JJAP Series 4
Proc. of 1990 Intern. MicroProcess Conference pp. 151–154

Novel Process for Direct Delineation of Spin on Glass (SOG)

Akira IMAI, Hiroshi FUKUDA, Takumi UENO
and Shinji OKAZAKI

Central Research Laboratory, Hitachi, Ltd.,
Higashi-koigakubo 1-280, Kokubunji, Tokyo 185

(Received July 18, 1990; accepted for publication September 22, 1990)

Some types of spin on glass (SOG) are radiationchemically sensitive and act as negative-tone resist for electron beam (EB) exposure. Using direct EB writing, 0.2 μm line and space (L/S) patterns are obtained with a 400 μC/cm² EB dose at an acceleration voltage of 30 keV. Although this material has high-resolution capability, the sensitivity is too low for practical resist applications. In order to improve sensitivity, an acid catalyzed system[6] is introduced. 0.3 μm L/S patterns are delineated with an EB exposure dose of 0.7 μC/cm² using a SOG-based chemically amplified material. This radiationchemically sensitive characteristic of SOG can be applied to a bi-layer resist system.

KEYWORDS: spin on glass, electron beam, sensitivity, negative-tone resist, acid catalyzed system, resolution, Bi-layer resist system

§1. Introduction

The minimum feature size of ULSI devices has become a quarter-micron. Multilayer resist systems[1] are one means of improving lithographic resolution technology. As the bi-layer resist system has an advantage over the tri-layer resist scheme in multilayer resist systems, it is the more practical scheme. A conventional bi-layer resist system is composed of a thick organic bottom layer (BL) and a radiation sensitive upper resist layer, which is resistant to O_2 RIE. In the bi-layer resist system, high-resolution, high sensitivity and high O_2 RIE resistant materials are required for the top resist layer. Many bi-layer resist system using materials containing silicon such as poly(vinylmethylsiloxane)[2] and ASTRO[3] have been tried and reported.[4] However, up to now, few materials meet the above mentioned requirements for electron beam (EB) and/or deep ultraviolet (DUV) exposure.

Spin on glass (SOG) is commonly used as the intermediate layer in tri-layer resist schemes and as the planarization layer for multilevel wiring systems.[5] In these systems, the SOG layer is usually patterned by ordinary lithographic processes. The authors' recent experiments have revealed that some types of SOG act as negative-tone resists by EB exposure.

This paper describes the basic EB exposure characteristics of the SOG material and a technique for improving sensitivity. Application to a bi-layer resist system is also shown.

§2. Experiment

OCD type 7 (Tokyo Ohka Kogyo Co.) was used as the SOG material. The SOG material was spin-coated on Si wafer substrates and soft-baked in a convection oven. Soft-baking was carried out for 0∼30 minutes between 70∼110°C. The SOG films were directly exposed to the EB and then developed. The acceleration voltage of the EB exposure was 30 keV. Methanol (CH_3OH) and an aqueous-base developer (20% dilution of NMD-3: 2.38% tetramethylammonium hydroxide obtained from Tokyo Ohka Kogyo, Co.) were used as developer solutions.

For chemically amplified resist applications, triphenylsulfonium triflate ($Ph_3S^+OTf^-$) was added to the SOG material as an acid generator (AG). Post exposure baking (PEB) was carried out at 80∼100°C for 0∼10 minutes before developing.

For a bi-layer resist process, SOG material was spin-coated on BL(1.6 μm film thickness)/Si substrates. After delineation of SOG patterns, hard-baking was carried out at 230°C for 3 minutes on a hot plate to enhance the resistance of SOG patterns to O_2 RIE. The O_2 RIE condition was 1.2 mTorr at 400 W power. The experimental procedure is shown in Fig. 1.

Sensitivity curves were obtained by measuring the remaining film thicknesses of 100 μm × 1000 μm rectangular patterns, delineated by various EB doses, using α-step (Tencor Inst. Co.). Infrared (IR) transmission spectra were measured by FTS-20C (Jasco International Co., Ltd.). A scanning electron microscope (SEM) S-800

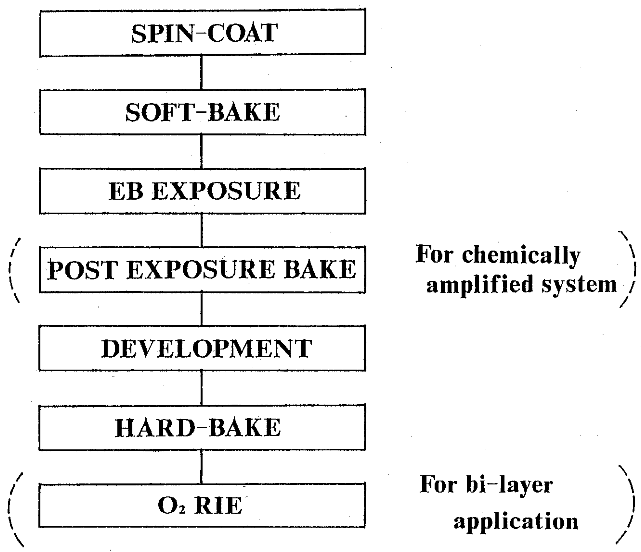

Fig. 1. Experimental procedure.

(Hitachi, Ltd.) was used for pattern investigation.

§3. Results and Discussion

3.1 *EB exposure characteristics of SOG material*

Sensitivity curves of SOG to EB exposure are shown in Fig. 2. The soft-baking temperature was set at 80°C and the soft-baking time varied from 0 to 10 minutes. Development was carried out in methanol for 30 seconds. As shown in this figure, the SOG itself acts as a negative-tone EB resist with a sensitivity of 150~300°C/cm^2. It also shows improvement in the sensitivity for longer soft-baking times. This improvement is due to the condensation reaction of silanol compounds promoted by soft-baking.

Table I shows the solubility of unexposed SOG film in methanol for various soft-baking conditions. For higher temperature and/or longer soft-baking time, SOG patterns can not be delineated because of residue left after development, and further soft-baking changes it to insoluble film in methanol. This is the result of the condensation reaction of silanol compounds. From this result, it can be seen that the soft-baking temperature should be chosen carefully.

The IR transmission spectra of SOG materials were measured to examine the reaction generated by EB exposure. The results are shown in Fig. 3. An upper curve shows the IR spectrum of SOG before EB exposure, and a lower curve shows the IR spectrum of the SOG after 500 μC/cm^2 EB exposure. As shown in this figure, large Si–O absorbance is observed both before and after EB exposure. On the other hand, Si–OH absorbance decreases after EB exposure. This change in the IR spectra suggests that the condensation reaction of silanol compounds is induced by EB exposure. This result supports the fact that the SOG film becomes insoluble in methanol and an aqueous-base developer after EB exposure because of an increase of molecular weight due to the condensation reaction.

An SEM photograph of SOG patterns delineated by direct EB writing is shown in Fig. 4. The soft-baking con-

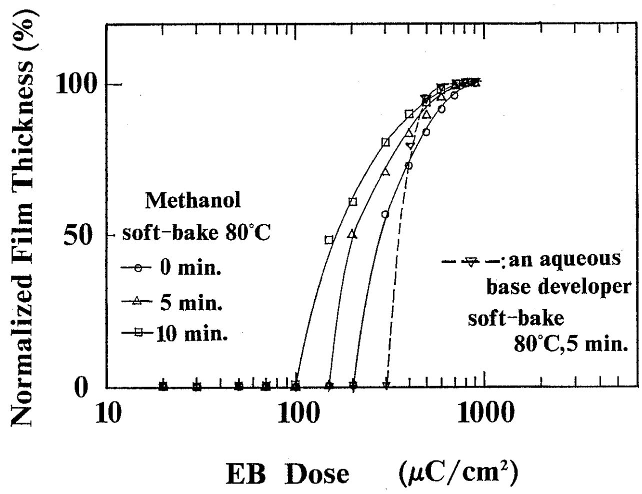

Fig. 2. Sensitivity curves of SOG. Soft-baking temperature: 80°C, Developer solution:methanol or 20% dilution of NMD-3(2.38%).

Table I. Solubility of SOG in methanol for various soft-baking conditions.

soft-baking temperature	soft-baking time (minutes)						
	5	10	15	20	25	30	35
70°C	○	○	○	○	○	△	×
80°C	○	○	○	△	×	×	–
90°C	○	×	–	–	–	–	–
100°C	○	×	–	–	–	–	–
110°C	×	–	–	–	–	–	–

○: soluble, △: residue after development, ×: insoluble soft-baking is carried out in a convection oven

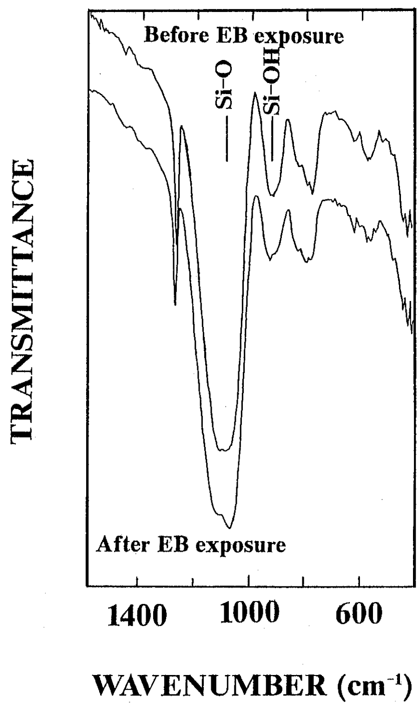

Fig. 3. FTIR spectra of SOG before and after EB exposure. EB dose: 500 μC/cm^2.

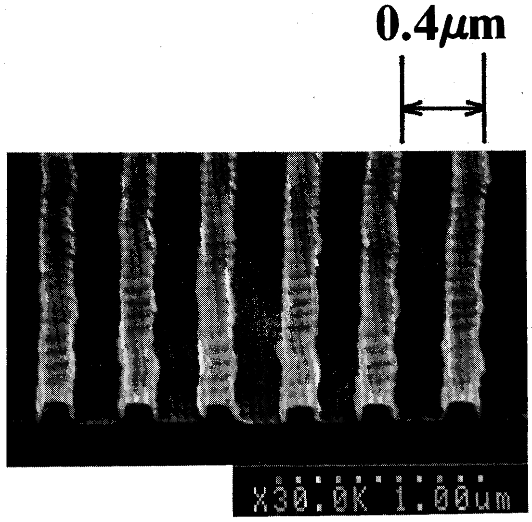

Fig. 4. 0.2 μm L/S SOG patterns delineated by direct EB writing. EB dose: 400 μC/cm^2, Film thickness: 0.2 μm.

dition was 80°C for 5 minutes and the development time was 30 seconds. 0.2 μm line and space (L/S) patterns are clearly delineated for a film thickness of 0.2 μm with a 400 μC/cm² EB dose.

The broken line in Fig. 2 shows the sensitivity curve of the SOG in an aqueous-base developer (20% dilution of NMD-3 2.38%). The development time was 10 seconds. Sensitivity in this development condition, 450 μC/cm², was lower than that in methanol while the contrast (γ) was higher. However, it was difficult to delineate fine patterns due to pattern degradations.

3.2 *Chemically amplified system application*

Although this material has high-resolution capability, the sensitivity is too low for practical resist applications. The chemical amplification scheme[6] was applied to improve the sensitivity.

A negative-tone chemically amplified resist system for DUV exposure, composed of triphenylsulfonium triflate ($Ph_3S^+OTf^-$) acid generator, a silanol compound and Novolak base resin, has been reported.[7] This system uses the condensation reaction of a silanol compound induced by an acid catalysis. Therefore, it can be expected that the condensation reaction of the silanol groups of the SOG material is also induced by an acid catalysis.

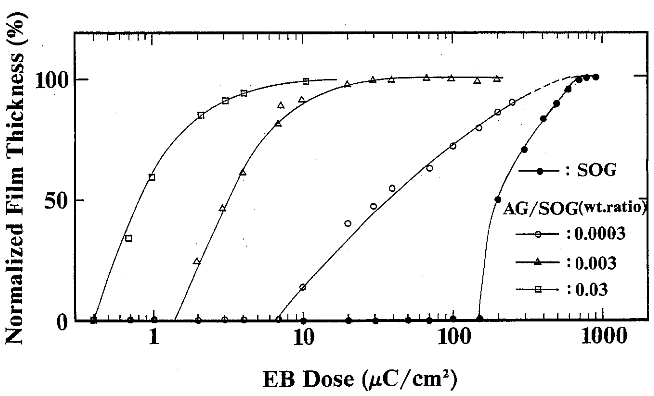

Fig. 5. Sensitivity curves of SOG-based chemically amplified materials for various AG/SOG wt. ratio. PEB temperature: 80°C, PEB time: 5 minutes, Development: in methanol for 30 seconds.

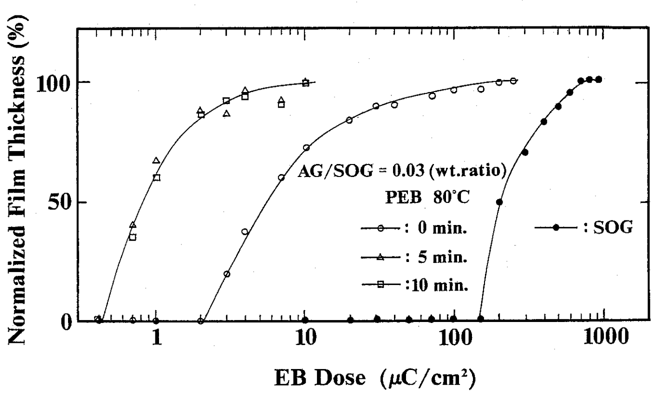

Fig. 6. Sensitivity curves of SOG-based chemically amplified materials (AG/SOG=0.03/1 in wt. ratio) for various PEB time. PEB temperature: 80°C.

In the experiment, a triphenylsulfonium triflate ($Ph_3S^+OTf^-$) is added to the SOG material as an acid generator to improve the sensitivity in EB and/or DUV exposure. SOG-based chemically amplified materials with various contents of the acid generator are spin-coated and exposed to direct EB writing. The soft-baking condition is set at 80°C for 5 minutes. The sensitivity curves of these materials are shown in Fig. 5. Post-exposure baking (PEB) is carried out at 80°C for 5 minutes before the development. It can been seen from Fig. 5 that sensitivity drastically improves. About 100 times higher sensitivity was achieved for the AG/SOG=0.03/1 (wt. ratio) sample as compared to the original SOG material. According to the increase of the PEB time, the sensitivity improved. However, no further improvement in the sensitivity was obtained beyond 5 minutes PEB time.

Figure 6 shows the PEB time dependence of sensitivity curves for SOG-based chemically amplified materials (AG/SOG=0.03/1 in wt. ratio). It can be seen from Fig. 6 that, when there was no PEB, the sensitivity of the SOG-based chemically amplified material was higher than that of the original SOG. This result suggests that the acid catalyzed reaction proceeded even at room temperature.

Although the sensitivity improved with increasing PEB time, the sensitivity for a PEB time of 10 minutes is almost the same as that for 5 minutes. This saturation phenomenon can be explained, if the acid diffusion length is somewhat limited. This also suggests that one approach to improve thermal stability is to use chemically amplified resists in this saturated region.

The IR transmission spectra of SOG-based chemically amplified materials (AG/SOG=0.03/1 in wt. ratio) are shown in Fig. 7. The upper curve shows the IR spectrum

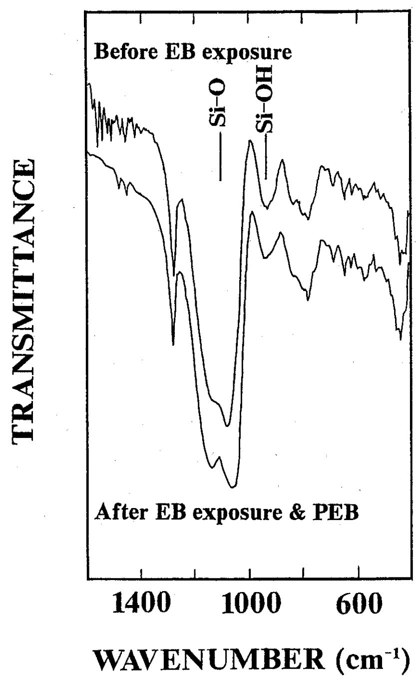

Fig. 7. FTIR spectra of SOG-based chemically amplified materials (AG/SOG=0.03/1 in wt. ratio) before and after EB exposure. EB dose: 10 μC/cm², PEB:80°C for 10 minutes.

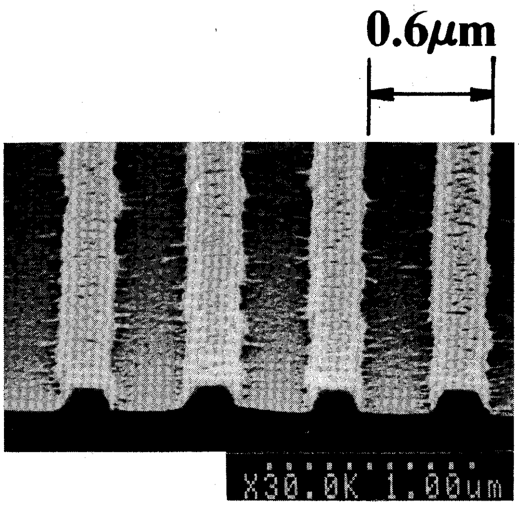

Fig. 8. 0.3 μm L/S patterns of SOG-based chemically amplified material. EB dose: 0.7 $\mu C/cm^2$, Post exposure baking: 100°C for 3 min, Film thickness: 0.3 μm.

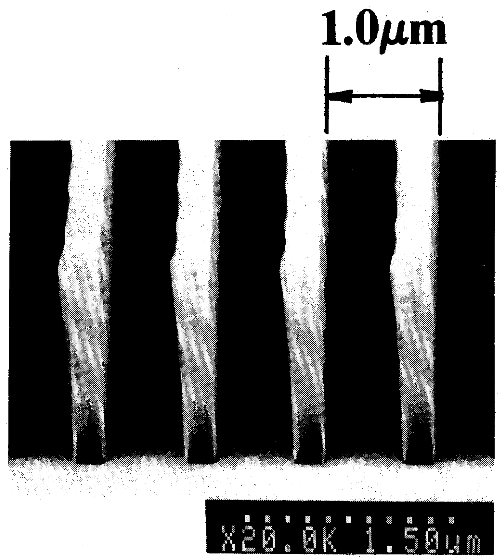

Fig. 9. Bi-layer resist patterns. Upper layer SOG, 0.3 μm film thickness, Bottom layer: hard-baked organic material, 1.6 μm film thickness.

before EB exposure and the lower curve shows the IR spectrum that of after an EB exposure dose of 10 $\mu C/cm^2$ followed by PEB at 80°C for 5 minutes. The decrease in Si–OH absorbance suggests that the condensation reaction of silanol compounds takes place upon EB exposure followed by PEB. Therefore, this drastic improvement in sensitivity can be attributed to an acid catalyzed condensation reaction of silanols.[7]

0.3 μm L/S patterns delineated with an exposure dose of 0.7 $\mu C/cm^2$ are shown in Fig. 8. The SOG-based chemically amplified material of AG/SOG=0.03/1 was used. PEB was carried out at 100°C for 3 minutes. High-sensitivity and high- resolution were achieved with this technique.

§4. Application to Bi-layer Resist System

SOG is commonly used as an intermediate layer of the trilayer resist scheme. Thus, the present method for direct delineation of SOG can be applied to a bi-layer resist system. The SOG patterns directly delineated by EB exposure can act as the etching mask of the bottom layer (BL) for O_2 RIE. Figure 9 shows bi-layer resist patterns after an etching of BL by O_2 RIE. The SOG film thickness was 0.2 μm. High aspect ratio 0.5 μm L/S bi-layer patterns were obtained. As can be seen from this figure, the SOG patterns show high resistancy against O_2 RIE.

SOG-based chemically amplified materials show very high resolution and high O_2 RIE resistant characteristics. Consequently, a bi-layer resist system with high-resolution capability and improved sensitivity can be created with these novel processes.

§5. Summary

The experiment showed that some types of SOG are radiationchemically sensitive. Fine patterns were directly delineated by EB writing. 0.2 μm L/S patterns were obtained with a 400 $\mu C/cm^2$ EB dose and an acceleration voltage of 30 keV. Sensitivity can be drastically improved by applying an acid catalyzed system. 0.3 μm L/S patterns were delineated with an exposure dose of 0.7 $\mu C/cm^2$ by adding an acid generator to the SOG materials. This radiationchemically sensitivity of SOG can easily be applied to a bi-layer resist system.

Acknowledgment

The authors would like to thank S. Itoh for the FTIR measurements, and I. Sakama and Y. Suzuki for the O_2 RIE process.

References

1) J. M. Moran and D. Mayden: J. Vac. Sci. Technol., **16** (1979) 1620.
2) M. Hatzakis, J. Shaw, E. Babich and J. Paraszczak: J. Vac. Sci. Technol. **B6** (6) (1988) 2224.
3) N. Hayashi, T. Ueno, H. Shiraishi, T. Nishida, M. Toriumi and S. Nonogaki: ACS Symp. Ser., **346** (1987) 212.
4) T. Iwayanagi, T. Ueno, S. Nonogaki, H. Ito and C. G. Wilson: Advances in Chemistry Series **218** (1988) 109.
5) P. Elkins, K. Reinhardt and R. Tang: IEEE V-MIC Conf., (1986) 100.
6) H. Ito and C. G. Wilson: Polym. Eng. Sci., **23** (1983) 1012.
7) T. Ueno, H. Shiraishi, N. Hayashi, K. Tadano, E. Fukuma and T. Iwayanagi: SPIE's 1990 Symposium Paper 1262–03.