Properties and Application Feasibility of an Osmium-Oxygen Thin Film Prepared by DC-Glow-Discharge Deposition from Osmium Tetraoxide

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An osmium-oxygen thin film was prepared by d.c.-glow-discharge deposition from osmium tetraoxide with a filming rate of 1 $\mathrm{nm\,s^{-1}}$. The fundamental properties of the films were investigated. The prepared films had a homogeneous amorphous structure and 10^{-4} Ω cm order of resistivity. Since the transparency of a 20 nm thick film was about 80% for visible light, a transparent conductive film could be obtained on glass or plastic substrates. X-Ray photoelectron spectroscopy measurements showed that the film contained 30 at.% of osmium and 70 at.% of oxygen, which might make the film be easily etched by an oxygen-plasma, or be electrically oxidized. Since the osmium film could be patterned by oxygen-plasma etching or by a lift-off method, which are familiar lithography techniques in the field of semiconductor devices, it is expected to be used as micro-electrode or micro-wiring materials. Low-temperature film preparation also makes it possible to be applied as an X-ray mask material for X-ray lithography.

Osmium is a heavy metal element belonging to the platinum group. It has the third-highest melting point next to tungsten and rhenium (ca. 3000 °C), high conductivity (8×10^{-6} Ω cm), and the highest density (22.6 $\mathrm{g\,cm^{-3}}$) among the metal elements.[1,2] In spite of such unique properties, because of difficulty to prepare a continuous film, the application of osmium has been limited to special fields, for example as an additive to alloys to improve hardness.

Recently, a new filming technique using d.c.-glow-discharge deposition was developed.[3,4] In this method, sublimated osmium tetraoxide gas is introduced into a vacuum chamber having a pair of electrode plates; the gas is decomposed in a d.c.-glow-discharge plasma generated between the electrodes. Osmium cations generated in the plasma are deposited on a substrate held in negative glow region, and a film is formed at room temperature. This method has been used for the pre-treatment of specimens to be observed by an electron microscope, utilizing its homogeneity and excellent covering quality.

We paid much attention to films prepared by this method, because osmium has many attractive characteristics, as mentioned above. A high melting point and high conductivity are very important properties for an electrode, or for a wiring material of semiconductor devices.[5] A low temperature process enables us to prepare films without internal stress, which would make it possible to be used as an X-ray mask material for X-ray lithography.[6,7] To realize such applications, it is necessary to clarify the fundamental properties of the film. In this paper, we report on some analytical results of films prepared by d.c.-glow-discharge deposition from osmium tetraoxide. We also mention the feasibility of patterning, which is an important point for applications to many kinds of devices.

Experimental

Materials. Osmium tetraoxide supplied by Nacalai Tesque Co. was used as received. A potassium bromide single crystal used for TEM sample preparation was supplied by Japan Spectroscopic Co. Positive-type novolac photoresist (Nagase Electronic Chemicals Ltd., NPR-9400) was used for patterning experiments.

Apparatus. A DC-plasma CVD apparatus made by Nippon Laser & Electronics Lab. was used for preparing the thin films. The structure of the apparatus is shown in Fig. 1.[4] Sublimated osmium tetraoxide was introduced into the vacuum chamber and decomposed in the plasma generated between two electrodes. The substrate surface was held at about 1—5 mm above the cathode, i.e. the negative glow region, so that cations were directly deposited on it. The deposition conditions are given in Table 1.

TEM Observation. For a high magnification transmission electron microscope (TEM) observation, a self-supporting film without a substrate is necessary. We prepared such films as follows: A KBr single crystal was cleaved in dry air, and the film was deposited on the cleavage surface by the method described above. After deposition, the KBr crystal was immersed in water, and then the deposited film was removed from the KBr surface and floated on the water surface. By picking the floating film on a copper specimen grid, washing with water, and drying in the air, we obtained a

Table 1. Deposition Condition of the Film

Discharge voltage	1.2 kV
Distance between electrodes	40 mm
Discharge current	40—60 $\mu\mathrm{A\,cm^{-2}}$
Gas pressure	10 Pa

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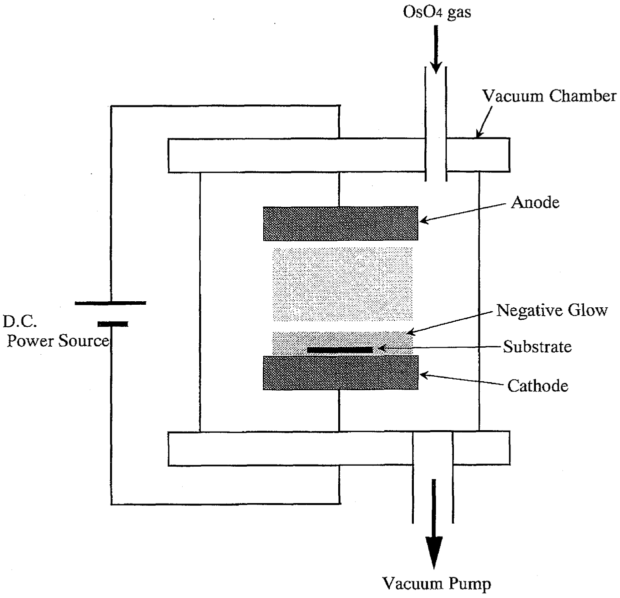

Fig. 1. Schematic picture of the deposition apparatus.

self-supporting sample.

We also prepared a sample for a cross-section observation. In this case, the film was deposited onto an epoxy-resin block. The deposited film was covered with another epoxy resin for protection, and sliced by a microtome (Reichert-Nissei, Ultracut S) to make a 60 nm ultra-thin cross-section film. TEM used was Hitachi, H-7100 type one.

Measurements. The light transmittance was measured by a UV/vis Spectrophotometer (Japan Spectroscopic Co, Ubest-50). An X-ray photoelectron spectroscopy (XPS) measurement was performed by a Shimadzu-Kratos XSAM-800.

The electrochemical properties were measured by a function generator (Hokuto Denko, HB-104) and a potentiostat (Hokuto Denko, HA-301). The film was deposited onto a platinum plate for a working electrode. A bared platinum plate and a saturated calomel electrode were used as a counter electrode and a reference electrode, respectively. A 1 M-Na_2SO_4 solution was used as an electrolyte (1 M = 1 mol dm^{-3}).

Patterning. Patterning of the film was performed by two methods: lift-off method and oxygen-plasma etching (Fig. 2). The details are as follows :

Lift-off Method:[8] A positive type photoresist was coated on a glass substrate and irradiated by a Xe lamp through a photomask by a Mask Aligner (Mikasa Co., M-2L type). The substrate was then immersed in a KOH solution to dissolve the part of the photoresist which had been exposed to light. After deposition of the film on a patterned photoresist, followed by whole exposure to light, the substrate was immersed in the KOH solution again. In the KOH solution, the remaining photoresist was dissolved together with the deposited film on it, leaving a patterned film. The obtained pattern was a negative one compared with the original photomask. Using a negative-type photoresist, we can obtain a positive pattern as well.

Oxygen-Plasma Etching : A film deposited from osmium tetraoxide by dc-glow discharge can be etched by an oxygen plasma (details are mentioned later). After a film deposited on a glass substrate was covered with a copper mesh (150 mesh), the sample was held 5 mm above the cathode of the CVD apparatus described in Fig. 1. About 10 Pa of oxygen gas was introduced into the chamber instead of osmium tetraoxide, and 1.2 kV voltage was added between the electrodes to generate an oxygen plasma for several minutes. The part of the film exposed to the oxygen plasma was removed, and a positive pattern was left on the glass substrate.

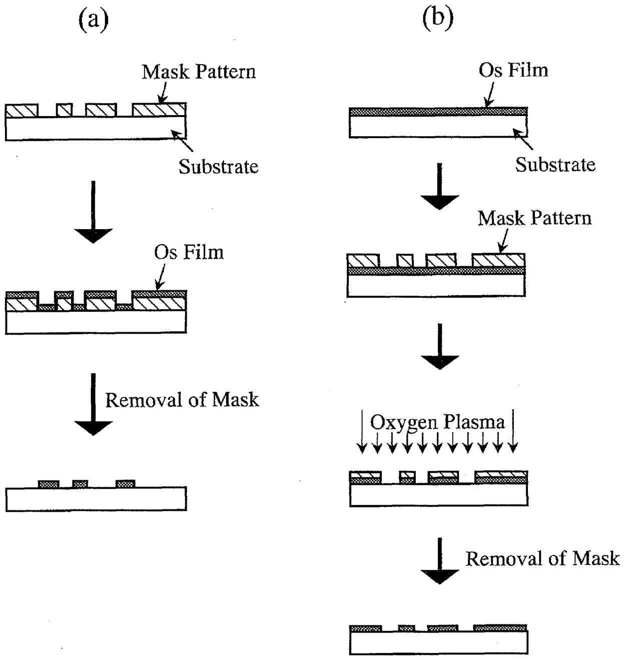

Fig. 2. Patterning processes of the films.
(a) Lift-off method. (b) Oxygen plasma etching.

Results and Discussion

Film Preparation. An osmium-containing film can be prepared according to the process described in the experimental section. Since the deposition rate is about 1 nm s^{-1} under the condition shown in Table 1, we can obtain several nm thick sample for a few seconds. Both higher and lower pressure of osmium tetraoxide gas make the discharge unstable. Moreover, deposition with a higher pressure brings about rough surface, perhaps due to the generation of particles in the gas phase. During deposition, the temperature of a substrate does not rise very much; for example, 1-min deposition causes only about a 5 degree rise in the temperature. It is therefore possible to deposit on thermoplastic substrates or on biological specimens.[4] That is why this method is used for conductive coating of SEM specimens, which are difficult to be pre-treated by other techniques, such as sputtering.

We succeeded in depositing a 30 nm thick film on a 10 μm thick poly(vinyl chloride) film without any deformation in the substrate, indicating that little heat damage was induced in the substrate. This fact would have great advantage in applications to X-ray mask material for X-ray lithography in which deformation of the mask brings about a serious problem in the accuracy of the lithography.

TEM Observation. We observed the morphology of the films by high-magnification TEM. Figure 3 shows a TEM image from the perpendicular direction to the film surface. The film is perfectly homogeneous without any obvious structure. Electron-beam diffraction shows a diffusing hollow pattern, indicating that the film is amorphous.

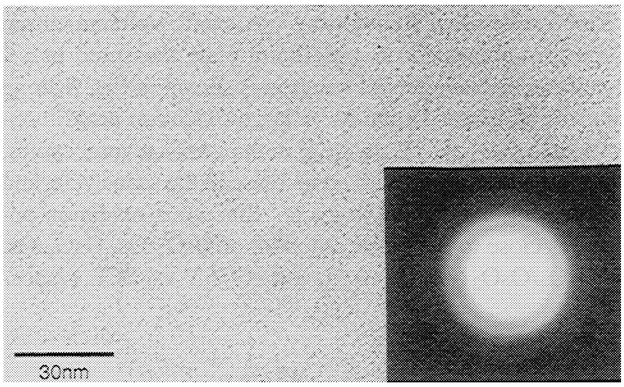

Fig. 3. High magnification TEM image of the film. The sample is self-supporting without any substrate. Electron beam diffraction pattern of this sample is shown at the right side of the picture.

A cross-section view is shown in Fig. 4. The observed structure is homogeneous amorphous, which is the same as the top-view image shown in Fig. 3. Moreover, it has been revealed that the homogeneity is maintained along the depth direction.

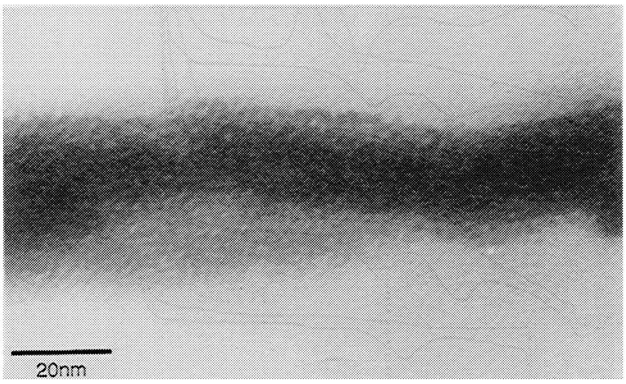

Fig. 4. Cross section TEM image of the film. The film is sandwiched between epoxy resin for protection.

XPS Spectrum. The XPS spectrum was measured for a 10 nm thick sample. Figure 5 shows the spectrum along with the signal assignment. The signals assigned to oxygen (O1s and Auger KLL) are observed along with those assigned to osmium. The shape of the spectrum did not change while the sample was being etched by Ar ion, until the signal of the substrate (SiO_2) was detected. This fact indicates that the existence of oxygen in the film can not be attributed to surface oxidation by air, but that the oxygen is enclosed during the deposition process from osmium tetraoxide.

Since we could not prepare a standard sample of osmium oxide for quantitative analysis, we roughly estimated the ratio of osmium and oxygen in the film from the XPS peak area and relative sensitivity for these elements. Since the obtained ratio of osmium and oxygen is about 30 : 70, we can describe the component of the film as being $OsO_{2.3}$. Including such an amount of oxygen would be one of the reasons why the resistivity of this film is rather higher than that of bulk osmium, as mentioned later.

Conductivity. The conductivity was measured by a patterned sample on a glass substrate (see Fig. 6) prepared by using a stainless-steel mask during deposition. The voltage between terminal A and terminal B was measured by a high-impedance voltmeter while a current was flowing from terminal C to terminal D. The specific resistivity (σ), of the film is given by

$$\sigma = w \cdot d \cdot V / L \cdot I, \qquad (1)$$

where V is the voltage between A and B, I the current from C to D, L the path length, w the path width, and d the thickness of the film. Using this equation, we obtained a resistivity of 2—5×10^{-4} Ω cm for a 10 nm thick sample.

We also used a conventional 4-probe method,[9] and ob-

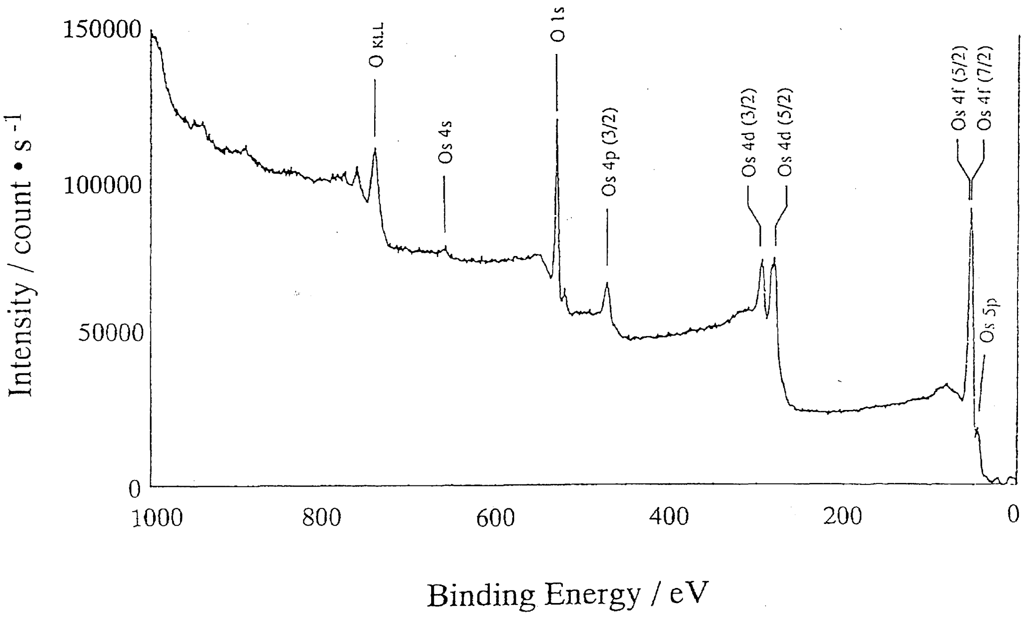

Fig. 5. XPS spectrum of the film. The sample was etched by argon ion for a few seconds to remove contamination on the surface.

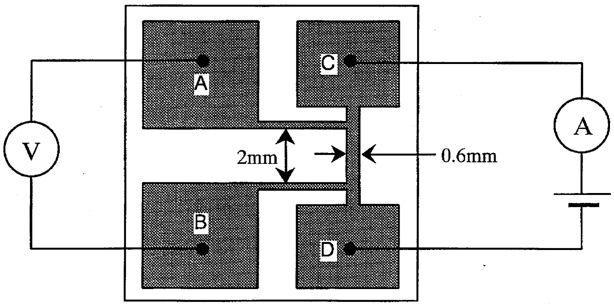

Fig. 6. Resistivity measurement of the film. The patterned film was prepared on a glass substrate.

tained a sheet resistivity of 400 Ω. Since the thickness of the film was 10 nm, a value of 4×10^{-4} $\Omega\,\mathrm{cm}$ was obtained as the specific resistivity, which almost corresponded to the value derived from Eq. 1.

These resistivity values are 50-times higher than the resistivity of bulk osmium metal (8×10^{-6} $\Omega\,\mathrm{cm}$), which would be due to the oxygen contained in the film, as shown by the XPS measurement. Besides, the thin-film resistivity is generally higher than the bulk resistivity. Supposing that the mean free path of an electron is 10—100 nm, and that the specularity parameter of the film is 0—1, we obtain 1—5 as the ratio of the thin-film (10 nm) resistivity and bulk resistivity, according to Sondheimer's theory. Therefore, a few percent of the resistivity rising would be ascribed to the thin-film effect. A reduction of the resistivity by reducing the oxygen content is required for applications to the electrode material or wiring material.

Transparency. The light-transmittance spectrum of a 20 nm thick film deposited on a glass substrate is shown in Fig. 7. As shown in the figure, the transmittance is 70—80% for entire the visible light region, corresponding to an absorbance of 50000 cm^{-1}. The transmittance value is rather high compared with that of ordinary metal thin films (10—40% for 20 nm thick film), which is perhaps due to the oxygen contained in the film. Since no specific absorption is observed in visible light, it is the so-called neutral density.

Electrochemical Behavior. A cyclic voltammogram of the film deposited on a platinum plate measured in a 1 M-sodium sulfate aqueous solution is shown in Fig. 8 along with that of bared platinum. A large oxidation peak is observed at +0.4—+0.7V vs. SCE in the initial several cycles, becoming small along with an increase in the scan cycle, and disappearing after the 20th cycle. Since this oxidation potential is close to the redox potential of OsO_2/Os, OsO_4/Os, and OsO_4/OsO_2 (+0.45, +0.61, and +0.76 V vs. SCE, respec-

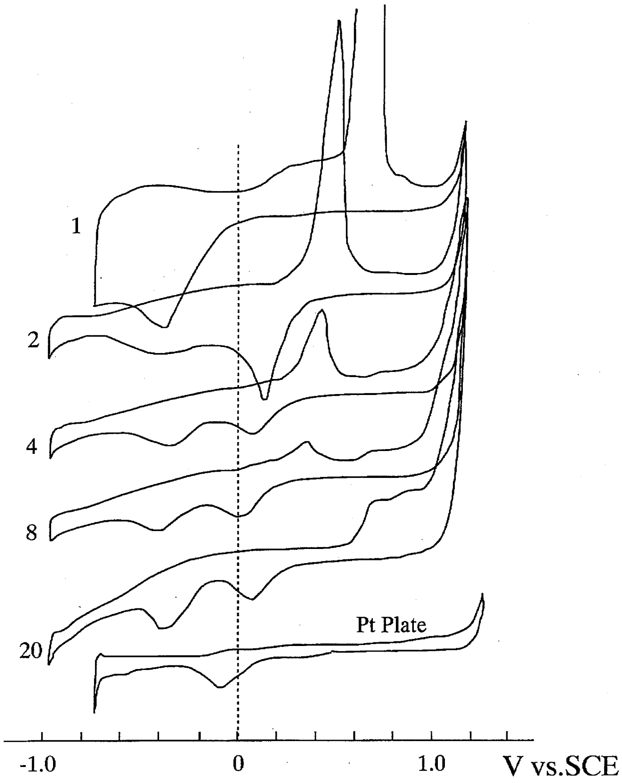

Fig. 8. Cyclic voltammograms of the film deposited on a platinum plate. Numeral at the left side of each voltammogram is a cycle number. The bottom one is the voltammogram of the bared platinum plate.

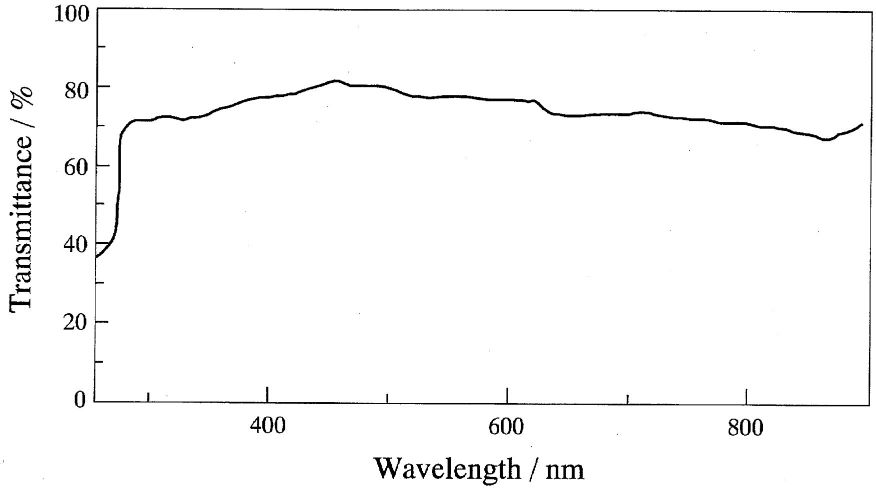

Fig. 7. Light transmittance spectrum of the film deposited on a glass substrate. The thickness of the film is 20 nm.

tively), the film is thought to be electrically oxidized and to dissolve into the electrolyte solution around this potential. After the 20th cycle, we can obtain a stable voltammogram having an oxidation peak at +0.7—+0.8 V vs. SCE and two reduction peaks at +0.1 and −0.4 V vs. SCE. We suppose that these peaks correspond to the oxidation and reduction of osmium contacting to platinum. The interaction between osmium and platinum may make the oxidation potential slightly higher and inhibit osmium to dissolve into the solution.

The oxidation and reduction peaks at each end of the voltammogram correspond to the oxidation and reduction of water. Compared to a bared platinum electrode, both peaks shift by about 0.2 V to a negative potential. This means that the deposited film has a lower overvoltage of oxygen generation and a rather higher overvoltage of hydrogen generation than bared platinum.

Heat Resistivity. The deposited film transfered to a TEM specimen grid was heated in air for 2 h to test the heat resistivity of the film. Figure 9 shows TEM images of the film after the heat treatment. Although the heat treatment at 200 °C in air had no serious influence (Fig. 9(a)), a 300 °C treatment caused a drastic change in the structure of the film (Fig. 9(b)). In Fig. 9(b), many particles having diameters on the order of 100 nm can be observed. These particles have a hexagonal habit, and were revealed to be single crystals of

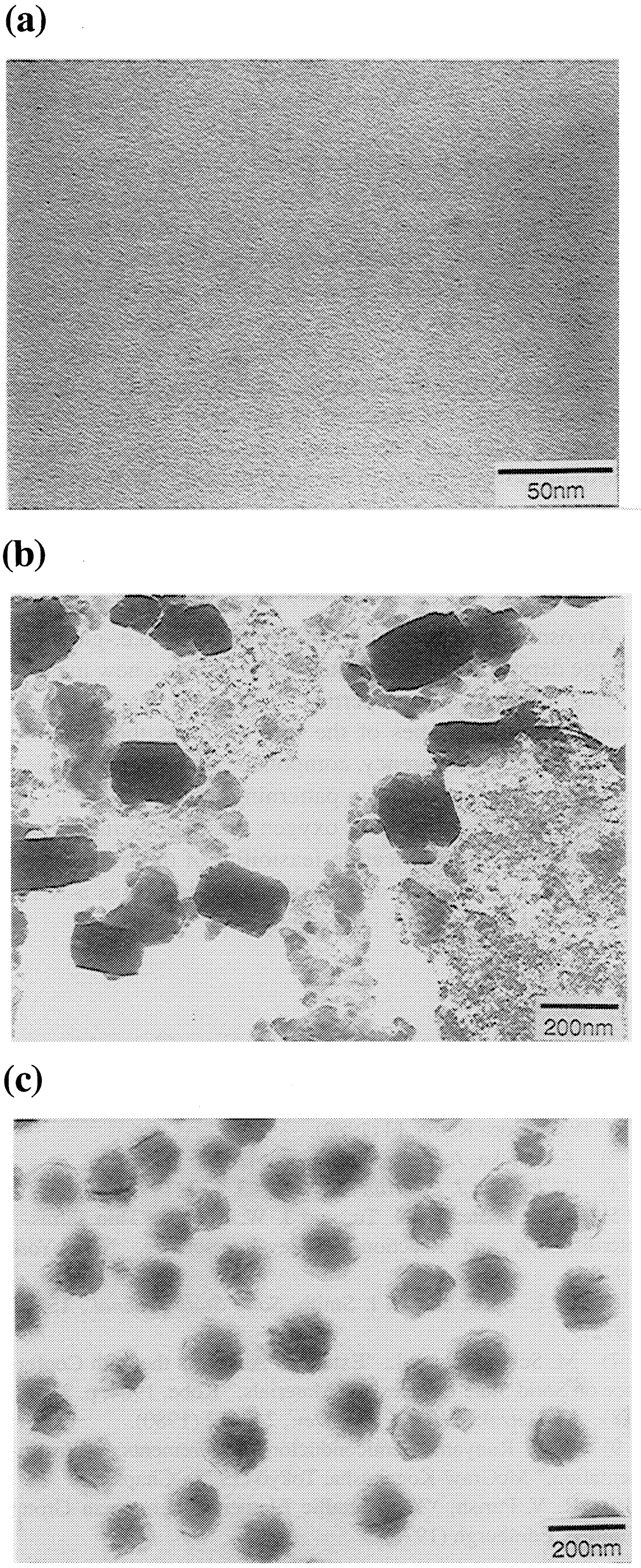

Fig. 9. TEM images of the films after heat treatment (a) at 200 °C in air, (b) at 300 °C in air, and (c) at 300 °C in vacuum for 2 h.

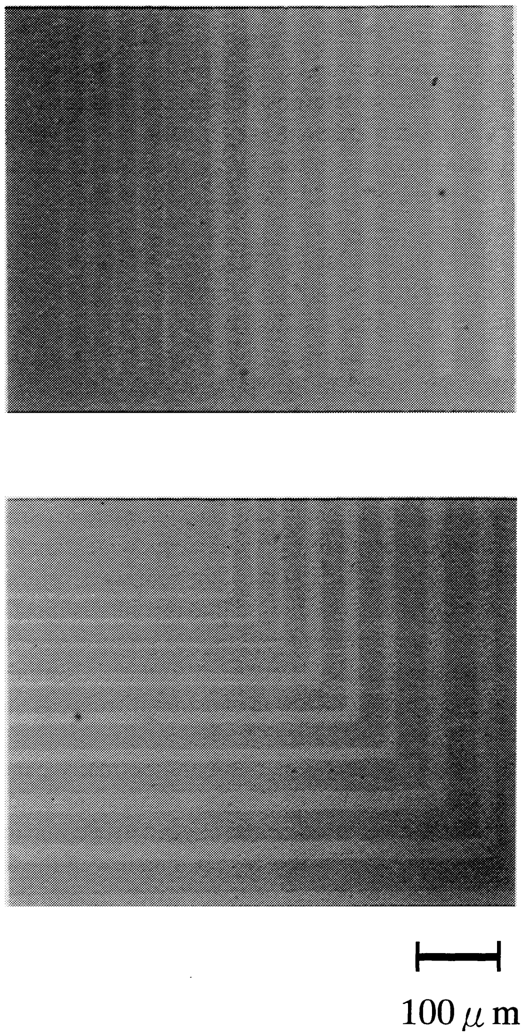

Fig. 10. Patterned film by lift-off method. Gray area corresponds to the remaining film.

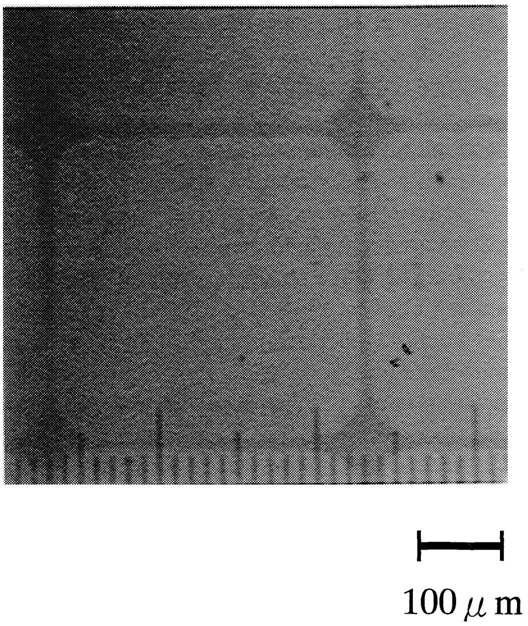

Fig. 11. Patterned film by oxygen plasma etching. Gray lines correspond to the remaining film.

metal osmium by electron-beam diffraction. Besides forming particles, the film structure is broken, and nuclei which are smaller than 10 nm are being generated. It is supposed that this nucleation occurs in the film at first, then the nucleus grows to be a hexagonal crystal particle by gathering osmium around it.

The heat resistivity of this film is much higher than that of osmium tetraoxide (boiling point, 131 °C), although the vapor pressures of other osmium oxides (OsO, Os_2O_3, OsO_2) are not clear. If such oxides evaporate at 300 °C, leaving metal osmium, the metallization and crystallization of the film should be accelerated by evacuation.

Nevertheless, a 300 °C treatment for 2 h in a vacuum (about 0.1 Pa) causes different result, as shown in Fig. 9(c) compared with a treatment in air. The aggregate of osmium is formed, but not completely crystallized, suggesting that the metallization and crystallization of the film are decelerated by evacuation, instead. Considering that osmium is most easily oxidized by oxygen among the platinum-group elements, and that osmium oxide is easily reduced to metal osmium, it is supposed that the crystallization of osmium proceeds through the following process.

At first, nuclei of metal osmium are thermally generated by the reduction of oxides in the film. Next, some oxides are further oxidized by environmental oxygen to become oxides, the vapor pressure of which is higher than that of the former one. This further oxidized osmium oxide evaporates and diffuses to the nucleus. On the nucleus of metal osmium, the osmium oxide vapor is reduced to a metal, and the nucleus grows to be a larger crystal particle. In a vacuum, such a process is not completely carried out, because of the lack of environmental oxygen.

Patterning. The capability of patterning is an important point to extend the application feasibility. At first, we used a lift-off method, which could be applied to almost all filming techniques and materials. The film patterned by the lift-off method is shown in Fig. 10. The narrowest line of the used photomask is 5 μm, and the removed line of the same width is formed in the film.

For patterning by oxygen-plasma etching, we performed just a primitive experiment using a copper mesh as a mask. The resulting pattern is shown in Fig. 11. Since the copper mask and the film did not perfectly contact each other, the plasma entered into the backside of the mask to etch the film under the mask as well as the exposed area. Therefore, the line width of the sample remaining on the substrate is narrower than that of the mask. If a photoresist pattern is used as a mask, the obtained film pattern should perfectly reflect the mask pattern. Being etched by oxygen plasma is one of the advantageous characteristics of this film compared with other metals, which require a special gas containing halogen for etching.[10)]

Conclusion

An osmium-oxygen thin film prepared by d.c.-glow discharge deposition from osmium tetraoxide is a new material having many unique properties. This study clarified many fundamental properties of the film, such as the structure, conductivity, transparency, component, and electrochemical behavior. We succeeded in patterning the film by a lift-off method or by conventional oxygen plasma etching, which would extend the application feasibility of the film, for example, as an electrode or a wiring material, or as a X-ray mask material for X-ray lithography.

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