Ion-Beam Deposition/Etching Using EMIM-N(CN)₂ Ionic Liquid Ion Source

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The effect of irradiating EMIM⁺ or N(CN)₂⁻ ion beams by using an ionic liquid ion source was discussed for application to metal-free negative-ion focused ion beams. We found that N(CN)₂⁻ ion beams exhibit substrate etching under an acceleration voltage greater than 1 kV. Especially, N(CN)₂⁻ irradiation at 4 kV yields large etching depth in Si substrates, as estimated by a Si/N(CN)₂⁻ sputtering yield of 10.0, and causes surface smoothing due to chemical etching, which was indicated by a decrease in the surface roughness of Si from 0.07 nm to 0.05 nm. In contrast, glass substrates were mainly etched with physical sputtering by incident ion beams. Moreover, the results of XPS and spectrophotometer measurements revealed that the irradiation of N(CN)₂⁻ at 1 kV forms a carbon-nitride film including g-C₃N₄.

Key words: dicyanamide, DCA, C₃N₄, ion beam deposition, ion beam etching

1. INTRODUCTION

Focused ion beams (FIBs), a technology crucial to the advancement of nanoscience and technology, has been increasing in importance. The commonly used FIB is a field-emission-type liquid-metal ion source (LMIS), which works with low-melting-point metals such as Ga.

Since the last decade, ionic liquid ion sources (ILIS) have attracted much attention because of their unique properties such as the easy generation of an ion beam by field emission[1-5]. The uniqueness is attributed to the characteristics of the ionic liquid (IL) known as room-temperature molten salt, which generally consists of organic cations and anions including halogens and shows moderate electrical conductivity (1-100 S/m), high thermal stability (up to ~300 °C), and extremely low vapor pressure (< 1×10⁻⁹ Pa). This may allow the ILIS to achieve a unique FIB with high-speed, metal-free chemical etching due to halogens and to provide negative ion beams resulting from anion emission. Furthermore, the ILIS-FIB may achieve not only nanoscale etching but also the formation of nanoscale 3D structures by ion-beam deposition, for example, the formation of carbon nitrides (C₃N₄) by using dicyanamide (DCA) anions.

Carbon nitrides are promising for use in various applications; they can be used as photocatalysts, fuel-cell electrodes, light-emitting devices, and chemical sensors. Diamond-like β-C₃N₄ is predicted to be of similar hardness and low compressibility as diamond[6]; on the other hand, graphitic C₃N₄ (g-C₃N₄) with a graphite-like structure is promising for use as a metal-free photocatalyst with a band gap of 2.7-2.9 eV[7], which can work under visible light[8].

We have previously developed an ILIS for application in a metal-free negative-ion FIB and have reported irradiation effects of ion beams obtained from 1-ethyl-3-methylimidazolium BF₄ (EMIM-BF₄) and

1-butyl-3-methylimidazolium PF₆ (BMIM-PF₆)[5,9-11]. In this report, irradiation effects of the EMIM-DCA ion beam, including the deposition of carbon nitrides and substrate-etching properties, were discussed.

2. EXPERIMENTAL

Figure 1 shows an image of the ILIS we previously developed[5]. The inset of the figure shows the chemical structure of 1-ethyl-3-methylimidazolium dicyanamide (EMIM-DCA), which was purchased from Sigma-Aldrich for our experiments and had a purity of 97%. The EMIM-DCA used as the source liquid is known as room-temperature molten salt; it consists of an imidazole cation and a dicyanamide anion and has a molar mass of 177 g/mol (EMIM 111 g/mol, DCA 66 g/mol), melting point of -21 °C, density of 1.1 g/cc, viscosity of 21 mPa·s, and electric conductivity of 27 mS/cm, respectively. The EMIM-DCA was supplied using a 100-μl syringe (Hamilton Company, 1710TLL) mounted on a syringe pump (YMC CO., LTD, YSP-201) that feeds the IL through a Polyether ether ketone (PEEK) tube when IL shortage occurs at the ion emitter. The IL feeding was usually performed at a rate of 0.5 μl/min before irradiation, until a stable emission current was obtained without unnecessary irradiation. Subsequently, the IL feeding was stopped until required again. The ion emitter is assembled with a 1/16-inch-O.D. stainless-steel tube and a custom-made mechanically sharpened graphite tip with a radius of 40 μm, which allows the ILIS to stabilize ion emission because of its good IL-wettability and chemical stability, as reported elsewhere[5,9]. These cations or anions in the IL were extracted individually from a Taylor cone formed by an electrical field applied between the extractor and the graphite tip and were focused by using an electrostatic lens. After electron screening by using

Fig. 1 Developed ionic liquid ion source (photo) and chemical structure of EMIM-DCA (inset).

magnets and a magnetic yoke, the transferred ions were irradiated to substrate targets, which were a single crystalline silicon substrate (Yamanaka Semiconductor, n-type 4-inch wafer (100)) and a non-alkaline borosilicate glass substrate (Matsunami glass, compatible with Corning #7059). The deflector made of 30-mm-length stainless steels was used for generating chopped beam to measure mass spectrum as mentioned later. The glass substrates were ultrasonically pre-cleaned using acetone, ethanol, and deionized water before irradiation and were finished by blowing with dry N_2 gas. The Si substrates were additionally rinsed in an 80 °C solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 1:4$) and were treated with 5% HF to remove the native oxidized layer.

Prior to the irradiations on the substrates, time-of-flight (TOF) mass measurement was carried out. Figure 2 shows TOF mass spectra for the IL ion beams with both polarities. The ions accelerated to 3–4 kV depending on current stability were chopped with a pulse of 5- μs width and 1-ms period by using an electrostatic deflector applied with voltages of -1 to -2 kV, as shown in Fig. 1. The chopped beam was passed through a 1.8-m-long drift chamber terminated with a

Fig. 2 TOF spectra of ions extracted from EMIM-DCA in positive- and negative-ion modes.

microchannel plate (Hamamatsu Photonics, F2222-21S, effective diameter: 20 mm) to detect the ion signal. Distinct peaks at mass/charge ratios of ~ 110 u/e and ~ 65 u/e are seen in the positive and negative polarities, respectively. These peaks correspond to the masses of EMIM⁺ (111 g/mol) and DCA⁻ 66 g/mol; therefore, the extracted ion was mainly composed of EMIM⁺ cation in the positive-ion mode and DCA⁻ anion in the negative-ion mode. The positive and negative ions were irradiated with acceleration voltages of 1, 2, 4, and 6 kV under a vacuum of 10^{-4} Pa. The irradiation fluences were set to 1×10^{15} - 1×10^{16} ions/ cm^2 , assuming the ions to be singly charged. The extraction voltage was adjusted in the range of 2–4 kV such that the beam current was stable. The ion beams were irradiated to a wide area 20 mm in diameter, wherein the substrates were mounted.

The deposition thickness or etching depth, obtained as the edge height at the masked-unmasked boundary on the irradiated substrates, was measured using a stylus surface profiler (Ambios Technology Inc., XP-2). Atomic force microscopy (AFM; SPM300 produced by SII NanoTechnology Inc.) was employed to observe the surface morphology of the irradiated samples and to

Fig. 3. Masked-unmasked boundary heights of (a) Si substrates and (b) glass substrates measured by the stylus profiler.

Fig. 4. Surface roughness of (a) Si substrates and (b) glass substrates estimated by using AFM.

estimate surface roughness as the arithmetic average of the absolute surface height. The elemental concentration and chemical state of the sample surfaces were determined using X-ray photoelectron spectroscopy (XPS; Quantum 2000 from ULVAC PHI Inc.).

3. RESULTS AND DISCUSSION

Figure 3 shows the masked-unmasked boundary heights of (a) Si substrates and (b) glass substrates. In the case of Si substrates, film deposition and substrate etching are observed at acceleration voltages of 1-2 kV and 4-6 kV, respectively. The etched depths of DCA⁻ irradiation are two times greater than those of EMIM⁺ irradiation, although DCA⁻ has no hydrogen atoms to generate SiH₄ gas and the molecular weight of DCA⁻ is 40% less than that of EMIM⁺. This implies that the DCA⁻ ion beam chemically etches the Si substrate. The estimated sputtering yields of Si/DCA⁻ is 4.8, 10.0, and 15.1 at 2, 4, and 6 kV, respectively. These sputtering yields are greater than that of Si/Ga, which is generally used in FIB applications and calculated as 1.2 by using TRIM code at the same acceleration voltages[12]. In the glass-substrate case of Fig. 3 (b), film deposition at 1-2 kV and substrate etching at 4-6 kV are observed for irradiation with EMIM⁺ and DCA⁻. Since the non-alkaline borosilicate glass is based on SiO_x and BO_x, which are chemically stable, the observed etching is probably caused by physical sputtering.

The surface roughness values estimated using the AFM observations are shown in Fig. 4 (a) and (b). In Fig. 4 (a), the surface roughness of the Si substrate for irradiation with DCA⁻ and EMIM⁺ at 2-4 kV decrease from 0.07 nm for the unirradiated substrate to about 0.05 nm, whereas the surface roughness at 6 kV increases to 0.14 nm for DCA⁻ and to 0.20 nm for EMIM⁺ with an increase in deviation. This trend is probably caused by physical sputtering and chemical etching. It is suggested that physical sputtering, which roughens the surface, is significant at 6 kV; in contrast, at low incident energies such as 2-4 kV, chemical etching, which smoothens the surface, is more prominent. The film deposition on the Si substrate at an acceleration voltage of 1 kV, as shown

in Fig. 3 (a), reduces the surface roughness from 0.07 nm for the unirradiated substrate to 0.05 nm. Thus, films deposited by irradiation have excellent smoothness.

As shown in Fig. 4 (b), for the glass substrates, surface roughness values at 2-4 kV for irradiation with EMIM⁺ and DCA⁻ are 0.1-0.15 nm, which is slightly greater than that of the unirradiated substrate, while that of 6 kV significantly increases to 0.3-0.4 nm with wide errors. The increased errors for the 6 kV are possibly due to surface waviness developed with the roughness by such high energy irradiation. Unlike the Si substrates, no decrease of roughness at 2-4 kV is detected for the glass substrates, even with DCA⁻ irradiation. This implies that the etching of glass substrates by irradiation with EMIM⁺ and DCA⁻ are mainly caused by physical sputtering. The glass substrates with a film deposition by DCA⁻ irradiation at 1-2 kV exhibits surface roughness values of about 0.1 nm, which is equivalent to that of the unirradiated substrate; this may be a result of the surface morphology of the unirradiated glass. On the other hand, the film obtained with EMIM⁺ irradiation at 1 kV shows a high roughness of 0.2 nm compared to those of the unirradiated and DCA⁻-irradiated substrates. This is possibly caused by the low density of the film structure induced with reduced beam energy; positive-ion irradiation usually develops electrical charge-up due to its accumulated charge and emission of secondary electrons, whereas negative-ion irradiation yields self-neutralization.

Figure 5 shows XPS spectra of (a) C1s and (b) N1s for the DCA⁻-irradiated Si substrates. In Fig. 5(a), several peaks related to C(sp²), C(sp³), C-N, and/or C-O bonds are observed at an acceleration voltage of 1 kV. Simultaneously, a C₃N₄ peak overlapping with a Si₃N₄ peak is detected for 1 kV, as shown in Fig. 5(b). These results indicate that the film obtained with DCA⁻ irradiation consists of C₃N₄ as well as graphitic and cubic carbons on a film/substrate boundary including Si₃N₄. For DCA⁻ irradiation at 2-6 kV, SiC peaks are observed in Fig. 5 (a) while C(sp³) and C-N and/or C-O peaks have decreased intensities. Hence, carbon nitrides do not remain on the surface and likely contribute to the

Fig. 5. XPS spectra of DCA^- -irradiated Si substrates for (a) C1s and (b) N1s.

chemical etching of Si substrates in the case of DCA^- irradiation at 2–6 kV. The estimated concentration between C and N were C:N = 4:1 and 2:1 for EMIM^+ and DCA^- , respectively. This contrast is probably caused by difference in N content for the irradiated ions, EMIM^+ and DCA^- .

In order to estimate the C_3N_4 structure, transparent spectra of a 100-nm film deposited on the glass substrate irradiated with 0.5-kV DCA^- was measured by using a UV-Visible spectrophotometer. Broad absorption was observed below 500 nm, which corresponds to a photon energy of over 2.5 eV. This is attributed to the band gap of g- C_3N_4 . Therefore, a film including g- C_3N_4 was probably formed by the DCA^- irradiation at 1 kV.

4. SUMMARY

In this study, the effect of irradiating $\text{EMIM}^+/\text{DCA}^-$ ion beams by using the ILIS was discussed for application to metal-free negative-ion FIBs. We found that DCA^- ion beams exhibit substrate etching under an acceleration voltage greater than 1 kV. Especially, DCA^- irradiation at 4 kV yields large etching depth in Si substrates, as estimated by a sputtering yield of 10.0, and results in surface smoothing due to chemical etching, which was indicated by the decrease in surface roughness from 0.07 nm of the unirradiated Si to 0.05 nm. In contrast, glass substrates were mainly etched with physical sputtering by the incident ion beams. Moreover, the results of XPS and spectrophotometer measurements revealed that the irradiation of DCA^- at 1 kV forms a carbon nitride film including g- C_3N_4 .

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