

X-Ray-Induced Reactions and Resist Features of Polydibutylgermane

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Synopsis

Polydibutylgermane undergoes oxidation reaction and chain scission under X-ray exposure. These reactions are the same as those observed for ultraviolet irradiation. Positive resist patterns can be fabricated by X-ray lithography.

INTRODUCTION

High molecular weight soluble organopolygermane was first synthesized by Trefonas and West.¹ They reported that polydibutylgermane (PDBG) undergoes photodegradation and photobleaching, which are commonly observed for organopolysilanes.^{2,3} From analogies based on photochemical properties, organopolygermanes are expected to become positive photoresists like organopolysilanes.⁴ However, the application of organopolygermanes to X-ray resists is a more interesting problem because organopolygermanes are evaluated to absorb more X-ray energy than organopolysilanes due to heavy germanium atoms. In this report, X-ray-induced reactions of polydibutylgermane (PDBG) are compared with photoreactions, and lithographic applications are discussed.

EXPERIMENTAL

PDBG was synthesized by the dechlorination of dibutylchlorogermanium in the conventional way.¹ Gel permeation chromatography (GPC) showed an elution profile of bimodal molecular weight distribution with the peaks at 650,000 and 13,000 on the basis of standard polystyrene. PDBG film was prepared by spin coating on a silicon wafer. X-ray and deep UV exposures were carried out in the atmosphere. A X-ray exposure system (SR-1) running with 5.4 Å X-ray (molybdenum L line) was used for flood exposure and mask pattern transfer.⁵ A spectro-irradiator (JASCO CMA-01) was used for deep UV (254 nm) irradiation. Infrared (IR) spectra were measured with a FT-IR spectrometer (Perkin-Elmer Model 1800).

RESULTS AND DISCUSSION

IR spectrum changes in the PDBG film caused by X-ray and deep UV exposures are shown in Figure 1. The Ge—O absorption band at 860 cm^{-1} appeared in the both spectra. The oxidation reaction from Ge—Ge bonds to Ge—O bonds was found to take place by X-ray and deep UV exposures.

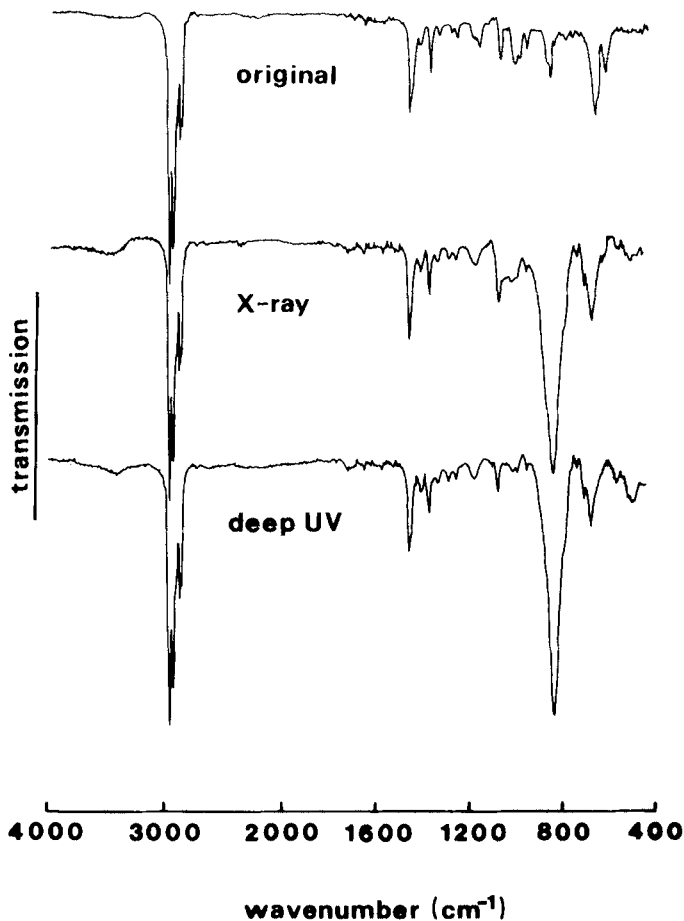


Fig. 1. IR spectrum changes of polydibutylgermane caused by X-ray and deep UV exposures. Doses of X-ray and deep UV were 2 J/cm^2 and 600 mJ/cm^2 , respectively.

Organopolysilanes also underwent oxidation as a result of X-ray exposure, whose spectrum change was the same as that for the previously reported photooxidation.⁶ Reactive species produced in organopolysilanes during the deep UV irradiation are thought to be silylene or radical fragments.^{7,8} Silylene reacts with oxygen in the atmosphere to produce siloxane structures, probably via silanone intermediates.⁹ We think that the X-ray-induced oxidation of PDBG investigated here proceeds similarly, via radical or biradical species.

Ge—O bonds produced in the exposed film were evaluated from the IR absorbance change. Area intensity of Ge—O absorption was normalized using the spectrum of sufficiently photooxidized film, according to the method used for the evaluation of organopolysilane photooxidation.⁶ A fraction of Ge—O bonds, $f(\text{Ge—O})$, was plotted against the dose in Figure 2, together with $f(\text{Si—O})$ of polymethylphenylsilane (PMPS). PDBG showed much higher reactivity than PMPS.

Accompanied with the oxidation, molecular weights of PDBG and PMPS decreased monotonously as the incremental X-ray dosage. Plots of the reverse

of number average molecular weight (M_n) against the dose showed a linear relationship, indicating that scission of PDBG and PMPS polymer chains was progressed in random process. The probability of scission per M—M bond (M denotes germanium or silicon atoms) per 1 J/cm² was calculated using the following equation:

$$p = (M_{n0}/M_n)/(1 + M_{n0}/w)$$

where M_{n0} is initial M_n and w is molecular weight per M—M unit. PDBG and PMPS having single modal molecular weight distributions were irradiated 0.5, 1, and 2 J/cm². Scission probabilities of PDBG and PMPS were 0.0015 and 0.0012, respectively. PDBG polymer chain was scissored a little more efficiently than PMPS.

In contrast to X-ray-induced reactions of PDBG and PMPS, the photooxidation of PDBG was only a little greater than PMPS as shown in Figure 3. The low glass transition temperature (T_g) of PDBG, ca. -20°C, may help increase reactivity because the produced radicals become more movable. But this factor does not contribute so much to the photooxidation as shown in Figure 3. The large difference in oxidation caused by the X-ray exposure between PDBG and PMPS as shown in Figure 2 is probably due to the higher sensitivity of PDBG to the X-ray.

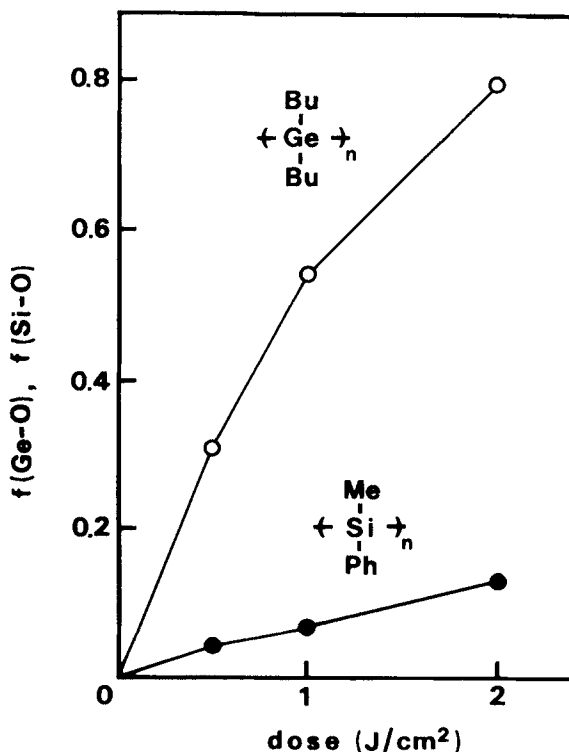


Fig. 2. X-ray dose dependence of the oxidation reaction: (○) fraction of Ge—O bonds in polydibutylgermane; (●) fraction of Si—O bonds in polymethylphenylsilane. Film thicknesses in both cases were ca. 0.6 μm.

PDBG positive resist pattern was able to be fabricated by the deep UV contact exposure and following development with methylethylketone-isopropanol mixture, similarly to organopolysilanes. So, the X-ray lithographic patterning process was applied to PDBG. Mask patterns were transferred using the SR-1 exposure system.⁵ Positive resist pattern was obtained by the X-ray lithography as shown in Figure 4. Thickness loss of the undosed area during the development with tetrahydrofuran-isopropanol mixture was ca. 35% of the initial 0.56 μm thickness. Resist sensitivity D_0 (where the irradiated region is completely removed by the development) was 1 J/cm^2 . The content of Ge—O bonds in PDBG at the dose of D_0 was estimated to be 54% from Figure 2. The positive resist pattern is generally fabricated based on solubility increase in the irradiated area. In the X-ray lithography process for PDBG, the oxidation and the molecular weight decrease are thought to enhance the solubility, as were discussed for the photolithography of organopolysilanes.⁶

Among the X-ray resists reported previously, poly(2,2,3,4,4,4-hexafluorobutylmethacrylate-co-glycidylmethacrylate)(FBM-G) is one of the most sensitive resists, with resist sensitivity of 80 mJ/cm^2 to the Mo L X-ray line.¹⁰ High sensitivity is the most important requirement for X-ray resists, because the incident power of current X-ray exposure systems is markedly low and the throughput directly depends on the resist sensitivity. The resist sensitivity of PDBG was not optimized in this report. However, it seems too difficult to improve it to the level of FBM-G.

CONCLUSION

X-ray-induced reactions and the lithographic application of organopolygermane were discussed. X-ray exposure caused the oxidation of Ge—Ge bonds

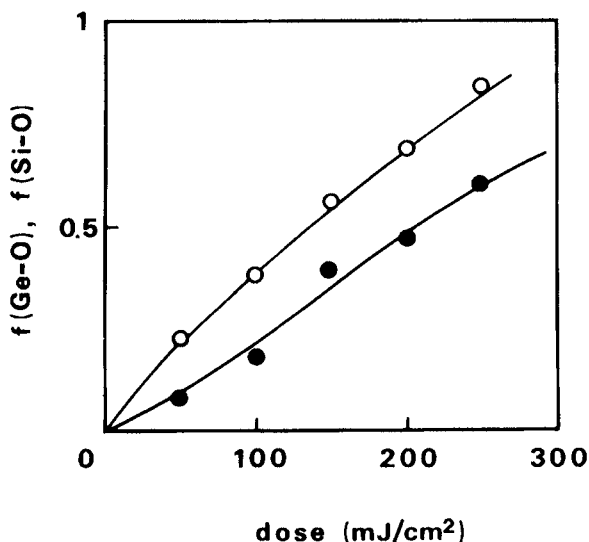


Fig. 3. Deep UV dose dependence of the oxidation reaction: (○) fraction of Ge—O bonds in poly(dibutylgermane); (●) fraction of Si—O bonds in polymethylphenylsilane. Film thicknesses in both cases were ca. 0.3 μm .

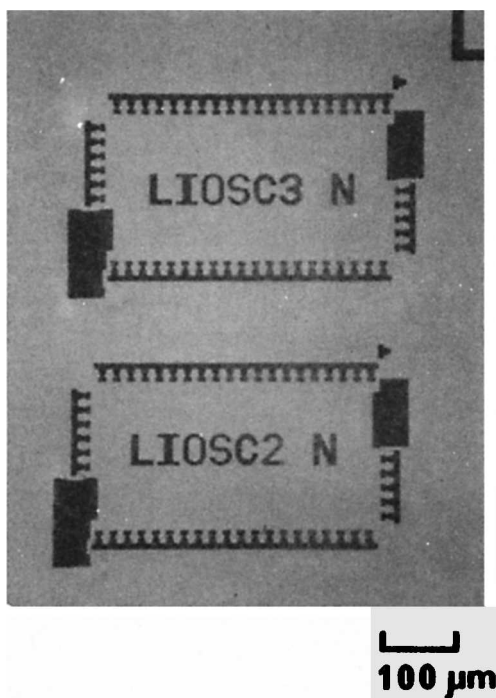


Fig. 4. Photograph of the polydibutylgermane positive pattern fabricated by the X-ray exposure and following development with tetrahydrofuran-isopropanol mixture.

and a molecular weight decrease. These reactions were same as those observed for photo irradiation. PDBG was more sensitive to the X-ray than PMPS. PDBG positive resist patterns was fabricated at a dose of 1 J/cm^2 using the SR-1 X-ray exposure system. Two factors of the oxidation and the molecular weight decrease were thought to contribute to the formation of positive resist patterns.

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Received January 4, 1988

Accepted April 25, 1988