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Irradiation of ionic liquid ion beams on silicon and glass substrates

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ABSTRACT

Irradiation of an ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF_6) ion beam on borosilicate glass and single crystalline Si(100) surface was demonstrated by using an ionic liquid ion source we developed. Surface smoothing on the glass substrates was produced by the irradiations at an acceleration voltage of 4 kV with both positive and negative ion beams, which include cation–anion pairs attached to a single ion of either polarity. Water contact angle measurements and X-ray photoelectron spectroscopy indicated that the surface smoothing was probably caused by surface modification involving nano-ordered chemical etching by Si–F reaction, implantation and deposition of P, N and C.

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1. Introduction

Polyatomic ion beam processing is an important technology because of its characteristics such as an equivalently high current, shallow implantation depth, and low implantation damage. In recent decades, ionic liquid ion sources (ILIS) have attracted much attention because of their unique characteristics: easy extraction of a negative ion beam and numerous combination of molecules. The ionic liquid (ILs), or room-temperature molten salt show moderate electrical conductivity (1–100 S/m), high thermal stability (up to ~300 °C) and extremely low vapor pressure (< 1×10^{-9} Pa). Several types of ILIS, such as an externally wetted needle made of tungsten [1,2] and a capillary [3,4], have been reported. We have also proposed an ILIS with an emitter consisting of a porous medium [5], which is known as a high-current, stable method in the field of liquid metal ion sources. ILISs are expected to be applied as an ion source in ion thrusters [6] and as a probe in secondary ion mass spectroscopy (SIMS) [7]. Because typical ILs includes halogens, ILISs are a potential ion source for reactive etching and surface modification of semiconductor materials such as Si [8] and SiO_2 and for focused ion beam processing (FIB) [9].

Glass, which is composed mainly of silicon dioxide, is also an important material for electronics devices such as flat panel displays and touch screens. However, typical glasses are generally electrical insulators, so irradiation of monomer ions onto the glass substrates tends to cause electric charge-up, which gives rise to an electrical breakdown. Polyatomic ions have a larger mass/charge ratio than monomer ions, which gives them the advantage of less charge-up. In particular, ILs, which are a type of polyatomic ion, are expected to be very effective for surface smoothing or sputtering because they encompass many types of molecules, especially boron, phosphorus and halogens, that considerably affect chemical reactions on glass. The surface smoothness is very important for a bendable glass applied to smartphones, watches, or other wearable connected devices. Nevertheless, irradiation or deposition of an IL ion beam onto a glass substrate has not been reported yet. Therefore, in this article, the effects of irradiation by an IL ion beam on the surface morphology of a glass substrate and on Si were investigated.

2. Experimental

2.1. Ionic liquid

Fig. 1 shows the structure of 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF_6), which was used as the source liquid in this study. BMIM-PF_6 is known as a room-temperature molten salt consisting of an imidazole ring with a butyl/methyl group as a cation; it contains a phosphorous fluoride as an anion, and has a molar mass of 284.2 g/mol, melting point of 6.5 °C, density of 1.38 g/cm^3, viscosity of 3.0 mPa s, and electric conductivity of 1.46 mS/cm. More details are available elsewhere [10–12]. Because the fluorine and the phosphor included in the anion are expected to react with silicon and silicon dioxide, BMIM-PF_6 was employed as the source liquid for ion beam irradiation.

2.2. Ion source and experimental chamber

Fig. 2 shows an illustration of the developed ILIS. This ion source is composed of an IL container of stainless steel (JIS-SUS304) connected with carbon felt and a mechanically sharpened carbon tip

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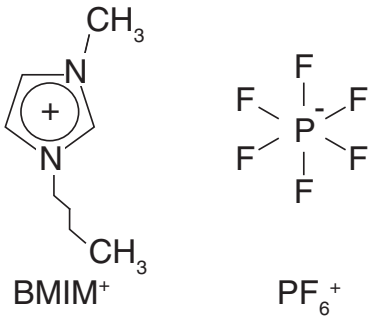

Fig. 1. Structural formula of BMIM-PF_6.

with diameter of 0.5 mm. The IL filled in the container is transported by capillary action through the porous medium of the carbon felt and is supplied to the carbon tip. Fig. 3 shows the developed experimental chamber with the ILIS, an electrostatic lens (einzel lens) to focus the ion beam, a pair of NdFeB magnets for removing undesired electrons, a deflector to align the beam trajectory, a Faraday cup and target holder, and a multichannel plate (MCP) as the detector for mass analysis. The setup of the electrical circuit in this figure shows the negative ion mode. A positive or negative IL ion beam is extracted from the ion source and accelerated by an extraction electrode with a ϕ2 mm hole 3 mm from the emitter tip. Then the ion beams are focused and irradiated to samples on the target holder. To protect the high voltage power supply of the extraction electrode and stabilize the ion current, a 40 MΩ resistor is connected in parallel.

To determine the mass/charge ratio of the generated IL ions, time-of-flight (TOF) mass spectrometry was employed. A bunched ion beam, with a pulse width of 1 μs and period of 1 ms, is produced by the deflector and moves to the MCP for a drift length of 1.7 m from the deflector. The experimental chamber is evacuated to 1×10^{-4} Pa by using turbo molecular pumps backed with rotary pumps before the TOF measurements and beam irradiation. Note that the mass resolution $M/\Delta M$ in this TOF system was about 10 at M = 100 u (unified atomic mass unit) and was about 138 at M = 1000 u. This shows that the ΔM of about 11 u at M = 200 u is due mostly to the pulse width.

Fig. 4 shows TOF spectra of BMIM-PF_6 ion beams in the positive and negative ion modes. Two peaks at mass/charge ratios of ~150 u and ~800 u are seen in both the positive and negative ion beam. The peak at 150 u corresponds to $BMIM^+$ cations with a molecular mass of 139 g/mol and PF_6^- anions with mass of 145 g/mol for the positive mode and negative mode, respectively. The mass/charge distribution around 800 u is likely caused by n cation–anion pairs attached to either a single cation or a single anion, where the value of n is estimated to be 3 or 4. According to many reports, a small cluster ions composed of cation–anion pairs seems likely to arise [3,4,13,14]. Charged droplets having a much lager mass/charge ratio (greater than 2000 u) were not observed in this measurement. However, the wet surface of the target holder, which was placed 200 mm downstream from the emitter tip, was detected, as described below. One of the reasons why the charged droplets were not observed by the TOF measurement is probably the low efficiency of MCP for detecting such a large mass. Furthermore, few droplets are thought to reach to the MCP at distance of 1.7 m owing to its large scattering cross section at that pressure.

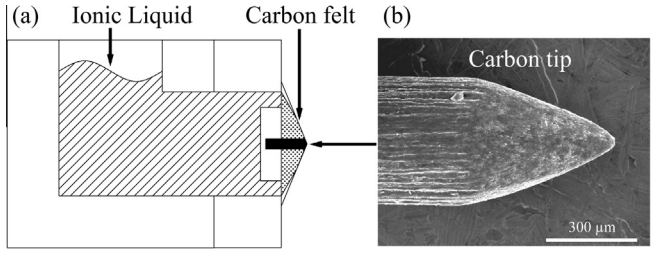

Fig. 2. Developed ionic liquid ion source: (a) schematic diagram of ionic liquid ion source and (b) SEM image of emitter tip made of graphite rod.

2.3. Sample preparation

Targets were irradiated by BMIM-PF_6 ion beams of both polarities under the following conditions: source liquid of BMIM-PF_6 with a purity of >97% purchased from Sigma–Aldrich, magnitude of acceleration voltage of 4 to 8 kV, fluence of 1.0×10^{15} ions/cm^2 assumed to be singly charged, and $< 1 \times 10^{-3}$ Pa vacuum. For the irradiation targets, non-alkaline borosilicate glass (Matsunami Glass Ind.,Ltd., comparable to Corning #7059) and a single crystalline Si(100) substrate were employed. The glass substrates were ultrasonically cleaned in acetone, ethanol and deionized water and were finished by blowing with dry N_2 gas. The Si substrates were additionally rinsed in a hot SPM solution (H_2SO_4:H_2O_2 = 1:4) and were treaded with 5% HF to remove the natural oxidized layer.

2.4. Analytical method

All the samples irradiated with the ion beams were wetted with an IL as mentioned above. Then, the IL was removed by ultrasonic cleaning in acetone for 2×30 min and in deionized water for 10 min before surface analysis. To examine the effect of this post-treatment cleaning, we prepared control samples that underwent the same procedure (i.e., were dipped in IL and then cleaned) without any ion irradiation.

The sputtering depth, obtained as the edge height at the masked–unmasked boundary on the irradiated substrates, was measured by a stylus surface profiler. Atomic force microscopy (AFM) was employed to observe the surface morphology of the irradiated samples and to estimate the surface roughness as the arithmetic average of the absolute value. The effect of irradiation on the surface energy was evaluated by measuring the contact angle of pure water on the samples by using the sessile drop method. The elemental concentration on the sample surfaces were determined by X-ray photoelectron spectroscopy (XPS).

3. Results and discussion

3.1. Surface morphology

The sputtering depth measurements yielded no measurable value over 1 nm in any of the samples. This reason might be that the IL wet layer acted as a protective coating against the incident ions.

Fig. 5 shows the surface roughness of the glass substrates irradiated with BMIM-PF_6 ion beam in positive or negative ion mode. The surface roughness increases is higher at acceleration voltages of $\geqslant$6 kV compared with the unirradiated sample, showing a roughness of 0.4 nm for both ion modes. In contrast, the surface roughness at an acceleration voltage of 4 kV in both ion modes clearly decreased to 0.17 nm compared to the unirradiated sample. This indicates that the BMIM-PF_6 ion beam induces surface smoothing of the glass. Because the ion beams of both polarities contain many cluster ions including cations and anions as shown in Fig. 4, their effects seem to show similar tendencies. It is possible that electric charge-up on the substrate surface, which is generally built up by incident positive ions, causes the differences in

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