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Surface modification of triacetylcellulose by low-energy nitrogen ions for diaphragm of environmental cell transmission electron microscope

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ABSTRACT

Triacetylcellulose (TAC) was subjected to surface modification by low-energy nitrogen ion irradiation for use as the diaphragm of an environmental cell transmission electron microscope (E-TEM). TAC films formed by the dipping method were placed on Cu grids for E-TEM and then irradiated by nitrogen ions with acceleration voltages of 1.0 and 1.5 kV and with ion doses between 5.9×10^{16} and 1.2×10^{17} ions/cm^2. The TAC films were removed by acetone after irradiation and the surface-modified layers at the top were kept for assessment as diaphragms. The thicknesses of the surface-modified layers, which varied depending on the acceleration voltage and dose of the nitrogen ions, ranged from around 12 to 29 nm. X-ray photoelectron spectroscopy revealed that the surface-modified layers mainly consisted amorphous carbon with a nitrogen-to-carbon atomic ratio of around 1%. These films were transparent to an electron beam accelerated to 300 kV. The pressure resistances of all samples were maintained at around 0.1 MPa.

1. Introduction

Environmental cells are small chambers used to study samples under pressure conditions that would otherwise be incompatible with ultrahigh vacuum techniques, such as transmission electron microscopy (TEM) and X-ray electron spectroscopy (XPS) [1,2]. In such systems, the diaphragm is the most important component of the environmental cell because it not only maintains the pressure difference between vacuum and high pressure (due to the gas, degassing solid, and liquid from the sample to be measured) but also allows the probing beam and subsequent signal to pass through. In addition, diaphragms for environmental cell TEM (E-TEM) are required to have high hardness and low electron scattering, be chemically inert, and exhibit no electron diffraction contrast. Thin amorphous films made of light elements can be particularly well suited for this application. We previously reported diaphragms for the environmental cell made from a nitride film deposited on a triacetylcellulose (TAC: $[C_6H_7O_2(OOCCH_3)_3]_n$, $\rho = 1.22$–1.34 g/cm^3) film by magnetic-field and pulsed-plasma-enhanced chemical vapor deposition (MPECVD) and low-energy ion-beam-induced chemical vapor deposition (LEIBICVD) [3,4]. After deposition of the nitride, the TAC film was removed by acetone so that electrons would be transmitted through only the nitride film. Although MPECVD has advantageous deposition rates and high coverage, these can lead to solid particle contamination on the surface, due to the so-called "dusty plasma" conditions [5,6]. Also, to obtain a continuous film, it was necessary to deposit roughly 100-nm-thick layers, which is not suitable for TEM applications. To overcome these problems, etching was carried out with nitrogen ions after film formation, and a diaphragm with a thickness of 15 nm and a pressure resistance of 0.3 MPa was successfully developed [7]. By contrast, in LEIBICVD, there is no problem associated with "dusty plasma", and the low-energy ion process is a promising technique to obtain flat surfaces [4,8]. Here, the TAC film surface was modified by irradiating it with low-energy nitrogen ions and it was attempted to use the surface-modified layer as a diaphragm without employing any deposition method. Surface modification of polymers by an ion beam has been reported previously [9]. For instance, in order to add a conductive layer on a polymer surface for use as LSI wiring, the decomposition and/or metal implantation of polymer surfaces by high-energy ion beam irradiation has been carried out [10–14]. Since the penetration depth of low-energy ions is extremely shallow, the surface modified layer is thought to be ultrathin. To investigate the usefulness of the surface-modified layer as a diaphragm, the layer was characterized by XPS and TEM, and the pressure resistance was measured.

2. Experimental

Fig. 1 illustrates the present procedure involving nitrogen ion

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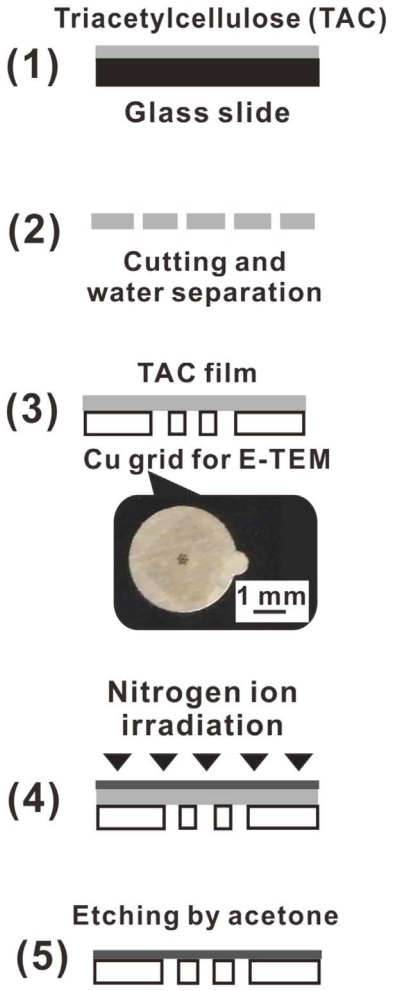

Fig. 1. Experimental procedure for fabrication of TAC surface-modified layer by low-energy nitrogen ion irradiation for use as a diaphragm.

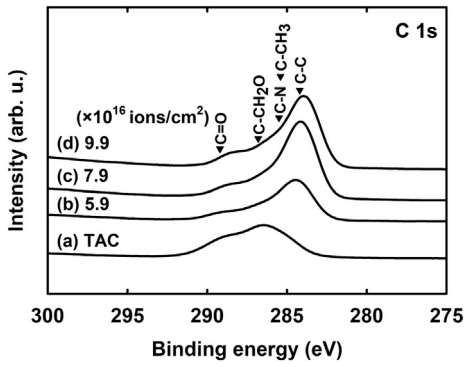

Fig. 2. C 1s XPS spectra of (a) TAC film and TAC surface-modified layers formed by nitrogen ion irradiation to ion doses of (b) 5.9, (c) 7.9, and (d) 9.9×10^{16} ions/cm^2 at an acceleration voltage of 1.0 kV after acetone etching.

irradiation, employed to fabricate surface-modified layers on a TAC film for use as diaphragms. The TAC film was prepared by a method similar to that reported in our previous paper [3]. The entire fabrication procedure can be summarized as follows: (1) a 150-nm-thick triacetylcellulose (TAC) film was formed on a glass slide by dipping the slide into a TAC solution (TAC: 0.595 mg; dichloroethane: 100 ml; methanol: 19 ml) (2) and cut to 2.5 × 2.5 mm. (3) The TAC film was peeled off from the glass slide and placed on a Cu grid for E-TEM (diameter: 3.5 mm; thickness: 1 mm; hole diameter: 100 μm). (4) TAC films on Cu

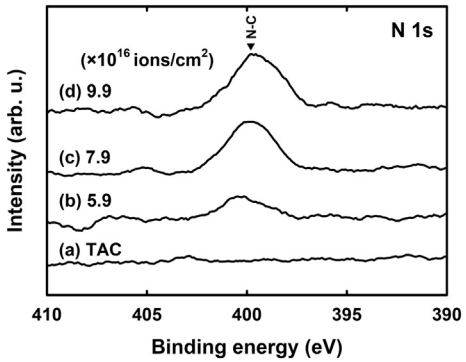

Fig. 3. N 1s XPS spectra of (a) TAC film and TAC surface-modified layers formed by nitrogen ion irradiation to ion doses of (b) 5.9, (c) 7.9, and (d) 9.9×10^{16} ions/cm^2 at an acceleration voltage of 1.0 kV after acetone etching.

grids were irradiated by nitrogen ions with acceleration voltages between 0.8 and 1.5 kV and ion doses between 3.0×10^{16} and 1.2×10^{17} ions/cm^2. An ion gun with an electron-impact-type ion source was used and the incident angle was set at normal. The emission voltage and current were 240 V and 50 mA, respectively. The ion irradiation area and ion density were fixed at 0.28 cm^2 and 1.8 μA/cm^2, respectively. Ion irradiations were performed at a chamber pressure of 1.0×10^{-5} Pa. (5) TAC films were removed by acetone after nitrogen ion irradiation so that electrons would be transmitted only in the surface-modified layer through the holes of the Cu grid.

The surface-modified layer was characterized by XPS (Axis-Nova, Kratos Analytical). The monochromatic Al-kα line was generated with an emission current of 10 mA and an acceleration voltage of 15 kV and used to excite photoelectrons. Measurements were performed at a pressure of 10^{-7} Pa. The incidence angle of the X-rays was 34.5°, and photoelectrons were detected normal to the substrate. The C 1s, N 1s, and Cu 2p spectra were obtained by five scans with a dwell time of 200 ms and an energy step of 0.1 eV. These spectra were calibrated with Cu 2p in the Cu grid and with reference gold foils. The nitrogen/carbon atomic ratio N/(C + N) was calculated on the basis of the peak area ratio of each spectrum, with software (vision processing) attached to an XPS equipment (AXIS Nova).

The capacity of the resistance pressure of the surface-modified layer was measured on a Cu grid. First, both sides of the edge of the Cu grid were sealed by a gasket at atmospheric pressure. One side of the Cu grid was evacuated to less than 100 Pa by a dry pump, while the other side was subjected to higher-than-atmospheric pressure by compressed air. The pressure at which the surface-modified layer broke and no pressure was applied was noted as the maximum pressure difference. The surface-modified layer portion in the Cu grid was determined by an optical microscope and the Cu grid was introduced into the E-TEM (H-9500, Hitachi). The acceleration voltage and emission current of the electron beam used for TEM observation were 300 kV and 5 μA, respectively.

The thickness of each surface-modified layer, controlled by varying the nitrogen ion energy and dose, was measured by TEM. Each surface-modified layer over the holes of the Cu grid was broken by a pin and a bent portion of the layer was observed. The thickness of the region of dark contrast observed in the bent region was taken to be the film thickness. Indeed, in this region, the electrons are transmitted through a greater length that is directly proportional to the film thickness.

3. Results and discussion

Fig. 2 shows the C 1s XPS spectra of (a) a TAC film and of TAC surface-modified layers formed by nitrogen ion irradiation to (b) 5.9, (c) 7.9, and (d) 9.9×10^{16} ions/cm^2 at 1.0 kV after acetone etching. The C 1s spectrum of the TAC film exhibited a broad peak that included several peaks, at 285.4 eV (C—CH_3), 286.8 eV (C—CH_2O), and 289.2 eV