Plasma Chemistry and Plasma Processing, Vol. 7, No. 2, 1987

Gold Particles Containing Plasma-Polymerized Styrene as an X-Ray Absorber

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Received November 7, 1985; revised October 20, 1986

Gold particles containing plasma-polymerized styrene film were formed simultaneously by plasma polymerization and evaporation using an inductively coupled argon gas flow type reactor. Gold was used as the evaporated metal and styrene as the monomer. The plasma etching characteristics of the film were evaluated by O_2 and CO_2 plasmas using a reactor with parallel-plate electrodes. A structure of lines and spaces of 4 μm width was successfully fabricated in the film on Si wafer by CO_2 plasma etching through a mask pattern of plasma-polymerized resist. A self-developed pattern was obtained through the X-ray mask with polyimide substrate by synchrotron radiation. The molecular structure and atomic composition of the film were investigated by ESCA and TEM.

KEY WORDS: X-ray mask; X-ray absorber; vacuum lithography; plasma polymerization; plasma etching.

1. INTRODUCTION

X-ray lithography is expected to be a promising technology for fabrication of VLSI devices with submicron size structure. In the development of X-ray lithography, many reports have been published since Smith *et al.* carried out the first experiment.[1] For the practical application of X-ray lithography, X-ray mask fabrication is considered to be one of the most important technologies.[2,3] The mask consists of an X-ray-transparent substrate and an X-ray absorbing microstructure formed on the substrate. The X-ray absorbing characteristics depend on the X-ray wavelength. Gold is a well-known material as an X-ray absorber for the X-ray mask because it is one of the fastest X-ray absorbers in a wide range of X-ray wavelengths. Gold is also the most inert material in a chemical process, but very complex

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0272-4324/87/0600-0155$05.00/0

processes such as ion sputtering,[4] electroplating,[5] and lift-off are needed to fabricate the fine patterns on a thick gold film for X-ray mask fabrication.

In this paper, a film consisting of a mixture of gold and polymer was formed as an X-ray absorbing material in order to increase the reliability and efficiency of X-ray mask fabricating processes.

Kay *et al.* have reported on gold containing plasma-polymerized fluorocarbon film deposited using a capacitively coupled r.f. diode type discharge system where the volume of gold in the polymer matrix could be controlled over a wide range.[6] Using this technique, gold foil is placed on the cathode and sputtered in the fluorocarbon plasma. The sputtered gold and polymer are simultaneously deposited on the counterelectrode where the substrate is mounted.

A different deposition technique combining gold evaporation with plasma polymerization of styrene was developed for the formation of the film. The film containing gold particles and carbon atoms was etched successfully by CO_2 or O_2 plasma. The X-ray mask pattern could be fabricated on the film by totally dry electron beam lithography.[7] The molecular structure and the composition of the film are investigated by ESCA and TEM.

2. EXPERIMENTAL

A schematic diagram of the apparatus is shown in Fig. 1, which combines two systems of a carrier gas flow type reactor for plasma polymerization and an apparatus for metal evaporation. First, the apparatus was evacuated by a diffusion pump down to a pressure of 5.3 mPa. Argon (Ar) as a carrier gas was introduced into the discharge tube, and the discharged was maintained by means of an external coil at a pressure of 0.2 Pa, a frequency of 13.56 MHz, and a power level of 10 W. Monomer gas of styrene was introduced into the downstream section of the discharge at a pressure of 0.6 Pa. Finally, the total pressure was kept at 0.9 Pa by controlling the main valve on the evacuation side. The monomer and Ar flow rates were measured by a flow meter and kept constant during the plasma polymerization by regulating the needle valves. When the polymerization of styrene started, gold (Au) was evaporated simultaneously by heating a tungsten boat which contained Au. A Si wafer and NaCl crystal placed further downstream of the discharge were used as substrate, and the substrate holder was cooled by liquid N_2.

Plasma etching of the film was performed using a sputtering machine with parallel-plate electrodes whose diameter was 100 mm. The film was set on the upper side of the electrode, which was cooled by water flow. The etched depth was measured by using a Tally Step. A structure of lines and

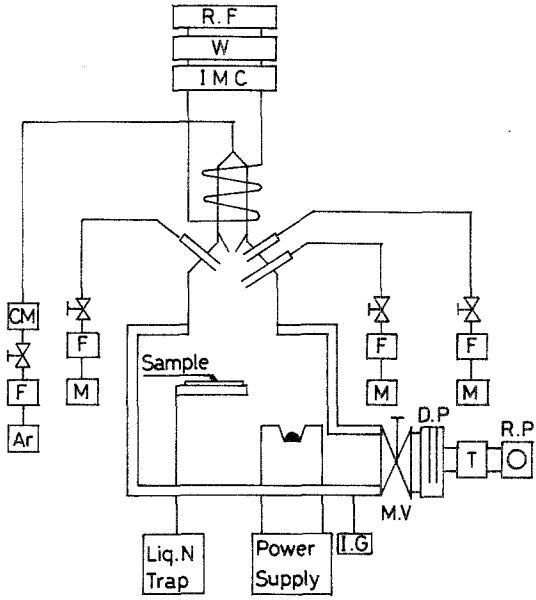


Fig. 1. Schematic diagram of the experimental apparatus. F: flow meter; M: monomer; Ar: argon; CM: capacitance manometer; IMC: impedance matching circuit; W: wattmeter; R. F.: R. F. generator; I.G.: ion gage; M. V: main value; D. P: diffusion; T: trap; R. P: rotally pump.

spaces of 4 μm width was engraved onto the film by using electron beam vacuum lithography.[7]

The resulting films were investigated by TEM, SEM, EPMA, and ESCA.

3. RESULTS AND DISCUSSION

3.1. Film Characterization

In the system, the film was prepared by simultaneous deposition of Au and polymer. When the depositions were performed individually, Au could be deposited successfully on the substrate at a lower pressure than 13.3 Pa. Under these conditions, the deposition rate of the plasma-polymerized styrene (PPstyrene) film was less than 100 Å/min. Therefore, the experimental sample was formed at a gas pressure of 0.9 Pa, and Au was incorporated uniformly throughout a thick film (greater than 0.5 μm thickness).

According to the ESCA spectra, the surface of the samples was composed of H, C, O, and Au atoms. The typical C_{1s}, Au_{4f}, and O_{1s} core level spectra are shown in Fig. 2. The C_{1s} peak was obtained at a binding energy of 285.0 eV, attributed to the hydrocarbon structure. When the C_{1s} spectrum

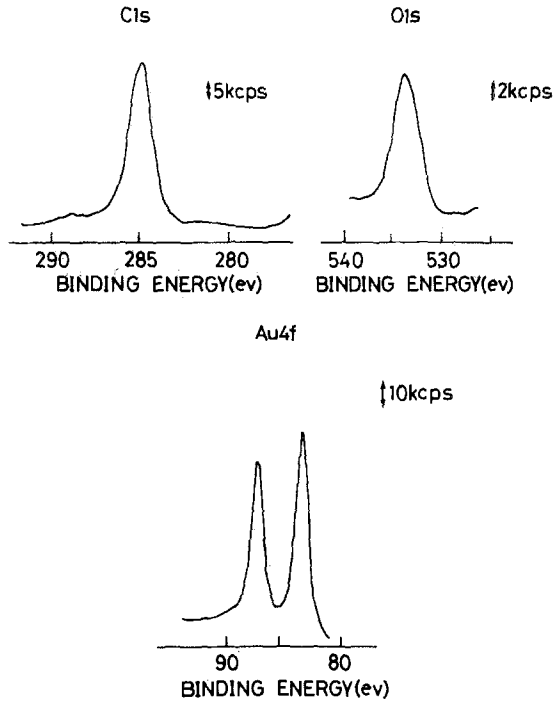


Fig. 2. ESCA spectra of Au_{4f}, C_{1s}, and and O_{1s} core level.

was compared with the spectrum of conventional polystyrene, the features of the spectrum were almost the same but the shake-up peak around the binding energy of 292.0 eV, owing to the π-π^+ transition of the benzene group, could be observed for the plasma-polymerized styrene.[8] This indicates that a large part of the benzene structure in the styrene monomer is destroyed during deposition.

Au_{4f} peaks at binding energies of 82.4 and 86.1 eV were observed. The peak position of Au coincided precisely with that of metallic Au for all of the samples, as expected from its chemical inertness. Oxygen gas was not introduced into the reactor, but an O_{1s} peak centered at 535 eV was observed. This oxygen peak was attributed to oxygen reacting with the residual free radicals in the film after exposure to air, and/or oxygen originating from the reacted air during the deposition.

Quantitative analysis of the resulting film was performed by calculating the integrated intensity of ESCA for each element derived from the core level relative to the total C_{1s} signal, correcting it with respect to the different photoionization cross sections, and relating it to the bulk composition derived from EPMA.

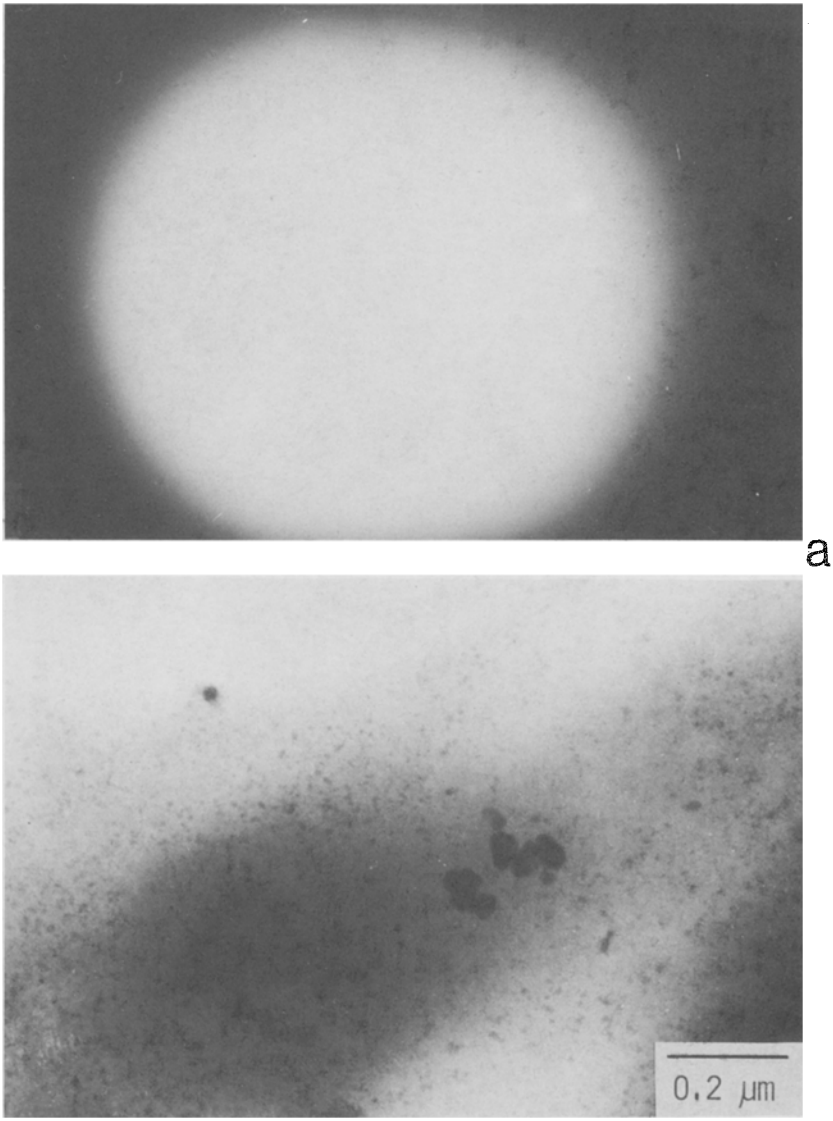
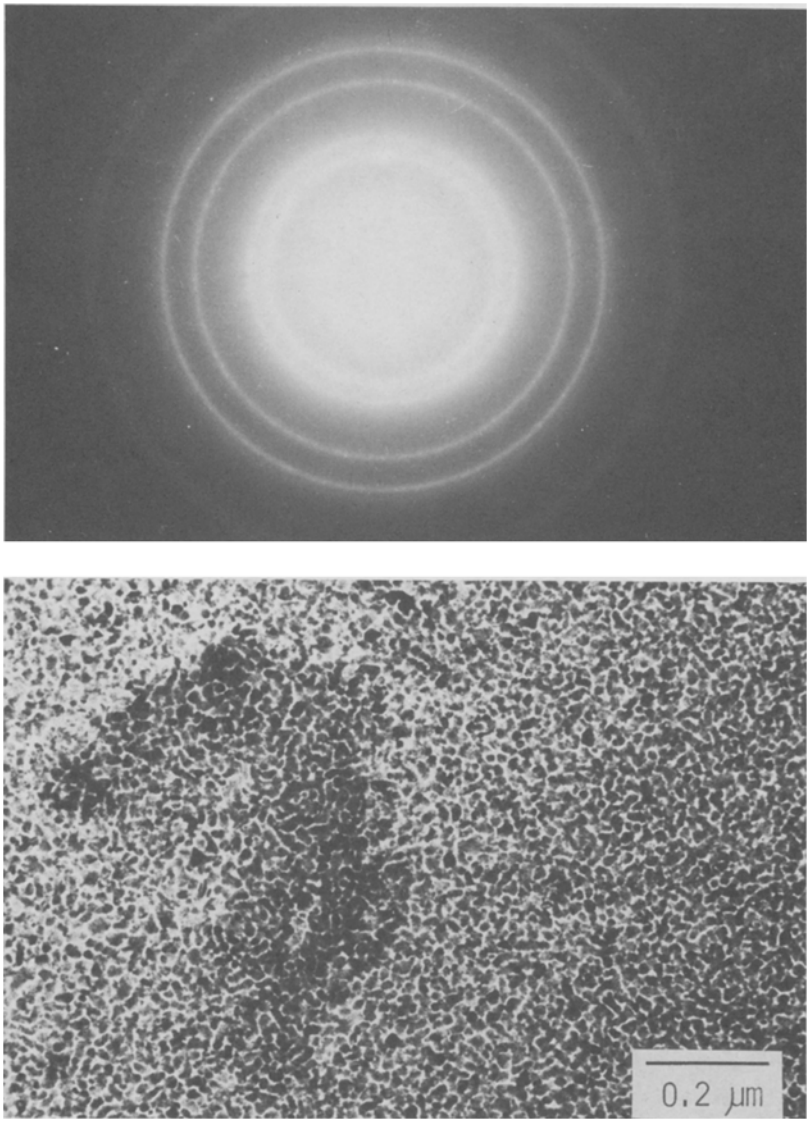


Fig. 3. TEM micrographs and diffraction patterns. (a) Styrene; (b) $Au_{50}C_{50}$; (c) Au.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0.2 μm

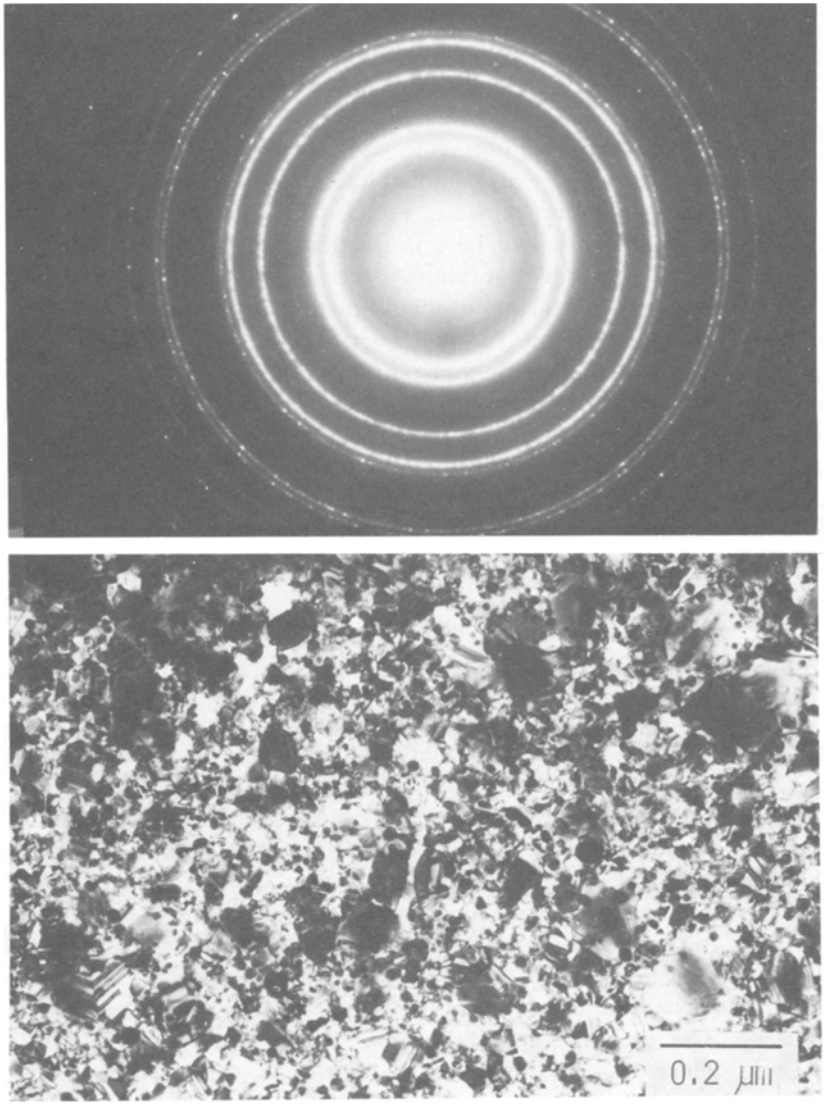

Fig. 3. Continued.

The atomic concentration of Au in the film was controlled by the heating current of the tungsten boat in the experiment. The film of 0.7 μm thickness, whose Au/C atomic ratio is 1 and which is denoted $Au_{50}C_{50}$ here and below, was formed at a gas pressure of 0.9 Pa, a heating current of the tungsten boat of 50 A, and a deposition time of 60 min.

Depositions of Au and PPstyrene were carried out individually in Ar plasma under the same conditions as those for $Au_{50}C_{50}$. The films of Au, PPstyrene, and $Au_{50}C_{50}$ were also studied by TEM. TEM micrographs and their diffraction patterns are shown in Fig. 3. The TEM micrograph of the PPstyrene showed smooth and halo diffraction patterns, whereas it was assumed that PPstyrene had amorphous structure and that the surface was smooth. For Au, the typical rings of the diffraction patterns were observed, which were attributed to a polycrystalline structure.

For $Au_{50}C_{50}$, a halo diffraction pattern containing many rings was observed. This indicates that Au particles in many small crystal structures were dispersed homogeneously in the amorphous polymer matrix. It was confirmed from TEM micrographs that the grain size of Au in $Au_{50}C_{50}$ film ranged from 80 to 200 Å, which was smaller than 300–1200 Å for Au particles formed in Ar plasma. Therefore, it is expected that the existence of organic vapor prevented the growth of large Au particles.

3.2. Plasma Etching Characteristics

Plasma etching of the film was performed at a pressure of 0.53 Pa, a frequency of 13.56 MHz, and a discharge power density of 0.6 W/cm^2. O_2 and CO_2 were used as the etching gas. The etched depths of Au, PPstyrene, and $Au_{50}C_{50}$ film are plotted against the plasma etching duration as shown in Fig. 4 along with a plasma-polymerized hexafluorobutylmethacrylate (PP6FBMA) resist.

The etching rate of Au for O_2 plasma was only 50 Å/min. The etching rate of PPstyrene for O_2 plasma was 1470 Å/min, which was almost 30 times that of Au. For $Au_{50}C_{50}$ film, the etching depth increased linearly as a function of the etching duration, and the whole film was etched off completely. The etching rate of $Au_{50}C_{50}$ was estimated to be about 600 Å/min, which was 12 times that of Au. $Au_{50}C_{50}$ film could also be etched by CO_2 plasma in the same manner as O_2 plasma, but the etching rate by CO_2 plasma was about 400 Å/min, which was lower than that of O_2 plasma.

There was a large difference in the etching rate of PP6FBMA resist between CO_2 and O_2 plasma etching. The etching rate of PP6FBMA for O_2 plasma was 4.4 times higher than that for CO_2 plasma.

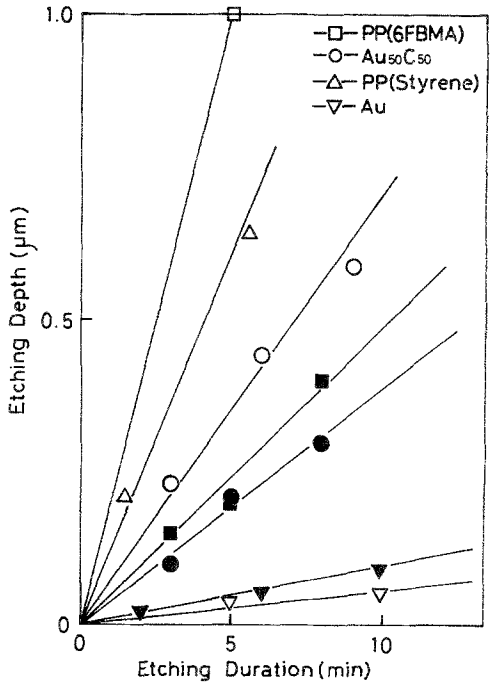

Fig. 4. Dependence of etching depth on the exposure dose. Open and closed symbols represent the etching characteristics of films for O_2 plasma and CO_2, respectively.

From the etching rate of $Au_{50}C_{50}$, it was estimated that the Au in $Au_{50}C_{50}$ film was etched off 6 times as fast as that in Au film. Such a high etching rate of Au in $Au_{50}C_{50}$ film is attributed to the smaller crystallized Au particles dispersed in the polymer matrix, which were easily etched off in the form of volatile compounds such as Au carbonyl or Au oxide in O_2 and CO_2 plasmas. However, more detailed study is necessary to elucidate the etching mechanism.

3.3. Patterned Structure Fabrication on $Au_{50}C_{50}$ Film

In order to use the Au containing plasma-polymerized styrene film as an X-ray absorbing material for an X-ray mask, the patterned structure fabrication must be demonstrated by a practical lithography process. In this experiment, an electron beam vacuum lithography process, as shown in Fig. 5, was applied to the film.

The film of $Au_{50}C_{50}$ was adopted for the fabrication. As a resist, a PP6FBMA resist was deposited on $Au_{50}C_{50}$ at an Ar pressure of 93 Pa, an

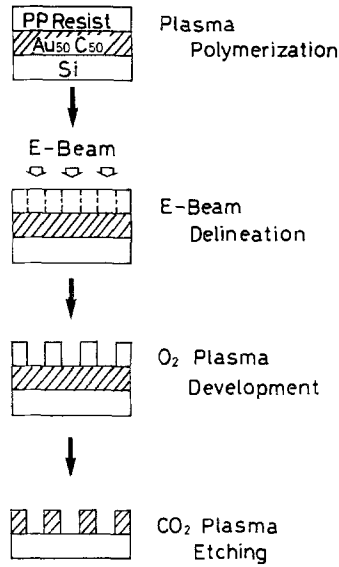

Fig. 5. Pattern fabrication processes with electron beam vacuum lithography.

Ar flow rate of 60 cm^3/min, a monomer flow rate of a few cm^3/min, and a discharge power level of 10 W, by using an inductively coupled flow type reactor.[9] The thickness of the PPMMA resist was 2.6 μm.

The electron beam-exposed part of the PP6FBMA resist was completely developed on the surface of the $Au_{50}C_{50}$ at a dose of 500$\mu C/cm^2$ by O_2

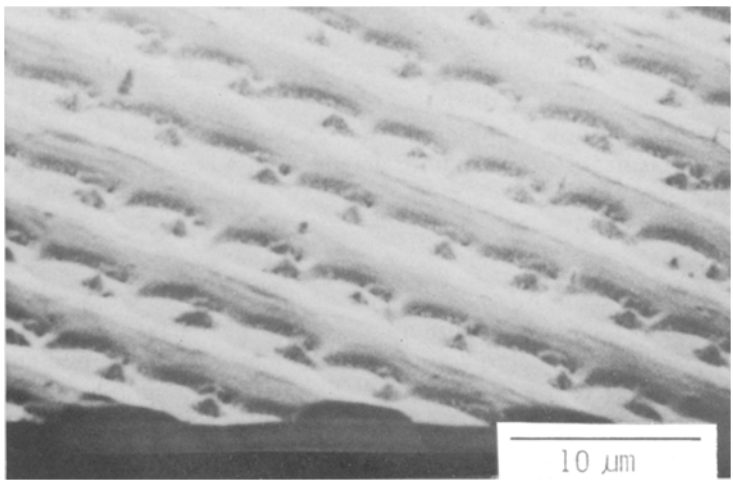

Fig. 6. SEM photograph of fabricated patterns.

plasma etching for a discharge duration of 8 min, and the residual film thickness on the unexposed part of the resist was about 1 μm. As shown in Fig. 4, it is effective to use CO_2 plasma for etching $Au_{50}C_{50}$ film because the ratio of etching rates between $Au_{50}C_{50}$ and the resist using CO_2 plasma was twice that using O_2 plasma, where the residual thickness of the developed resist was sufficient to serve as a mask layer for etching $Au_{50}C_{50}$ film.

The X-ray mask pattern was replicated precisely in $Au_{50}C_{50}$ film through the developed window on the PP6FBMA resist by CO_2 plasma. A SEM photograph of the fabricated structure is shown in Fig. 6. This figure shows that the test X-ray mask pattern of lines and spaces of 4 μm width could be successfully fabricated on the $Au_{50}C_{50}$ film by CO_2 plasma etching in electron beam vacuum lithography. The microvilli between the 4 μm-beam spots were observed to remain in the open areas of the mask patterns. The microvilli were caused by the nonuniformity of the electron density in the beam spot.

3.4. Evaluation as an X-Ray Mask

In order to confirm the possibility of using the gold containing plasma-polymerized film as an X-ray absorber, the mask pattern was actually transferred to the conventional resist. The X-ray mask was fabricated as follows. The gold containing plasma-polymerized styrene film was formed at a thickness of 0.5 μm on a polyimide substrate which in turn was formed at a thickness of 5 μm on Si wafer by a conventional method.[10]

The pattern of 5-μm lines and spaces was fabricated on the X-ray absorber by conventional photolithography.[11] Then the Si wafer was back-etched by a solvent.[12]

For the experiment, conventional PMMA resist (Tokyo-Oka OEBR-1000) was formed on Si wafer. As an X-ray source, an electron storage ring from the Institute for Molecular Science, Okazaki, was used. Through the X-ray mask, the resist was irradiated by synchrotron radiation (RS) for 120 min at a beam energy of 750 MeV and a beam current of 30 mA. The self-developed pattern was successfully developed in the resist, as shown in Fig. 7.

4. CONCLUSION

A plasma-polymerized styrene film was deposited simultaneously with evaporation of gold. A film containing gold as high as 50% atomic ratio was formed that could be etched using only simple O_2 and CO_2 reactive ion etchings at a higher etching rate than that of pure gold film. Furthermore,

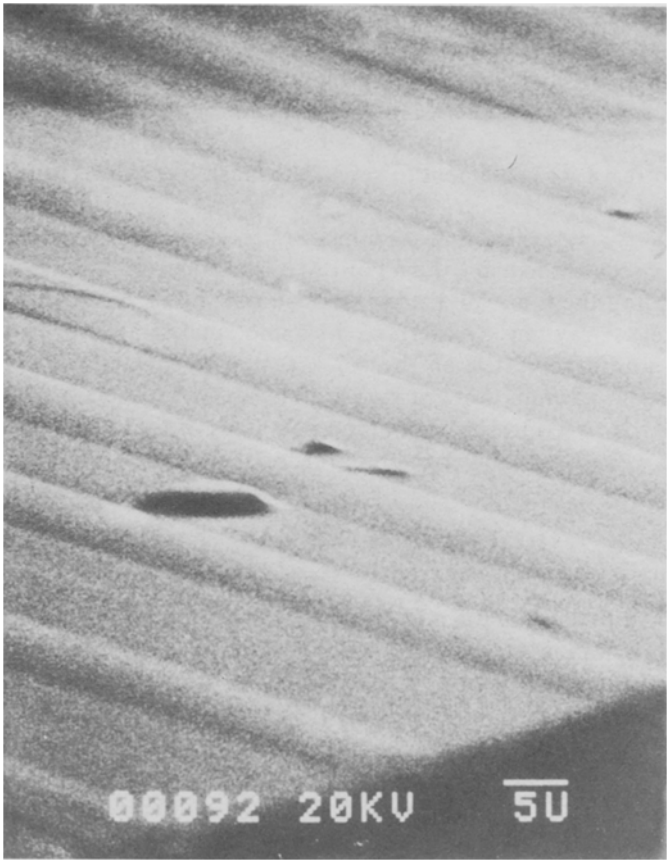

Fig. 7. SEM photograph of self-developed patterns through the X-ray mask using SR.

a structure of lines and spaces of 4 μm width was successfully fabricated in the film by CO_2 plasma etching through the mask pattern of plasma-polymerized resist.

In addition, an X-ray mask was fabricated using gold containing plasma-polymerized styrene as an X-ray absorber, and the mask pattern was successfully transferred to the resist using SR.

ACKNOWLEDGMENT

The authors thank Dr. A. Isogai and Mr. T. Suzuki of the Toyota Central Research and Development Laboratories for the ESCA measurement, and Dr. Y. Ando of Meijo University for help with the TEM analysis.

This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan.

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