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# Fullerene Film Resist for Electron Beam Nanolithography

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Electron beam (e-beam) irradiation has been found to reduce the dissolution rate of evaporated $C_{60}$ films in organic solvents such as monochlorobenzene, which shows that this material serves as a negative e-beam resist. In addition, the rate of thermal sublimation in vacuum is also reduced by the exposure. This means that the $C_{60}$ resist can be developed with the sublimation process as well. These observations indicate that e-beam irradiation causes polymerization of $C_{60}$ molecules leading to resist action. This resist exhibits good resolution and high dry-etch durability. The performance of this resist was demonstrated by defining 20 nm dot patterns in $C_{60}$ films and fabricating Si nanopillars by subsequent plasma etching. Since this material has the molecular size of less than 1 nm, it may be possible to yield the resolution of a few nm.

## 1.Introduction

Electron beam (e-beam) lithography has been and will continue to be a major technique for the fabrication of fine structures, even if the required feature size decreases from $\mu$m to nm dimensions. Many investigation into nanolithography have been carried out using e-beam lithography[1,2]. Negative resist materials also have a comparatively long history. Their action is due to cross-linking and polymerization caused by e-beam irradiation. This operation principle results in the disadvantage that the resolution is limited by the molecular size. Thus a resist material with a low molecular size is required for nanofabrication. Fullerenes such as $C_{60}$ and $C_{70}$ have attracted considerable attention since their discovery by Kroto *et al.*[3] in 1985, and many investigations have been made into the properties of this new class of material. Among these properties, chemical sensitivity to light has already been reported. Rao *et al.*[4] found that irradiation of a $C_{60}$ film with visible or ultraviolet (UV) light induces polymerization of the molecules, and makes the film insoluble in organic solvents such as toluene. This suggests that $C_{60}$ can be used as a negative photoresist. Hebard *et al.*[5] showed that sublimed fullerene films can be used for photolithography. In their work, UV exposure of fullerene films in an oxygen-rich ambient led to an increase in the cohesive energy and resulted in negative-type resist action. Although the reported pattern size is large, the small molecular size implies that this material might have an ideal resolution for nanolithography if it is sensitive to e-beam irradiation in a vacuum.

## 2. Resist Properties of $C_{60}$

We have already reported that e-beam irradiation reduces the dissolution rate of $C_{60}$ films in organic solvents[6]. Namely, $C_{60}$ films can serve as a negative-type e-beam resist with developer of organic solvents. In addition, we have found that the development can be done also with thermal sublimation process in vacuum. Here we compare the

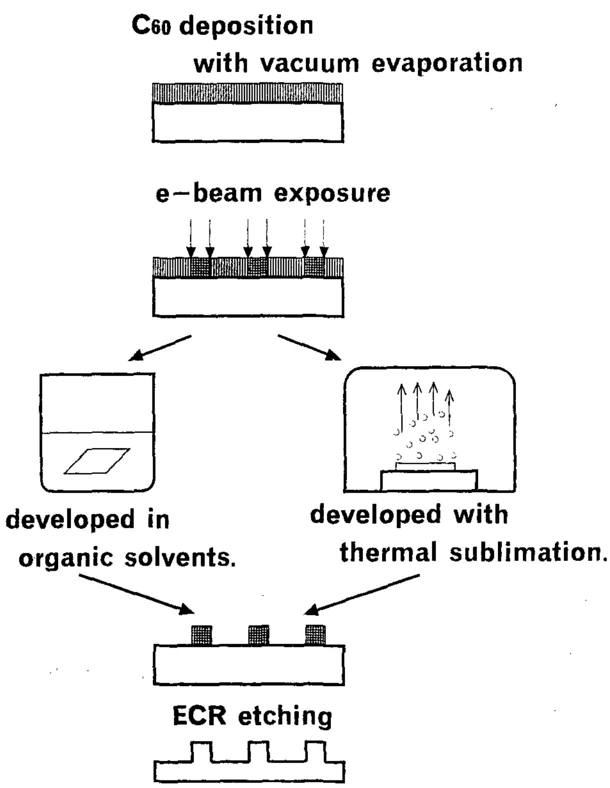


Fig.1 Procedure for nanolithography using fullerene films.

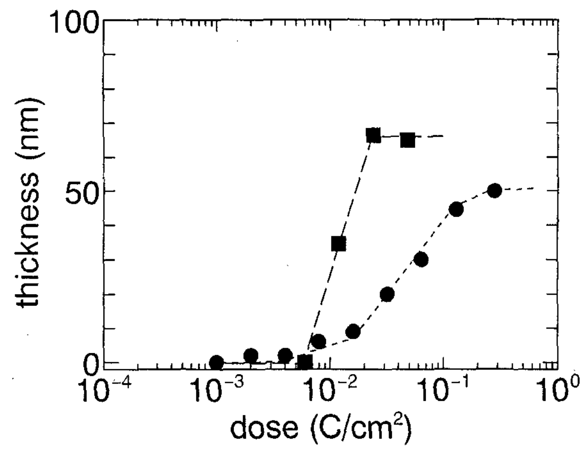


Fig.2. Response curves of the $C_{60}$ films for 20−keV e−beam exposure. The thickness remaining after development in different method is plotted as a function of the e−beam dose. Squares (■): developed in mono−chlorobenzene (MCB) for 1 min. Circles (●): developed with thermal sublimation at 450℃ for 1 hour.

two development processes of the $C_{60}$ negative resist and demonstrate the performance of this resist by defining nanopatterns in Si. Since deposited $C_{60}$ molecules are polymerized by e−beam irradiation and may have graphite−like structures[6] at last, their film can be used as a negative resist for nanolithography according to the process shown in Fig.1. Two different processes are available for pattern development: dissolution in organic solvents and thermal sublimation in vacuum. In our actual experiments, $C_{60}$ films were prepared on HF−cleaned Si substrates by sublimation of $C_{60}$ powders in vacuum at 500−700℃ with thickness of 50−60 nm. After exposed to 20 keV e−beams, wet development was done in monochlorobenzene (MCB) for 1 min followed by rinsing in isopropanol (IPA) for 10 s. The dry development was performed by heating the exposed sample in vacuum at 450℃ for 1 hour. During this heating process, $C_{60}$ in the unexposed area is sublimed from a Si substrate, but not in the exposed area. Figure 2 compares response curves of the $C_{60}$ films for these two development process. The sensitivity with the dry development is 0.05 C/cm$^2$, which is lower than that with development in MCB (0.01 C/cm$^2$) and the onset slope is slightly poor. However, the development with sublimation in vacuum has an advantage that it enables us to carry out all the process in vacuum.

To know the exposure mechanism of fullerene, we observed PL spectra of $C_{60}$ before and after e−beam irradiation (0.046 C/cm$^2$). As seen in fig. 3, PL intensity decreased drastically after the irradiation. This is consistent with the idea that $C_{60}$ film has graphite−like structures after e−beam irradiation.

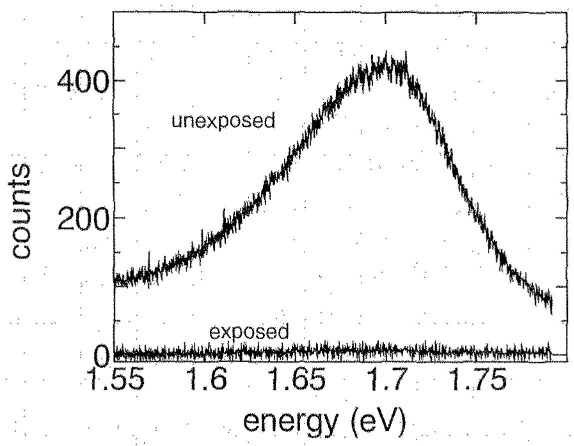


Fig.3 Photoluminescence spectra of a $C_{60}$ film at room temperature before and after e-beam exposure of 0.046 C/cm$^2$.

**3.Fabrication of Nanostructures**

In order to demonstrate the performance of the $C_{60}$ resist, pattern definition was carried out using development with MCB. Figure 4 is a scanning electron microscope (SEM) micrograph of the patterns fabricated in the resist after developing in MCB for 1 min and rinsing in IPA for 10 s. Pillars with a diameter of 20–30 nm and height of ~30 nm are observed. The sidewalls of the pillars are sharp, which proves that $C_{60}$ films can be used as a high-resolution resist. Next we fabricated nanopillars in Si

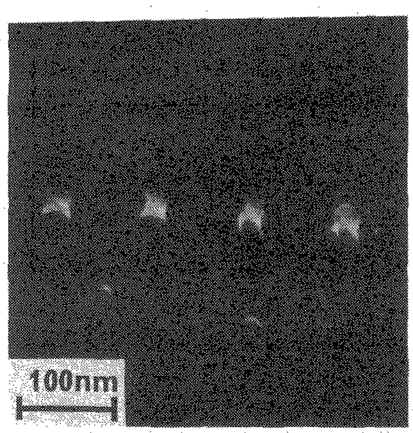


Fig.4 An SEM micrograph of dot patterns defined in a 35-nm thick $C_{60}$ layer. The tilt angle is 40°.

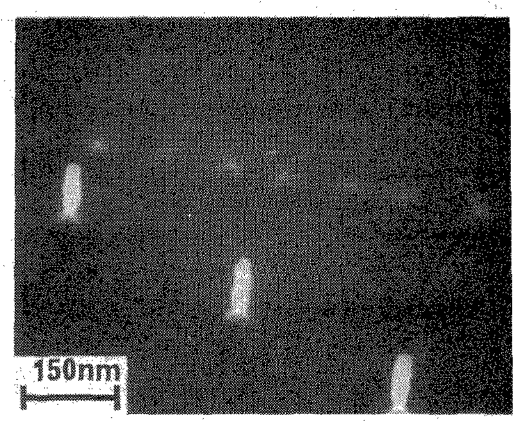


Fig.5 An SEM micrograph of the pillars fabrica in a Si substrate. The tilt angle is 40°.

using ECR etching with $C_{60}$ dot patterns defined above. The etching gas was $SF_6$ and the etch temperature was −135℃. The etch rate ratio of S the $C_{60}$ resist is greater than 10 and the dry-e durability of $C_{60}$ is found to be higher than that the conventional novolac-based e-beam resist, S 601 (Shipley). Figure 5 is an SEM micrograph of fabricated Si pillars with a diameter of 20–30 and height of 100 nm. This shows that the $C_{60}$ re: is suitable for nanofabrication of Si and possibly other materials.

**4. Summary**

We have shown that evaporated $C_{60}$ films as a negative e-beam resist with a sensitivity of 0 C/cm$^2$ for development in an organic solvent, MC and 0.05 C/cm$^2$ for thermal sublimation in a vacuu This resist exhibits good resolution and high dr etch durability. The etch rate ratio of Si to the resist is greater than 10 for ECR etching with gas. The performance of this resist was demonstrat by defining 20 nm dot patterns in $C_{60}$ films a fabricating Si nanopillars by subsequent E( etching. Since this material has the molecular size less than 1 nm, it may be possible to yield resolution of a few nm.

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**References**

[1]. T. Tada and T. Kanayama: J. Vac. Sci. & Technol. B **11** (1993) 2229.

[2]. W. Chen and H. Ahmed: J. Vac. Sci. & Technol. B **11** (1993) 2519.

[3]. H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, and R.E. Smalley: Nature **318** (1985) 162.

[4]. A.M. Rao, P. Zhou, K.-A. Wang, G.T. Hager, J.M. Holden, Y. Wang, W.-T. Lee, X.-X. Bi, P.C. Eklund, D.S. Cornett, M.A. Duncan, and I.J. Amster: Science **259** (1993) 955.

[5]. A.F. Hebard, C.B. Eom, R.M. Fleming, Y.J. Chabal, A.J. Muller, S.H. Glarum, G.J. Pietsch, R.C. Haddon, A.M. Mujsce, M.A. Paczkowski, and G.P. Kochanski: Appl. Phys. A **57** (1993) 299.

[6] T.Tada and T. Kanayama: Jpn. J. Appl. Phys. **35** (1996) L63.