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Anisotropically conducting films consisting of sub-micron copper wires in the ion track membranes of poly(ethylene terephthalate)

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Abstract

Ion track membranes of poly(ethylene terephthalate) (PET) are applied to the production of anisotropically conducting films possessing copper wires of less than sub-micron in diameter. The membranes possessing cylindrical pores of 1.9 μm and 200 nm in diameter were prepared by irradiation of $^{129}Xe^{23+}$ ion beams followed by etching in an aqueous NaOH. Copper wires were deposited into the pores by electrochemical plating in aqueous copper sulfate solution to prepare the PET/Cu hybrid membranes. The copper wires with 1.9 μm in diameter showed wavelike surface roughness, resulting from the roughness of the pore side wall, whereas the copper wires with 200 nm in diameter showed smooth surfaces. The resistances of the membranes measured by a four terminal resistance method are in good agreement with the calculated values, indicating that the hybrid membranes possess conductivity perpendicular to the membrane surfaces but not parallel to the surfaces.

Keywords: Ion track membrane; Anisotropically conducting film; Electroplating

1. Introduction

Ionizing radiation sources such as ion and electron beams have attracted a great deal of attention as promising tools for nano-fabrication of electronic devices of the next generation, since these beams are able to be focused to a diameter in nanometer scale and scanned at high speeds [1–6]. The ionizing radiation is superior to optical lithography, which has limited resolution due to its wavelength. When polymeric membranes are irradiated by heavy ion beams, each single heavy ion particle deposits its energy to a substrate in a region of less than 10 nm in diameter along the ion-path through membranes (an ion track). The damaged region is susceptible to a proper etchant, resulting in the formation of through-holes with nanoscopic diameters, which are called 'ion track membranes' (Fig. 1) [7–13].

There have been many reports for manufacturing metallic wires by electrochemical template synthesis in the pores of ion track membranes for technological applications [14–16], such as electron field emitters, solar absorbers [17], vertical magnetic materials [18], and optical fibers [19]. Among them, copper wires have been prepared by electrochemical template synthesis mainly using the ion track membranes made of polycarbonate (PC); then, the PC membranes were removed after copper preparation for investigating structural and physical properties of copper wires [20–22]. However, there have been no attempt for applying the electroplating with ion track membranes to fabricate conductive and insulating hybrid membranes.

The anisotropically conducting films, which consist of a insulating polymer with cylindrical conductive copper wires, have been used as conductive adhesive films in manufactures of printed circuits and multi-tip modules [23,24]. These pores have been prepared by laser beam ablation, which has resolution limitation of several microns in diameter due to surface roughness caused by heat damages. Since, smaller size pores with smoother surfaces are required for manufacturing high-density and high-capacity electronic devices, we report herein the application of the ion track membranes to the fabrication of anisotropically conducting films consisting of copper wires of a diameter which is 100 times smaller than those of commercially available films.

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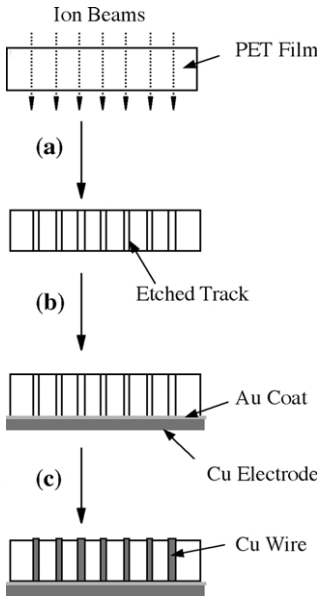

Fig. 1. Schematic illustration for the preparation of an ion track membranes and electroplating of copper wires within the pores of ion track membranes. (a) Ion beam irradiation and etching. (b) Thin gold layer deposition and successive electroplating of copper electrode. (c) Electroplating of copper wires within the pores of the ion track membrane.

2. Experimental section

2.1. Preparation of ion track membranes

PET films were purchased from Hoechst (thickness: 12 and 38 μm) and cut into pieces of 4×4 cm^2. Six sheets of film samples were set on the turntable-type film-carrier in a vacuum chamber, which is connected to the Azimuthally Varying Field (AVF) cyclotron on the Takasaki Ion Accelerators for Advanced Radiation Application (TIARA), Japan Atomic Energy Research Institute (JAERI), Japan. $^{129}Xe^{23+}$ion beams with an energy of 3.5 MeV/n were used with fluxes of 3.0×10^5 and 3.0×10^7 ions/cm^2. The irradiated films were etched at 60 °C in 0.2 or 1.0 M NaOH aqueous solution without stirring. The specimens were washed with a large amount of water and dried at a room temperature. The surface of the films was coated with gold using a Giko IB-3 ion coater and observed with a JEOL JXA-733 scanning electron microscopy (SEM).

2.2. Electrochemical deposition of copper wires

One side of PET ion track membranes were coated with gold (25 nm) using a Giko IB-3 ion coater. The membranes were set in the electrochemical plating cell shown in Fig. 2; electrochemical plating was conducted with Hokuto Denko Potentiostat/Galvanostat HA-501 in conjunction with TOA Electronics Ltd. Precision Recorder INR-6062B. A copper layer was deposited onto the thin gold-coated surface by the electroplating in a pH1 aqueous solution of 1.3 M copper

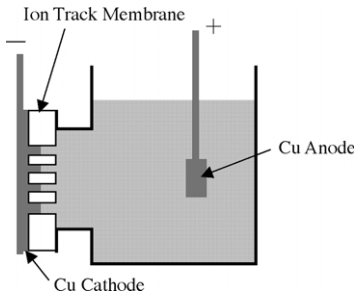

Fig. 2. Schematic illustration for an electrochemical deposition cell.

sulfate with −0.2 V for 3 h and determined to be 20 μm in thickness using Mitutoyo Digimatic Indicator [21]. The thick layer is required for a thick and continuous current collector on top of deposited gold as well as a cathode of the subsequent electroplating of copper wires. The opposite side of membranes was attached to face the inside of the cell so that copper wires grew within the pores of ion track membranes onto the copper electrode. Electrochemical copper plating into the pores was made in the same copper sulfate solution with periodic potential modulation (−0.2 V; 6 s, 0.2 V; 1 s) generated with Hokuto Denko Function Generator HB-104 in order to avoid termination of copper deposition at a growth point in the pores due to defects on the copper surfaces. The PET films were removed from the copper electrode using a 10 M KOH/ethanol (3:7 w/w) mixed solution at 70 °C for 30 min; then, the geometry of copper wires on the copper electrode was estimated by SEM measurement.

2.3. Conductivity measurements

The conductivity of hybrid membranes was measured using a contact probe method to obtain conductive information of restricted area at different positions throughout the membranes to ensure homogeneous conductivity, which is one of the most important characteristic for anisotropically conducting films. The gold-coated surfaces of the hybrid membranes were set onto a thin gold plate of 2×5 cm^2 with 0.35 mm in thickness, which was connected to milliohm-meter (Hioki 3540 mΩ Hitester) via four-terminal leads. The resistance of the membranes were measured by attaching needle probes with head areas of 2.5×10^{-4} and 6.3×10^{-6} cm^2, which were connected with the milliohm-meter.

3. Results and discussion

3.1. PET/Cu hybrid membranes with 1.9 μm copper wires

PET films with 38 μm in thickness were irradiated by $^{129}Xe^{23+}$ion beams with a flux of 3.0×10^5 ions/cm^2. The irradiated films were etched in 1.0 M NaOH aqueous solution at 60 °C for 10 h to dissolve the ion tracks. The

clear hole patterns with 1.9 μm in diameter were observed in the SEM image of the surface of the PET ion track membrane, as shown in Fig. 3(a). The film thickness decreased to 36 μm during etching due to the dissolution of the original film.

Successive layers of gold (25 nm) and copper (20 μm), which were used for the subsequent electroplating of copper wires as a cathode, were coated at one side of the PET ion track membranes. The copper wires were deposited into the pores of 1.9 μm in diameter by electrochemical plating in pH1 aqueous solution of 1.3 M copper sulfate with periodic potential modulation (−0.2 V; 6 s, 0.2 V; 1 s). Since, an electroplating current is proportional to the surface area of electrochemically growing materials, the electroplating current was constant at the first stage of the electroplating of ion track membranes, corresponding to the growth of wires into the pores of the membranes; then, the current rapidly increased owing to the electrodeposition on the surfaces of membranes to form hemispherical caps over the end of each wires [18,21]. Accordingly, the pores can be fully filled with copper wires with hemispherical caps by the termination of electroplating after the rapid current increases. In this experiment, the electroplating of copper wires was conducted for 68 min, resulting in the formation of the PET/Cu hybrid membrane, as shown in Fig. 3(b).

In order to observe the copper wires which grew into the pores of the ion track membranes, PET films must be removed from the copper electrode. Unlike the treatment of the hybrid membranes in an alkaline solution, in which both PET films and copper wires are easily dissolved, only PET films were swelled with partial dissolution and totally removed without the damage of the copper wires when the hybrid membranes were soaked in a 10 M KOH/ethanol (3:7 w/w). Accordingly, the copper wires on the copper electrode can be observed using SEM; then, the geometry of the wires was confirmed to be almost the same as that of the pores as shown in Fig. 3(c).

Although the height and diameter of the wires are in good agreement with the geometry of the membrane pores, the wavelike roughness was observed on the surface of the cylindrical copper wires. Fig. 4 shows the SEM image of the cross-section of the PET ion track membrane, which was obtained by congelation in liquid nitrogen followed by mechanical cutting (Fig. 4). It should be clear that the surface roughness on the cylindrical copper wires results from the roughness of the pore side wall. The most suspicious reason for the surface roughness of the membrane pores is fillers in commercial PET films. Nevertheless, the ion track membranes made of filler free PET films by the same method possessed the pore surface with the same wavelike roughness. Accordingly, the surface roughness of the wires is probably due to heterogeneous morphology consisting of partially crystallized and amorphous regions.

3.2. PET/Cu hybrid membranes with 200 nm copper wires

PET films with 12 μm in thickness were irradiated by $^{129}Xe^{23+}$ion beams with fluxes of 3.0×10^7 ions/cm^2. The irradiated films were etched in 0.2 M NaOH aqueous solution at 60 °C for 10.5 h. As shown in Fig. 5(a), the clear hole patterns with 200 nm in diameter were observed in the SEM image of the surface of the PET ion track membrane.

The copper wires were deposited into the pores with 200 nm in diameter according to the same electroplating method. The electroplating of copper wires was conducted for 32 min to ensure that copper wires were filled in the pores of the membrane. After removing the PET film from the copper electrode in the same mixed solution, the geometry of the copper wires was observed by SEM and was found to be 200 nm in diameter and 12 μm in height, which were in good agreement with the size of the pores as shown in Fig. 5(b). The surface of copper wires with 200 nm in diameter seems to be smooth although the surfaces of 1.9 μm copper wires exhibit wavelike roughness resulting from the roughness of the pore internal wall. This difference is probably because the membrane with 200 nm diameter pores was etched in a milder condition (0.2 M) than that in the membrane with 1.9 μm diameter pores, resulting in

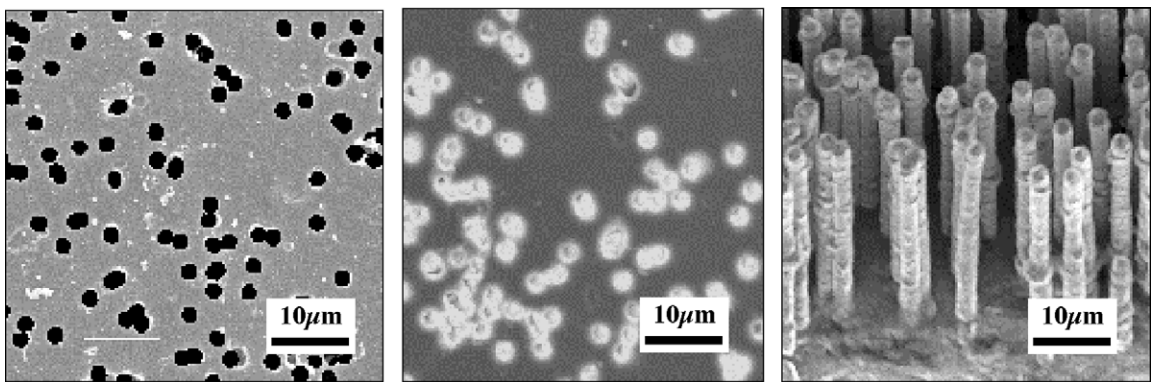

Fig. 3. SEM photographs of (a) the surface of the PET ion track membrane possessing through-holes with 1.9 μm in diameter. (b) The top surface of the hybrid membranes consisting of PET film with cylindrical copper wires. (c) The corresponding copper wires with 36 μm in height and 1.9 μm in diameter on copper electrode after removing the PET film.

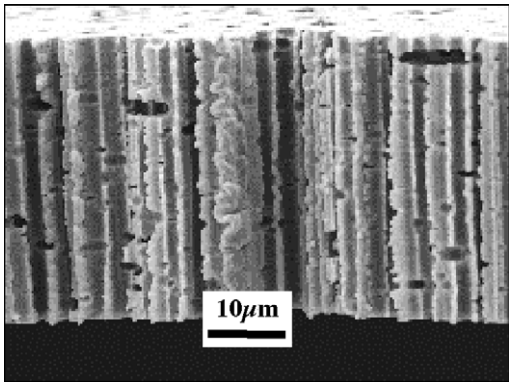

Fig. 4. The SEM image of the cross-section of the PET ion track membranes, which were obtained by congelation in liquid nitrogen followed by mechanical cutting.

smooth surfaces of the pore internal wall. These observation confirms the successful formation of the hybrid membranes consisting of insulating PET film and perpendicularly aligned cylindrical copper wires with high aspect ratio (height/diameter = 50).

3.3. Conductivity measurements

The conductivity of the PET/Cu hybrid membranes consisting of PET with 36 μm in height and 1.9 μm in diameter was evaluated by the measurement of the membrane resistance in the directions perpendicular and parallel to the surfaces by a four terminal resistance method, as shown in Fig. 6. The gold-coated surfaces of the hybrid membranes were set onto a thin gold plate, which was connected to a milliohm-meter; then, the resistances (Ω/cm^2) of the membrane were measured at randomly selected 40 points on the surfaces.

As shown in Fig. 7(a), the PET/Cu membranes exhibited the resistances ranging from 3.6×10^{-7} to 1.2×10^{-6} Ω/cm^2 and the average resistance of $6.3 \pm 3.9 \times 10^{-7}$ Ω/cm^2. The theoretical resistance (Rt, Ω/cm^2) is derived from the

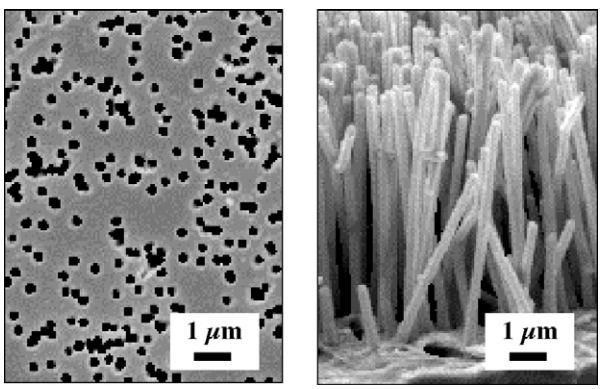

Fig. 5. SEM photographs of (a) the surface of the PET ion track membrane possessing through-holes with 200 nm in diameter. (b) Copper wires with 12 μm in height and 200 nm in diameter on copper electrode after removing the PET film.

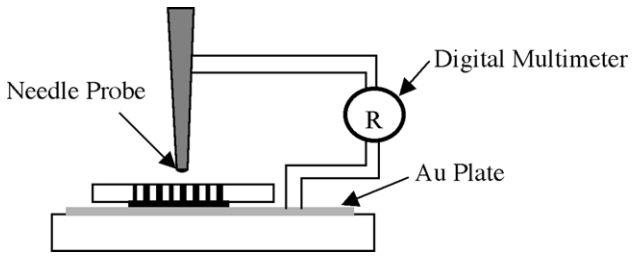

Fig. 6. Schematic illustration for the apparatus for the resistance measurement of hybrid membranes in the direction perpendicular to the surfaces by a four terminal resistance method.

following equations

$$R_t = 1/S = \rho L/(\pi(r/2)^2 F) \quad (1)$$

where ρ is copper resistivity (1.67×10^{-6} Ω cm), L is wire length (3.6×10^{-3} cm), r is cross-sectional diameter of copper wires (1.9×10^{-4} cm), and F is an ion flux (the number of pores = 3.0×10^5 ions/cm^2). The calculated R_t (7.1×10^{-7} Ω/cm^2) is quite good agreement with the average of the measured resistance of the membrane. Contrary to the conductance perpendicular to the surfaces, the conductivity parallel to the membrane surfaces were zero at any points. This result clearly shows that the membranes consisting of PET film and copper wires with 1.9 μm in diameter work as an anisotropically conducting membranes perpendicular to the surfaces.

The resistances of the membrane consisting of copper wires with 200 nm in diameter at randomly selected 40 points on the surfaces were evaluated using the above method. As shown in Fig. 7(b), the membrane showed the resistances perpendicular to the surfaces in the ranges from 1.5×10^{-7} to 1.5×10^{-8} Ω/cm^2 and the average resistance

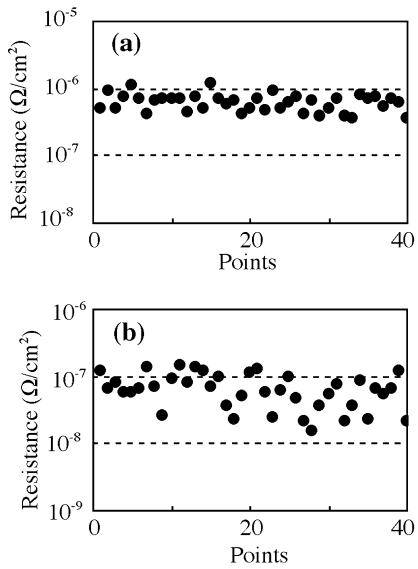

Fig. 7. The resistances of the hybrid membranes consisting of PET film with cylindrical copper wires in the directions perpendicular to the surfaces by a four terminal resistance method. (a) Copper wires with 36 μm in height and 1.9 μm in diameter. (b) Copper wires with 12 μm in height and 200 nm in diameter.

is estimated to be $6.9 \pm 3.7 \times 10^{-7}$. This average resistance of the membrane is about three times higher than the theoretical resistance ($2.1 \times 10^{-7}\ \Omega/cm^2$) estimated using Eq. (1). Such lower conductivity of the PET/Cu hybrid membranes compared with the calculated value is likely to result from the defects in copper wires during the electroplating preparations, influence of the interfaces between copper wires and the pore surfaces of PET, and/or the contact resistances between the needle probe and the top of copper wires. In contrast, as is the case of the membrane consisting of copper wires with 1.9 μm in diameter, the resistance of the membrane parallel to the surfaces were zero at any points. From these results, it is evident that anisotropically conducting membranes possessing copper wires with less than sub-micron in diameter are prepared by electroplating of copper into the cylindrical pores in the ion track membrane made of PET.

4. Conclusion

PET/Cu hybrid membranes consisting of insulating polymer (PET) with 36 and 12 μm in thickness and perpendicularly aligned cylindrical copper wires with 1.9 μm and 200 nm were prepared by electrochemical plating of copper wires into the pores of PET ion track membranes. The PET films could be selectively removed from the copper electrode without the damage of the copper wires; then, the geometry of copper wires was confirmed to be 1.9 μm and 200 nm in diameter, respectively. The copper wires with 1.9 μm in diameter showed the wavelike surface roughness, resulting from the roughness of the pore side wall, whereas the copper wires with 200 nm in diameter showed smooth surfaces. The resistance of the membranes was measured by four terminal resistance method indicating that the hybrid membranes possessed conductivity perpendicular to the membrane surfaces but not parallel to the surfaces. From these results, it is confirmed that anisotropically conducting membranes possessing copper wires of less than sub-micron in diameter can be prepared by electroplating of copper into the cylindrical pores of the PET ion track membranes.

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