Departure Process of Ga from DLC Films Fabricated Using Ga Focused Ion Beam Assisted Deposition by Heat Treatment

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The departure process of residual Ga in diamond-like carbon (DLC) film synthesized by focused-ion-beam chemical vapor deposition (FIB-CVD) was investigated by measuring Rutherford backscattering (RBS) spectra of FIB-CVD DLC films after heat treatment in various conditions. The annealing temperature and annealing time were varied in the range of 473-973 K and 0-64 h, respectively. The decrease in Ga concentration and transfer of Ga in the FIB-CVD DLC film were not observed due to heat treatment at less than 573 K. The transfer of residual Ga from inside the film to the surface, and the formation of Ga spheres, which were surrounded by a graphite shell, were observed after heat treatment at 673 K, but Ga concentration did not vary much. When the annealing temperature was higher than 773 K, a decrease in the Ga concentration was observed. The depth profile of Ga in the DLC film in the RBS spectra was observed to divide into two peaks when treated with heat at temperatures higher than 673 K. This splitting can be interpreted as the difference in the desorption rate of Ga in the DLC, graphite shell, and Si substrate.

KEYWORDS: focused-ion-beam chemical-vapor deposition (FIB-CVD), diamond-like carbon (DLC), annealing effect, Rutherford backscattering spectrometry (RBS), thermal expansion

1. INTRODUCTION

A Ga focused-ion-beam chemical vapor deposition (FIB-CVD) method was developed as an effective technique for fabricating three-dimensional (3D) nanostructures [1]. Using this method, a pillar 80 nm in diameter can be fabricated by irradiating a focused Ga ion beam under a phenanthrene gas atmosphere, which was used as a carbon source, and a complex shape with an overhung, hollow, bridging structure can be formed by scanning a Ga ion beam. The fundamental structure of the carbon material formed by FIB-CVD is diamond-like carbon (DLC) by Raman spectroscopy [1] and near edge X-ray absorption fine structure spectroscopy [2]. The Young's modulus of a pillar fabricated using the FIB-CVD technique was reported to exceed 600 GPa [3, 4], which is sufficiently large that nanodevices fabricated using this technique offer great possibilities in various applications, such as in the biochemical and electromechanical fields.

The pillar fabricated by FIB-CVD had a double structure such that the core region coexisted with C and residual Ga from the source ion and with its outer diamond-like carbon shell that did not contain Ga. In addition, this residual Ga in the core-region transferred to the surface and produced Ga spheres there, which finally vaporized from the film by annealing at temperatures higher than 873 K [3, 5, 6]. These movements of Ga were known to cause a change in the fundamental structure and several material properties, such as density [4], elemental composition [7], local structure [2, 8], Young modulus [3, 7] and hardness [8]. As noted above, the properties of nanodevices fabricated using the FIB-CVD technique can be controlled by heat treatment. However, the details on the departure process of Ga in the FIB-CVD DLC film have not been

fully understood. We therefore investigated the behavior of Ga atom in FIB-CVD DLC films during annealing. Sample films fabricated using the FIB-CVD method were annealed under various conditions, such as annealing temperatures in the range of 473-973 K and annealing times in the range of 0-64 h. The Ga concentration and depth profile of FIB-CVD DLC films after heat treatment were measured using Rutherford backscattering spectrometry (RBS) techniques.

2. Experimental

An FIB-CVD DLC film was formed on a Si substrate surface using a commercially available FIB-CVD system (SMI2050MS: SII Nano Technology Inc.). The details of the method used to fabricate the FIB-CVD DLC films are described in a previous paper [1, 9]. Briefly, the accelerating voltage of a Ga⁺ ion beam and ion beam currents were at 30 keV and 28 nA, respectively. The system was equipped with two gas nozzles; a source gas, phenanthrene (C₁₄H₁₀), was supplied through these nozzles, and phenanthrene molecules were adsorbed on the Si substrate. The base pressure of the sample chamber was 9×10^{-5} Pa, and the chamber pressure during introduction of the source gas was 1×10^{-4} Pa. The FIB was scanned to write a square pattern $200 \text{ m} \times 200 \text{ m}$ using a computer-controlled scanning system. The produced FIB-CVD DLC was covered with these squares, resulting in a total area that $5 \times 5 \text{ mm}^2$. We intended to deposit FIB-CVD films with thickness of a 200 nm. The actual thickness of the formed individual films was estimated using a surface profiler (ULVAC: DEKTAK 6M). The formed FIB-CVD DLC films were annealed in a vacuum using a furnace (ThermoRIKO: GFA430). The back pressure and pressure during annealing in the furnace were $\approx 1 \times 10^{-5}$ and $\approx 5 \times 10^{-5}$

Pa, respectively. The annealing temperature ranged from 473 K to 973 K, and the annealing time ranged from 2 to 64 h. We observed the surface of the FIB-CVD DLC film and roughly estimated the Ga/C ratio using a scanning electron microscope energy dispersive x-ray spectrometer (SEM-EDX) (JEOL: JSM6700F).

An RBS measurement with MeV-He⁺ irradiation was performed using an electrostatic accelerator (Nissin-High Voltage: NT-1700HS) at the Extreme Energy Density Research Institute, Nagaoka University of Technology. The details of RBS measurement are described in refs. 9-11. Briefly, the He⁺ ions accelerated to 2.5 MeV were used as incident beam at 72° with respect to the surface normal of samples. A He⁺ beam current was maintained at 6 nA. A small fraction, ~0.1 %, of high-energy He⁺ ions scattered elastically by the sample were captured with a solid-state detector (SSD) arranged at 12° with respect to the surface normal of samples toward the incident beam. No signal, except for signals corresponding to C, Ga, and Si, which was due to the substrate, was observed in the RBS spectra. The content of these atoms was determined using the RBS fitting calculation package (Nissin High Voltage Co.: ERNIE ver. 1.0) on the basis of film thickness, estimated with a profiler, and Ga/C ratio, estimated with the SEM-EDX. The estimation error was 0.5 at.%, because the content examination was simulated at 1 at.% steps.

3. Results and discussions

The dependence of the Ga/C ratio on annealing-time is plotted in Fig. 1. The Ga/C ratio in the as-deposited FIB-CVD DLC film was ≈4 at.%. The Ga concentration in the film is expected to be slightly different in each film, because the deposition conditions were not identical. The Ga concentration in the FIB-CVD DLC film maintained its initial value after the annealing at 573 K. The annealing at 673 K caused a slight decrease in the Ga concentration in the annealing time range from 0 to 16 h and a slight increase from 16 to 32 h. These variations can be considered as a small desorption of Ga from the DLC surface, and the formation of Ga spheres on the DLC surface, as described below. On the other hand, the Ga concentration decreased remarkably by annealing at temperatures higher than 773 K with an increase in the annealing time. The desorption temperature of Ga from the

Fig. 1 Dependence of Ga/C ratio of FIB-CVD DLC film on annealing time determined by the RBS measurements. Open circle indicates Ga/C ratio of FIB-CVD DLC film as deposition. Closed circles, closed triangles, and closed squares indicate the Ga/C ratios of FIB-CVD DLC films after heat treatment at 573, 673, and 773 K, respectively. Closed inverse triangle and closed diamond indicate the Ga/C ratios of FIB-CVD DLC films after 32 h of heat treatment at 873 and 973 K respectively

FIB-CVD DLC film agreed well with the thermal desorption spectroscopy (TDS) study [6].

Fig. 2 Ga profiles in the RBS spectra of FIB-CVD DLC films as- deposited and after heat treatment at 773 K. Annealing times are noted in the upper part of each spectrum. The plots indicate the measured RBS spectra, and the solid lines indicate the fitting curves reproduced using the RBS fitting calculation package.

Figure 2 depicts the Ga profiles in the RBS spectra of the FIB-CVD DLC film (a) as deposited, and annealed FIB-CVD DLC film at 773 K for (b) 2 h, (c) 15 h, and (d) 64 h. The X- axis indicates the energy of He⁺ ion back-scattered by the Ga in the FIB-CVD DLC film; namely, the high energy side and low energy side correspond to the Ga atoms near the surface and Ga atoms at the bottom of the film, respectively. The Ga profile of the FIB-CVD DLC film as- deposited (a) has a rectangular shape, which indicates that Ga atoms were distributed uniformly. However, the Ga profile in the FIB-CVD DLC film was divided into peaks by the 2- h heat treatment at 773 K (b). In other words, the concentration of Ga in the middle part of the film decreased earlier than at the near-surface part and bottom part of the film. The peak intensity of the near-surface part was larger than that of the bottom part in the film after 2 h of heat treatment at 773 K (b), while the peak intensity of the near-surface part was less than that of the bottom part in the film after 15 h of heat treatment at 773 K (c). After 64 h of heat treatment at 773 K, only a small amount of Ga was left, in the bottom part (d). These Ga profiles indicate that the desorption rate of Ga increased in the order of the middle part, upper part, and bottom part.

Some studies have reported that Ga segregated from an FIB-CVD device by annealing treatment formed Ga spheres by agglomerating [3, 5, 12]. These Ga spheres were surrounded by a graphite shell. Figure 3 shows an SEM image of the DLC film after 32 h of heat treatment at 673 K. The squares with 200- m sides indicate the deposition area of one scan of the FIB beam, as described in the experimental section. A lot of Ga spheres were observed on the surface of the FIB-CVD DLC film. The increase in Ga concentration after 32 h of heat treatment at 673 K in Fig. 1 can be attributed to the formation of these Ga spheres; in other words, a lot of Ga existed near the surface, where the detectivity of the RBS apparatus is higher. The slight decrease in Ga concentration of the FIB-CVD film after heat treatment in the range of 0-16 h at 673 K indicated that the Ga atoms from the inner part of the FIB-CVD film transferred to the surface, and a small quantity of them departed. The desorption rate from a Ga sphere is thought to be smaller than that from DLC, namely amorphous carbon, because the Ga spheres were surrounded by a graphite shell, which was composed of a large amount of graphite, namely crystalline carbon. On the other hand, the bottom part, where some Ga remained after long heat treatment, is thought to be the Ga-implanted Si substrate. The desorption rate of Ga from this region was expected to be smaller than that from the DLC, because the

diffusion constant of the Si substrate is smaller than that of DLC, even if the Si substrate is damaged by the Ga ion beam.

Fig. 3 SEM image of FIB-CVD DLC film after 32 h of heat treatment at 673 K.

We can summarize the departure process of Ga from the FIB-CVD DLC film as follows. Figure 4 shows a schematic illustration of the annealing effect on the FIB-CVD DLC film. In the chemical vapor deposition by FIB, the Ga was implanted into the Si substrate. The ion range of 30- kV Ga ions into the Si substrate was calculated to be ≈ 35 nm by Monte Carlo simulation [13]. On the other hand, the DLC layer, which contains no Ga, is formed near the surface. The thickness of this region is ≈ 35 nm [4, 6]. Therefore, the structure of the FIB-CVD DLC film deposited on the Si substrate was consisted of four kinds of layers, a DLC layer ≈ 35 nm in thickness neighbouring the surface without Ga, a DLC layer containing Ga in the middle part, Ga-implanted Si substrate of ≈ 35 nm thick, and a Si substrate without damage (Fig. 4(a)). The heat treatment at ≈ 673 K caused residual Ga to expand. Ga atoms in the inner part of the film then transferred to the surface (Fig. 4(b)). The Ga segregated by the annealing

treatment formed Ga spheres by agglomerating. The desorption rate increased sequentially starting with the Si substrate, inner graphite shell, and then the inner DLC (Fig. 4(c)). Therefore, the Ga concentration first decreased in the middle part of film, which was composed of DLC, then in the upper part, where Ga spheres surrounded by a graphite shell were formed. Finally, the Ga departed from the bottom part, where Ga ions were implanted in the Si substrate.

In conclusion, we investigated the departure process of Ga after applying an FIB-CVD process by preparing samples at various annealing temperatures and annealing times. The Ga atoms in the FIB-CVD DLC film did not move at heat treatment of 523 K. At 673 K, residual Ga transferred to the surface and formed Ga spheres, although the evaporation rate was very low. With heat treatment at temperatures higher than 773 K, the residual Ga was evaporated, and the Ga concentration decreased as the annealing time increased.

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References

- [1] S. Matsui, T. Kaito, J. Fujita, M. Komuro, K. Kanda, and Y. Haruyama, *J. Vac. Sci. Technol. B*, **18**, 3181-3184 (2000).
- [2] K. Kanda, J. Igaki, Y. Kato, R. Kometani, and S. Matsui, *Radiat. Phys. Chem.* **75**, 1850-1854 (2006).
- [3] J. Fujita, M. Ishida, T. Ichihashi, T. Sakamoto, Y. Ochiai, T. Kaito, and S. Matsui, *Jpn. J. Appl. Phys.*, **41**, 4423-4426 (2002).
- [4] J. Fujita, M. Ishida, T. Ichihashi, Y. Ochiai, T. Kaito, and S. Matsui: *Nucl. Instrum. Methods Phys. Res. B*, **206**, 472-477 (2003).
- [5] R. Kometani, S. Ishihara, K. Kanda, Y. Haruyama, T. Kaito, and S. Matsui, *Jpn. J. Appl. Phys.*, **47**, 5032-5035 (2008).
- [6] T. Nagata, Y. Sakuma, M. Haemori, K. Nakajima, R. Kometani, K. Kanda, S. Matsui, and T. Chikyow, *Jpn. J. Appl. Phys.*, **47**, 9010-9012 (2008).
- [7] K. Kanda, J. Igaki, A. Saikubo, R. Kometani, T. Suzuki, K. Niihara, H. Saitoh, and S. Matsui, *Jpn. J. Appl. Phys.*, **47**, 7467-7469 (2008).
- [8] A. Saikubo, K. Kanda, Y. Kato, J. Igaki, R. Kometani, and S. Matsui, *Jpn. J. Appl. Phys.*, **46**, 7512-7513 (2007).
- [9] J. Igaki, A. Saikubo, R. Kometani, K. Kanda, T. Suzuki, K. Niihara, and S. Matsui, *Jpn. J. Appl. Phys.*, **46**, 8003-8004 (2007).
- [10] Y. Ohkawara, S. Ohshio, T. Suzuki, H. Ito, K. Yatsui, and H. Saitoh, *Jpn. J. Appl. Phys.*, **40**, 3359-3363 (2001).
- [11] Y. Ohkawara, S. Ohshio, T. Suzuki, H. Ito, K. Yatsui, and H. Saitoh, *Jpn. J. Phys.*, **40**, 7007-7012 (2001).
- [12] R. Kometani, T. Ichihashi, S. Warisawa, and S. Ishihara, *Jpn. J. Appl. Phys.*, **48**, 06FE01-4 (2009).
- [13] R. Kometani, Ph. D. Thesis, University of Hyogo, (2007) 31-37.

Fig. 4 Schematic illustration of Ga departure from FIB-CVD DLC film. (A) FIB-CVD DLC film as- deposition. (B) With heat treatment at temperatures higher than 673 K, residual Ga transferred toward the surface and agglomerated into Ga spheres. (C) Ga concentration in the middle part of the FIB-CVD DLC film decreased, because the desorption rate decreased in the order of DLC, graphite shell, and Si substrate.