig. 2. This effect can have a two-fold explanation: (i) the NaSi precursor was transformed directly to the diamond-structured Si, or (ii) the Si clathrate recrystallized into the diamond-structured Si. The re-grown Si showed a stacking fault at the boundary and had a larger (111) d value compared to the Si substrate. In any case, no buffer layer (e.g., an amorphous phase) was detected at the boundary separating the Si clathrate crystal film and the substrate, suggesting the presence of a chemical bonding between the clathrate film and the diamond-structured Si. The insets of Fig. 2 show the fast Fourier transformation (FFT) images of the lattice patterns corresponding to the Si clathrate and substrate, respectively. The FFT images result from the diffraction pattern of the crystal lattice. For the diffraction pattern in the Si substrate region, the direction normal to Si [111] in the Si substrate area, was determined to be $[2\bar{1}\bar{1}]$ from the theoretical simulation of the electron diffraction pattern of the diamond-structured silicon crystal. At the same time, the observed diffraction pattern of the Si clathrate film was in agreement with the theoretically simulated pattern for the Si₁₃₆ clathrate crystal without any Na atoms. In this case, the crystalline structure is cubic with the space group $Fd\bar{3}m$ [18]. The Miller indices of the diffraction spots for the Si clathrate were identified as shown in Fig. 2. In this case, the [113] direction of the Si clathrate tilts 4° relative to the Si substrate [111] toward the $[2\bar{1}\bar{1}]$ direction. Thus, we identified the crystal orientation and then we calculated the d values of the type-II Si clathrate, close to the interface with the substrate.

The above analyses were performed for several TEM images obtained in different positions.

Afterwards, we estimated the induced strains at the interface between the Si clathrate and the substrate. Concerning the 3 and 6 cycles I₂-treated samples, the observed lattice spacing (d_{obs}) values and the tilt angles relative to the Si [111] direction for each set of the Miller indices of the collected diffraction patterns, are summarized in Figs. 3 (a) and (b). The d_{obs} value were estimated by the comparison with the d value ($= 3.1355 \text{ \AA}$) of the Si (111) obtained from the same FFT image [19]. The vertical axis shows the strain ε as defined by (Eq. (1)):

$$\varepsilon = (d_{\text{obs}} - d_{\text{calc}}) / d_{\text{calc}} \times 100 \quad (1)$$

where, d_{calc} was calculated using the lattice constant ($a = 14.65$) reported for the Na_{1.5}Si₁₃₆ with $Fd-3m$ space group [20]. The data obtained from each grain of different growth directions were indicated by the same marks.

As seen in Figs. 3(a) and (b), many diffraction spots with different lattice planes were detected and analyzed in both samples. This means that the Si clathrate crystals are randomly orientated with respect to the crystal axes of the Si substrate. It is worth mentioning that no signs of epitaxial growth of the Si clathrate were identified.

We noted that some crystal grains are highly strained while others are less strained. For example, the crosses in Fig. 3(b) are all located nearby the horizontal axis, indicating that the corresponding grain has a little strain. On the other hand, the grain corresponding to the circles in Fig. 3(b) possesses large strain. Moreover, not only the existence of grains with stretching strain (positive sign) can be identified in Fig. 3, but also the presence of grains with a compressive one (negative sign) is detected. The strains existing in the samples after performing the I₂-treatment for 3 and 6 cycles reached values up to 3.5 and 3.0%, respectively. Concerning the directions of the large strain, as can be seen in Fig. 3(a), a grain is strained toward to the [202] axis, while to $[1\bar{3}1]$ axis, suggesting the lack of a preferred strain axis. San-Miguel *et al.* had reported the isotropic volume change of Si₁₃₆ clathrate crystals under high pressures [21]. Applying the pressure of 10 GPa yields isotropic and compressive strain

of about 3.5 % in the lattice constant, which is comparable to the maximum strain in this study. Although the strict comparison is difficult because of the uniaxial (anisotropic) strain in the present sample, some of the present crystal grains are likely to have large strain corresponding to applying the pressure of several GPa.

As for the tilt angle, i.e., the angle between the strained axis and the normal of the Si (111) plane of the substrate, the strained [111] axis tilted at $\sim 90^\circ$, as per the data shown in Fig. 3(b) (triangles). On the other hand, the strained $[31\bar{1}]$ axis (triangle) tilted at $\sim 30^\circ$. Thus, the angle between the direction of the strained axis and the crystal axis of the Si substrate is likely to be random. Furthermore, the comparison of Figs. 3 (a) and (b) suggests that the strain and the crystal orientation are not dependent on the number of cycles of the I_2 -treatment.

Consequently, it was observed that the randomly strained Si clathrates crystals were grown on the Si substrate without any preferred orientation. This result can be explained considering that the strain was randomly induced when the Si clathrate crystalline nuclei in the NaSi precursor bonded with each other. The resulting crystalline orientation is considered to depend strongly on the initial sticking direction of the NaSi precursor on the substrate. Therefore, further optimization on the NaSi growth processes is required, in order to achieve the epitaxial growth of Si clathrate single-crystalline films.

4. Conclusion

We investigated the effect of the I_2 treatment applied to Si clathrate thin films, on the residual Na contents and on the induced crystal strains in guest-free samples. The elemental analyses performed by the STEM-EDX mapping indicated that type-II (without any Na inclusion) Si clathrate thin films were obtained by the I_2 -treatment repeated for more than 3 cycles. In addition, the presence of amorphous carbon was observed in the films. The cross-sectional HR-TEM observations demonstrated that Si clathrate film was grown on the

Si substrate, and was strictly bonded to it. The Si clathrate crystal grains present both stretching and compressive strains. The observed strains were about 3.5%. In addition, we found no correlation between the strains and the crystal growth directions of the Si clathrate at the Si substrate interface. However, detailed TEM observations and analyses provided us important knowledge on the initial nucleation of the Si crystal in NaSi. This result will be useful in the production of high quality Si clathrate thin films usable as a material for solar cells.

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Figure Captions

Figure 1. Cross-sectional STEM images and elemental maps of carbon and sodium in Si clathrate films subjected to the I_2 -treatment for: (a) 1 cycle, (b) 3 cycles, and (c) 6 cycles. The top layer, the middle layer, and the bottom layer in the STEM images are the Si substrate, the obtained film, and the adhesive layer, respectively.

Figure 2. HR-TEM image of the I_2 -treated Si clathrate thin film (3 cycles) lattice, at the interface with the Si substrate. The left layer, the middle layer, and right layer are the Si substrate, the re-grown Si layer, and the Si clathrate film, respectively. The insets show the fast Fourier transformation (FFT) results of the lattice patterns, that is, the electron diffraction patterns of the Si substrate and the Si clathrate.

Figure 3. Variation of the induced strains of the Si clathrate crystal at the interface with the Si substrate, for samples subjected to the I_2 -treatment for: (a) 3 cycles, and (b) 6 cycles. The vertical axis is the induced strain (%) of the Si clathrate crystal, and the horizontal axis is the tilt angle relative to the Si [111] toward: (a) Si $[2\bar{1}\bar{1}]$, and (b) Si $[11\bar{2}]$.

Figure 1

Figure 2

Figure 3