C_{60}-incorporated nanocomposite resist system for practical nanometer pattern fabrication

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We propose a nanocomposite resist system that incorporates sub-nm size fullerene C_{60} molecules into a highly sensitive and moderately dry-etching resistant electron-beam positive resist, ZEP520. C_{60} incorporation leads to carbon reinforcement in the original resist material and enhances resist performance for nanometer pattern fabrication. 10 wt % C_{60} incorporated ZEP520 shows enhancements of etching resistance (~15%), thermal resistance (~30 °C), and mechanical resistance (3.5–5.5 in the aspect ratio). By applying this new resist system to x-ray mask fabrication, an ultrafine mask with the minimum dimension of 45 nm has been successfully fabricated. © *1997 American Vacuum Society.* [S0734-211X(97)14606-6]

I. INTRODUCTION

The fabrication of nanometer patterns with dimensions smaller than 0.1 μm at a practical level has been increasingly in demand for research and development in ultralarge scale integrates (ULSIs), quantum devices, or diffractive optical elements. In such device fabrications, further improvement of resists performance is accordingly required. Resist performance is generally characterized by three qualities: resolution, sensitivity, and resistance. In the nanometer range, resistance will play a critical role more and more in actual device fabrication. Although resistance in a general sense means etching resistance, it could be classified by its characteristics into two kinds: chemical and physical resistance. Chemical resistance is essentially etching resistance. Physical resistance can be further divided into thermal and mechanical resistance. Low thermal resistance results in pattern deformation in heat processes, while low mechanical resistance leads to pattern collapse during development. Because the etching resistance of conventional materials is moderate and a large decrease of the aspect ratio of patterns is not expected, mechanical resistance has been increasingly a factor limiting resolution in nanometer pattern fabrication.

We have recently proposed a nanocomposite resist system that incorporates sub-nm fullerene C_{60} molecules into a conventional resist material to realize an ultrathin films resist process by enhancing etching (or chemical) resistance.[1,2] This new resist system also has the potential to enhance physical resistance by the reinforcement effect of C_{60} incorporation. This article presents a nanocomposite system composed of C_{60} and a highly sensitive and moderately dry-etching resistant electron beam positive resist, ZEP520,[3] and shows some characteristics of the system, focusing on the mechanical and thermal resistance.

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II. CONCEPT

The basic idea of the nanocomposite resist system is shown in Fig. 1. A spin-coated film of a conventional resist material appears to be a closely packed film, but actually such a thin polymer film has space, called free volume, which is not occupied by resist molecules and is porous in nature. Although etching resistance is increased by introducing etching resistant functional groups into resist molecules in conventional resist, etching reactants easily pass through the unoccupied space among the resist molecules and react

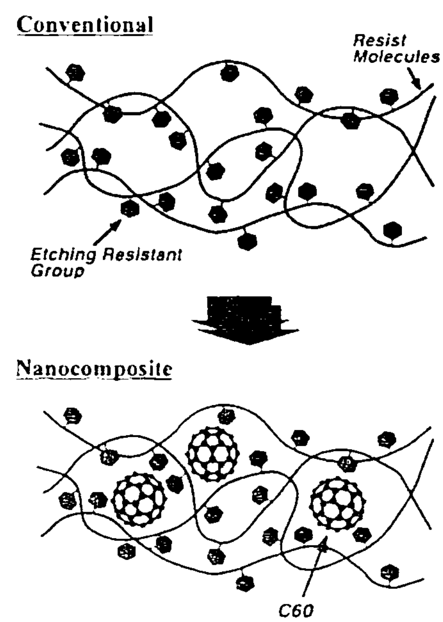

FIG. 1. Concept of the nanocomposite resist system, where sub-nm size fullerene C_{60} molecules are incorporated into a conventional resist material. C_{60} incorporation leads to a carbon-reinforcement effect by making the original film rigid and hard and enhances resist performance for nanometer pattern fabrication.

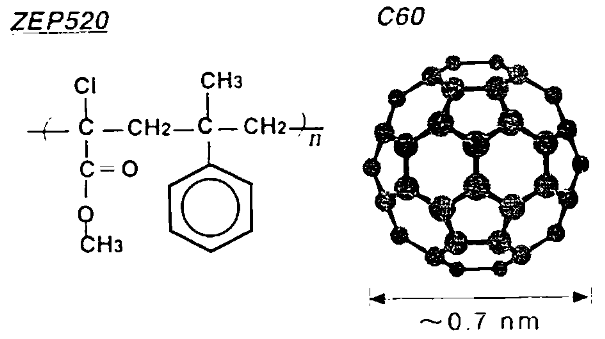

FIG. 2. Molecular size comparison for ZEP520 and C_{60}. The diameter of C_{60} is about 0.7 nm, which corresponds to the length of the four or five C–C unit bonds in the ZEP520 molecule

with molecules in deeper regions of the film, inducing etching defects in unwanted areas. By reducing the free volume with highly etching resistant C_{60} molecules,[4] the intrusion of the etching reactants is blocked, and a further increase in the etching resistance of the original resist material is achieved. In addition, filling the free volume with C_{60} molecules, which have a high melting point (>700 °C), would hinder thermal motion and enhance the thermal resistance of the film. Close packing by C_{60} incorporation could also increase the rigidness or strength of the film by increasing the density of the film, thereby enhancing its mechanical resistance.

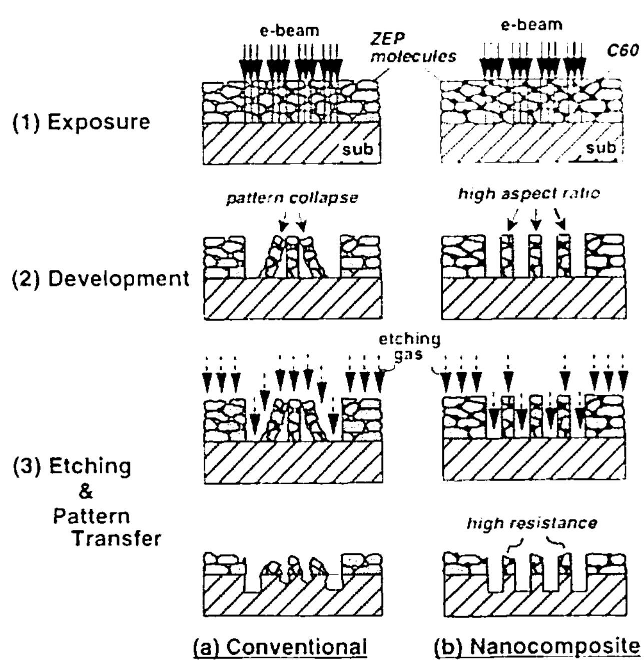

FIG. 3. Schematic of *e*-beam resist processes for densely packed patterns. In a conventional process (a), nanometer patterns with high aspect ratio tend to collapse during development due to their poor mechanical strength or resistance. On the other hand, in the nanocomposite process (b), those patterns are properly formed by C_{60} reinforcement.

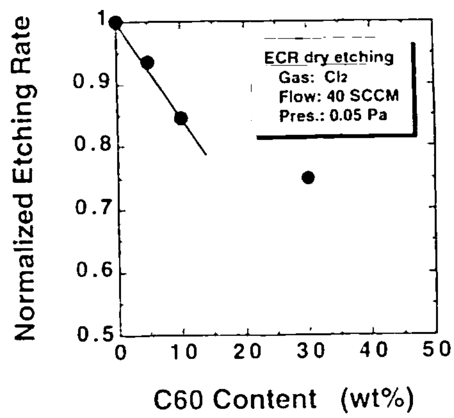

FIG. 4. Enhancement of etching resistance of C_{60} @ ZEP as a function of C_{60} content evaluated by ECR dry etching under Si etching conditions (gas: Cl_2, gas flow: 40 SCCM; pressure: 0.05 Pa; microwave power: 200 W).

The molecule structures of both ZEP520 and C_{60} are shown in Fig. 2. C_{60} has several advantages for incorporation. First, C_{60} is an ultrafine particle with a diameter of ~0.7 nm, which corresponds to the length of the four or five C–C unit bonds in the ZEP520 molecules. Second, it is pure carbon material consisting of 60 carbon atoms. Third, it dissolves in most aromatic solvents. Fourth, it is chemically and physically stable. When C_{60} is incorporated into ZEP resist to make a composite, these qualities lead to substantial improvements of resist properties, including chemical and physical resistance, without the need for a significant process change.

Figure 3 shows a schematic of *e*-beam resist processes. In the fabrication of densely packed patterns like equal lines and spaces, resolution is, in most cases, limited by pattern collapse caused by surface tension during the drying by rinse solvents.[5,6] In the conventional system (a), nanometer patterns with high aspect ratio tend to collapse during the development due to their poor mechanical strength or resistance. Empirically, the threshold of pattern collapse has been an aspect ratio of 5, but in sub-100 nm dimensions, it will go down to 3 or 3.5 due to the lack of mechanical resistance in such small patterns. On the other hand, in the nanocomposite process (b), patterns with a aspect ratio of >5 are properly formed by C_{60} reinforcement.

III. EXPERIMENT

We used commercially available fullerene C_{60} (Kanto Chemicals) and incorporated it into ZEP520 (Nippon Zeon). C_{60} powder was first dissolved in o-dichlorobenzene and then mixed with the ZEP resist solution. We prepared 0, 5, 10, and 30 wt % C_{60} solutions (to the solid content of the original resists solution) for C_{60}-incorporated ZEP520 (C_{60} @ ZEP) samples. Each C_{60} @ ZEP resist solution was spin-coated on a Si substrate and prebaked at 165 °C in an oven for 30 min. Exposure experiments were carried out with a 25 kV Gaussian electron beam machine (JEOL-5FE).

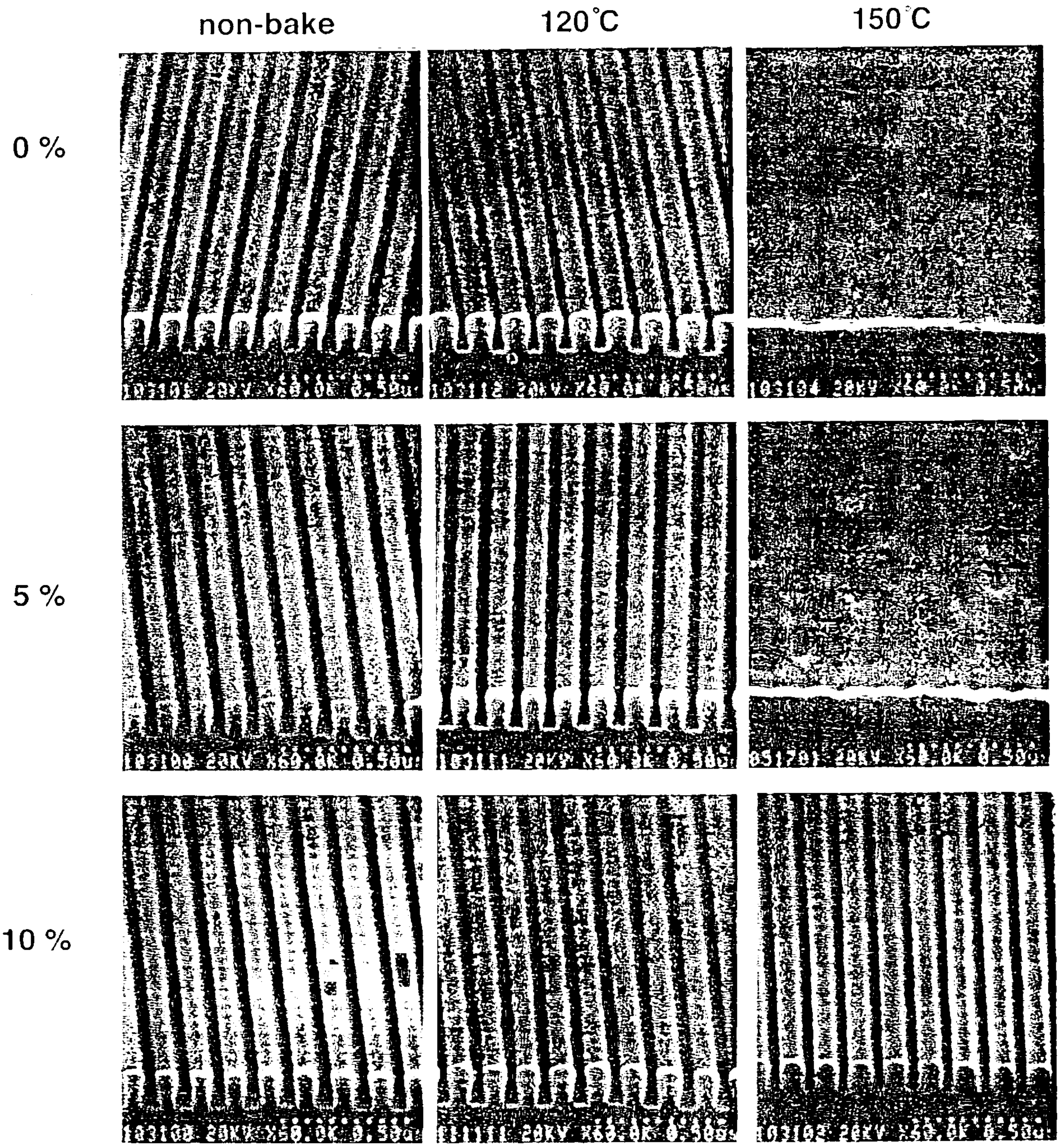

FIG. 5. Enhancement of thermal resistance of C_{60} @ ZEP. SEM micrographs of 150 nm pitch patterns of 0, 5, and 10 wt % C_{60} @ ZEP sample baked at 120 and 150 °C are shown with nonbaked patterns as a reference.

Exposed samples were developed in the ZEP developer ZED-N50 (*n*-amyl acetate). The sensitivities of all the samples were adjusted to ~50 $\mu C/cm^2$ by controlling development time.

The enhancement of etching resistance was evaluated by an electron cyclotron resonance (ECR) dry etching technique under Si etching conditions (gas: Cl_2; gas flow: 40 sccm; pressure: 0.05 Pa; microwave power: 200 W). Thermal resistance was evaluated by the scanning electron microscope (SEM) observation of 150 nm pitch patterns heated in an oven for 30 min. Mechanical resistance was evaluated by measuring the aspect ratio of various nanometer patterns observed with the SEM.

X-ray mask fabrication was done by technologies developed at NTT.[7] The mask substrate was composed of, from top to bottom, SiO_2 (150 nm), Ta (0.4 μm), SiN (200 nm), and Si (0.38 mm). The thickness of 10 wt % C_{60} @ ZEP was 100 nm and the patterning process was carried out in the same manner as described above. The SiO_2 layer was etched through the resist patterns by reactive ion etching using C_2F_6 gas, and the Ta layer was etched with the SiO_2 mask by ECR etching using a $Cl_2/Ar/O_2$ gas mixture.

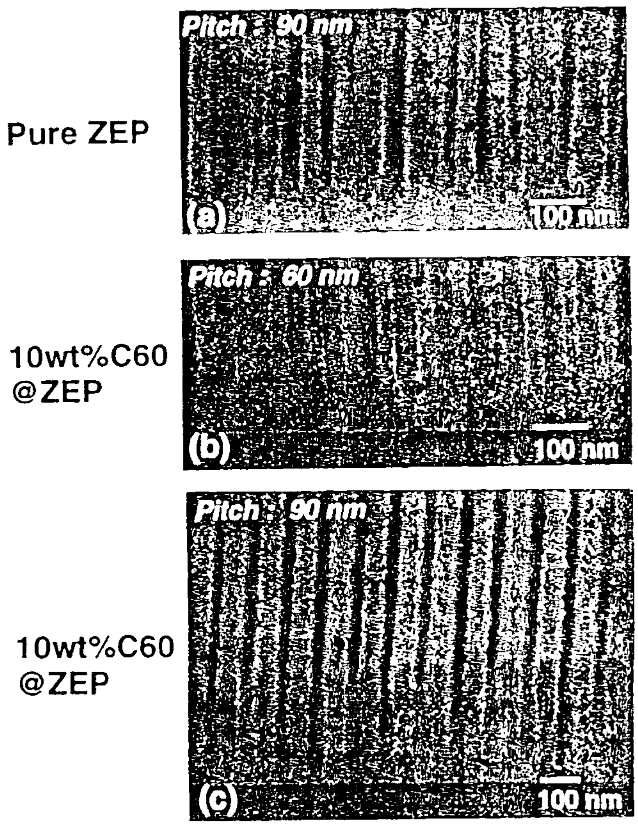

FIG. 6. Example of the enhancement of mechanical resistance. (a) 130-nm-thick pure ZEP patterns (pitch: 90 nm). (b) 130-nm-thick 10 wt % C_{60} @ ZEP patterns (pitch: 60 nm). (c) 250-nm-thick 10 wt % C_{60} @ ZEP patterns (pitch: 90 nm).

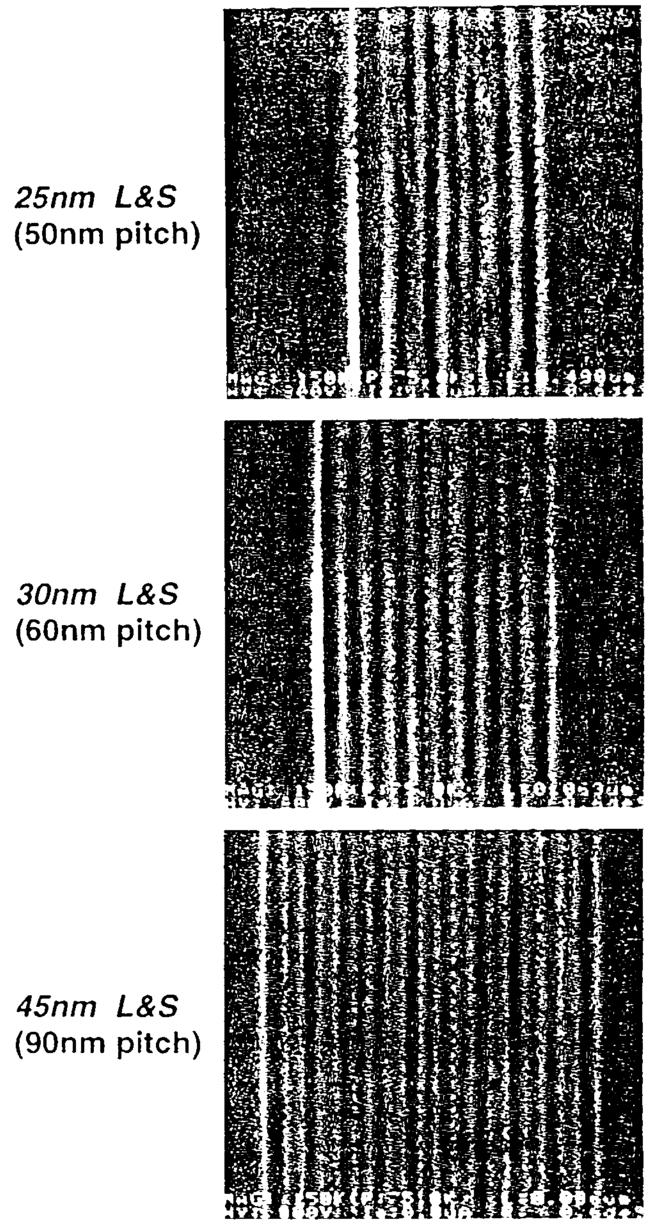

FIG. 7. SEM micrographs of sub-50 nm patterns of 10 wt % C_{60} @ ZEP formed in a 100 nm film on the SiO_2 layer for x-ray mask fabrication. Pattern dimensions are 25, 30, and 45 nm in equal lines and spaces from top to bottom.

IV. RESULTS AND DISCUSSION

Figure 4 shows the normalized etching rate of C_{60} @ ZEP against C_{60} content. The rate decreases linearly with C_{60} content up to around 15 wt % and then tends to level off. This proves that C_{60} incorporation enhances etching resistance. Under the present development conditions, we could not obtain good quality patterns at 30 wt %. The best quality patterns were obtained at 10 wt %, which correspond to an etching resistance enhancement of ~15%.

Figure 5 shows SEM micrographs of 150 nm pitch patterns of 0, 5, and 10 wt % C_{60} @ ZEP samples after being baked at 120 and 150 °C for 30 min. Nonbaked samples are also shown for reference. Although ZEP520 resist has a relatively high glass transition temperature of 145 °C, the pure (0 wt % C_{60}) ZEP sample showed pattern swelling at around 120 °C and completely flowed at 150 °C. The 5 and 10 wt % C_{60} samples showed no practically adverse swelling at 120 °C, but the former sample flowed at 150 °C as did the pure sample, whereas the latter one showed strong thermal resistance even at 150 °C. This enhancement of thermal resistance could, by allowing us to remove an additional protecting layer, simplify the compound semiconductor process in which a thermal step such as high-melting point metal deposition for gate lift-off or substrate heating dry etching is usually employed.

Figure 6 shows nanometer patterns formed in the pure ZEP and 10 wt % C_{60} @ ZEP systems. In the pure ZEP system, 90 nm pitch patterns which were 130 m thick collapsed as shown in Fig. 6(a). Since the actual pattern width by SEM measurement was a little smaller than 40 nm, we estimated the aspect ratio at about 3.5 for these patterns. In the 10 wt % system, 60 nm pitch patterns were resolved in the same thickness of the film as shown in Fig. 6(b). We tried patterning in the thicker film of 250 nm as shown in Fig. 6(c). This thickness is partically viable for fabrication of a substrate even by conventional dry etching. The micrograph shows 90 nm pitch patterns with a high aspect ratio of

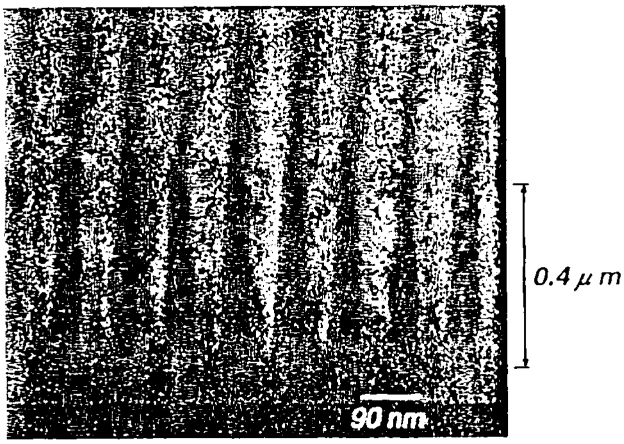

FIG. 8. Cross-sectional view of a fabricated ultrafine x-ray mask. The pattern dimension is 45 nm, and the height of the Ta absorber is 0.4 μm.

5.5 were successfully created in the 10 wt % C_{60} @ ZEP. This result shows an increase in aspect ratio from 3.5 to 5.5 and demonstrates the enhancement of mechanical resistance.

We applied our new resist system to x-ray mask fabrication and obtained good results. Figure 7 shows 10 wt % C_{60} at ZEP patterns on the SiO_2 layer. Patterns down to 30 nm were formed. Figure 8 shows a fabricated x-ray mask with the minimum dimension of 45 nm. The Ta thickness is 0.4 μm, so the aspect ratio is more than 8. Under the present Ta etching conditions, we could not fabricate a mask with dimensions smaller than 45 nm. As C_{60} can be easily removed by ultraviolet (UV) ozone ashing and contains no harmful impurities, no process change was needed during the fabrication.

V. CONCLUSIONS

We propose a nanocomposite resist system that incorporates sub-nm size fullerene C_{60} molecules into a highly sensitive and moderately dry-etching resistance electron-beam positive resist, ZEP520. This new resist system leads to enhancements of resist performance that are required for nanometer pattern fabrication. The enhancement of chemical resistance, or etching resistance, was evaluated by ECR dry etching and ~15% enhancement was observed at ~10 wt % C_{60} content. Physical resistance, i.e., thermal and mechanical resistance, was evaluated by SEM measurement of pattern deformation upon heating (for the former) and by measuring by the aspect ratio (for the latter) of nanometer patterns, and enhancements of ~30 °C and 3.5–5.5 were obtained, respectively. By applying this new resist system to x-ray mask fabrication, an ultrafine mask with the minimum dimension of 45 nm and an aspect ratio of more than 8 has been successfully fabricated. This example of application shows that our new resist system promises to provide an improved resist process for wide areas of nanometer pattern fabrication.

[1] T. Ishii, H. Nozawa, and T. Tamamura, Micro- and Nano-Engineering, Glasgow, Abstract 21 (1996).
[2] T. Ishii, H. Nozawa, and T. Tamamura, Appl. Phys. Lett. 70, 1110 (1997).
[3] T. Nishida, N. Notomi, R. Iga, and T. Tamamura, Jpn. J. Appl. Phys., Part 1 31, 4508 (1992).
[4] T. Tada and T. Kanayama, Jpn. J. Appl. Phys., Part 2 35, L63 (1996).
[5] K. Deguchi, K. Miyoshi, T. Ishii, and T. Matsuda, Jpn. J. Appl. Phys., Part 1 31, 2954 (1992).
[6] T. Tanaka, M. Morigami, and N. Atoda, Jpn. J. Appl. Phys., Part 1 32, 6059 (1993).
[7] A. Ozawa, S. Ohki, M. Oda, and H. Yoshihara, IEICE Trans. Electron. E77-C(2), 255 (1994).