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Oxygen quenching effect in ultra-deep x-ray lithography with SU-8 resist

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Abstract

An ultra-thick (1.5 mm) SU-8 resist was prepared and patterned using synchrotron x-rays. The lithographic sensitivity of the SU-8 resist is over 100 times higher than that of the traditional PMMA resist. However, preliminary results showed that the standard resist process produced poor lithographic quality. The fluorescence induced by high-energy x-ray irradiation was believed to blur the transfer pattern. The lithographic quality improved significantly if the resists were relaxed in an oxygen atmosphere before being soft baked. The FTIR spectrum displayed new absorption peaks, corresponding to the C=O bond, in the oxygen-relaxed resists. The development rates of the low-dosed resists increased if they were held in the oxygen atmosphere, implying that trapped oxygen restrains the cross linking of the SU-8 resist. Based on these observations, this study proposes an oxygen quenching mechanism for interpreting these phenomena. When the SU-8 is oxygen relaxed, the oxygen molecules will gradually diffuse into the resist. Oxygen is a strong free-radical scavenger, and thus kills the free radicals generated by fluorescence, providing a clear pattern defined by x-ray irradiation. After the SU-8 resist was properly oxygen treated, the maximum dimension error was only about 2 μm for a 1.5 mm-thick SU-8 resist. This lithographic quality is good enough to meet the micromachining requirements for mm-wave RF (radio frequency) cavity applications.

1. Introduction

LIGA is an abbreviation of the German words, 'lithographie', 'galvanik' and 'abformung', which mean lithography, electroforming and molding, respectively [1–3]. Highly intense and collimated synchrotron x-rays are used as the light source for deep x-ray lithography (DXL). The LIGA process is then an effective means of fabricating highly precise microstructures with high aspect ratios for use in innovative applications, such as the mm-wave klystron.

A klystron is a high power RF (radio frequency) amplifier for electron acceleration, with applications in radars, satellite communications or synchrotron sources. To reduce the dimension of the klystron for widespread applications, the applied RF frequency must be elevated to increase the acceleration gradient. For example, an acceleration gradient

of 1 GeV/m can be achieved using a 95 GHz RF source. However, the dimension tolerance of the RF cavity becomes critical as the applied frequency is increased. The required thickness of the 95 GHz RF cavities always exceeds 1 mm, but the machining precision and surface quality (R_a) must be less than 2 μm and 0.2 μm , respectively. Among various micromachining processes, the LIGA technique has been identified as the most appropriate method for fabricating an mm-wave klystron [4, 5].

In the DXL procedure, PMMA is always used as the resist because it can yield excellent lithographic quality with high resolution, high precision and low surface roughness. However, PMMA has poor sensitivity to x-ray irradiation. Exposure time over 10 h is always required to pattern a mm-thick microstructure. A multi-exposure scheme has been developed to improve DXL efficiency, but progress in this

area remains limited [6]. The ultimate solution to improve the DXL efficiency is using a highly sensitive x-ray resist.

SU-8 is a negative-tone, chemically-amplified resist that has been extensively used in MEMS applications [7, 8]. The epoxy-based SU-8 resist has excellent thermal and chemical stability, adhesive strength and stress corrosion resistance. SU-8 is normally exposed to a UV light source (i-line, 365 nm); however, Fresnel diffraction raises a difficulty in patterning highly precise, mm-thick SU-8 resists just using UV lithography.

In fact, the SU-8 resist is also sensitive to e-beam and x-ray irradiation. Bogdanov *et al* examined the lithographic behavior of SU-8 under x-ray irradiation [9]. They found that the sensitivity of SU-8 was approximately 70 times higher than that of the PMMA resist. Many researchers have successfully x-ray patterned SU-8 resists with a resist thickness of below 600 μm [10, 11]. However, our preliminary studies show that when the resist thickness exceeds 1 mm, the transferred pattern is blurred for unknown reasons. In this work, a 1.5 mm-thick SU-8 resist was prepared and patterned using synchrotron-radiated x-rays to form mm-wave RF cavities. The possible mechanism yielding poor pattern transfer is proposed and controlled to provide excellent lithographic quality with ultra thick SU-8 resists.

2. Resist process

SU-8 resists with a thickness of 1.5 mm were prepared on a glass substrate. Spin coating was not used; instead, resist with a constant weight was directly poured onto the substrate to prepare a thick resist layer. The resist was then soft baked at 120 °C for 5 h. Since the SU-8 resist has very low viscosity at elevated temperatures, the resist spread all over the substrate to produce a uniform thickness.

SU-8 resist has high sensitivity and contrast compared to PMMA resist [12]; therefore, the resist can be well patterned even using a 'robust' x-ray mask with thick membrane and thin absorber. This fact markedly improves the fabrication yield of the membrane x-ray mask. In this work, an x-ray mask with a wet-etched Si-membrane and electrodeposited gold absorbers was used to transfer the pattern onto the SU-8 resist. The thickness of the silicon membrane and the gold absorber were 20 and 15 μm , respectively.

X-ray exposure was performed at the micromachining beamline of the NSRRC. The electron energy of the synchrotron source is 1.5 GeV, and the characteristic photon energy of the synchrotron radiation is 2.3 keV. Under x-ray exposure, the fluorescence induced from the mask membrane always yields an icing-like film on the top of the developed resist. Thin graphite foil was then placed between the x-ray mask and the resist to absorb the fluorescence. The resists were x-ray exposed through the mask to achieve a minimum dosage of 25 J cm⁻³ [12]. The resists were then post-exposure baked (65 °C, 1 h), ultrasonically developed for 30 min and blown dry for subsequent inspection.

3. Effects of the atmosphere

The preliminary results showed that lithographed SU-8 resists have very poor pattern definition, as illustrated in figure 1(a).

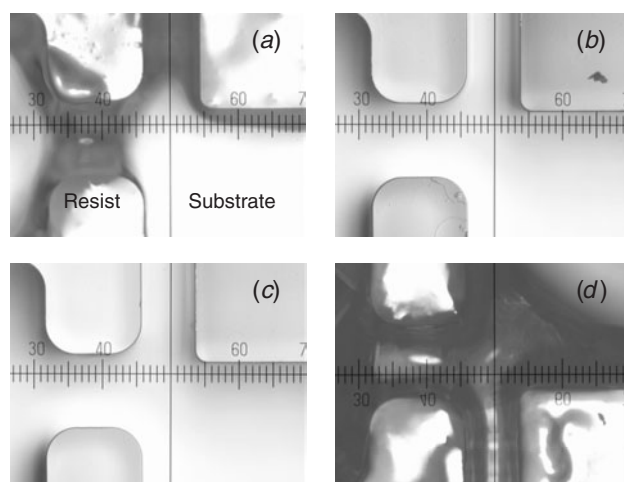


Figure 1. Top view of the SU-8 resists after deep x-ray lithography. The resists were held in air before soft baking for various times: (a) 0 h, (b) 3 h, (c) 6 h and (d) 12 h.

Gel-like resist, which should be removed during development, is observed in the masked area even if the absorber thickness is increased. As is well known, when the SU-8 resist is irradiated by high-energy photons, the photoactive compound (PAC) in the resist undergoes a photochemical reaction and generates a free radical. The radical opens the ring of the SU-8 epoxy molecules, and initiates a cross-linking reaction during the subsequent baking process. However, the high-energy x-rays also cause fluorescence on penetrating the resist. The fluorescence can travel laterally into the masked area and initiate excessive cross-linking of the SU-8 resist. This process may blur the transferred pattern as illustrated in figure 1(a).

If the resists were left in air (at room temperature) for hours before soft baking, then the lithographed resists exhibit better pattern definition, as shown in figures 1(b) and (c). Detailed examination under an optical microscope reveals that the resist left in air for 6 h has the best lithographic quality (figure 1(c)). Further extending the holding time degrades the DXL quality, probably because the resist is too dry to develop, just as when the resist is over-baked (figure 1(d)).

Two possible causes exist for the improvement of DXL quality when the resist is stored in the air before soft baking. One is the mechanical effect: the orientation of the molecules in the resist may change to form a low-stress layer, which helps improve lithographic quality [13]. The other is the atmosphere effect, since the resists were placed in air for hours before soft baking. Gas molecules may dissolve in the resist and thus influence its photochemical reaction.

In order to identify the key factor controlling the DXL qualities, the resists were placed in both N₂ and O₂ atmospheres for 6 h before soft baking. Following the DXL process, the results indicated that the resists held in N₂ atmosphere had poor pattern definition, as illustrated in figure 2(a). In contrast, the resists held in O₂ atmosphere exhibited clear and well-defined microstructures (figure 2(b)). Obviously, the oxygen atmosphere, rather than the mechanical effect, dominated lithographic quality.

The oxygen molecule can be supplied to the resist via diffusion [14]. Under ideal conditions with constant surface oxygen concentration (C_s) and diffusion coefficient (D), the

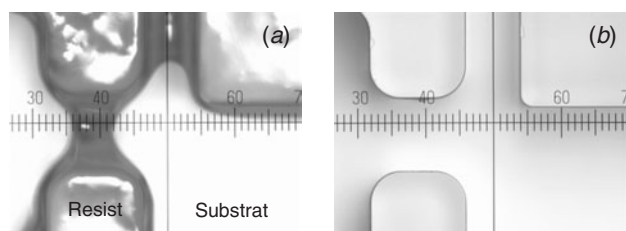


Figure 2. Top view of the SU-8 resists after deep x-ray lithography. The resists were held in (a) nitrogen and (b) oxygen atmosphere for 6 h before soft baking.

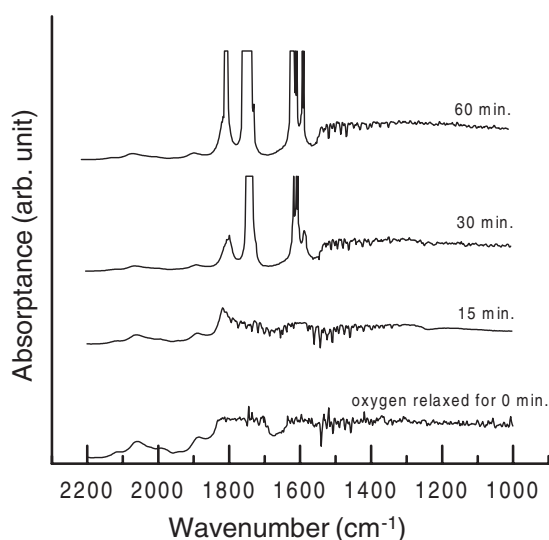


Figure 3. FTIR spectrum of the SU-8 resists for various oxygen-relaxing times.

oxygen concentration (C_z) at a depth of z and a time of t can be solved from Fick's second law as

$$C(z, t) = C_s[1 - \text{erf } Z/2\sqrt{Dt}]. \quad (1)$$

For a reasonable first-order approximation, the diffusion distance Z_c (where $C(z, t)/C_s$ is a constant) can be simply estimated as \sqrt{Dt} . It means when the resist thickness is doubled, the oxygen relaxing time must be increased four-fold.

FTIR was also used to elucidate the effect of the oxygen atmosphere on the chemical properties of the SU-8 resists. In this experiment, the SU-8 resists ($\sim 250 \mu\text{m}$ thick) were spin coated on the IR-transparent KBr substrate and then 'relaxed' in the oxygen atmosphere for various times before soft baking. A conventional UV light source was used to expose the resists to a relatively low dose (approximately one tenth of the standard dosage). The transmission spectra of the resist were then detected at various wave numbers. From figure 3, the FTIR spectra of the resists change when the resists are oxygen relaxed. Some new absorption peaks, at wave numbers from 1590 to 1900 cm^{-1} , appeared and became more pronounced with increasing oxygen-relaxing time. The band positions of the new peaks are correlated with the stretching vibrations of the C=O bond. The analytical results indicate that the oxygen concentration in the resist increased with the relaxing time, and that the oxygen molecules participate in the cross-linking reaction of the SU-8 resists.

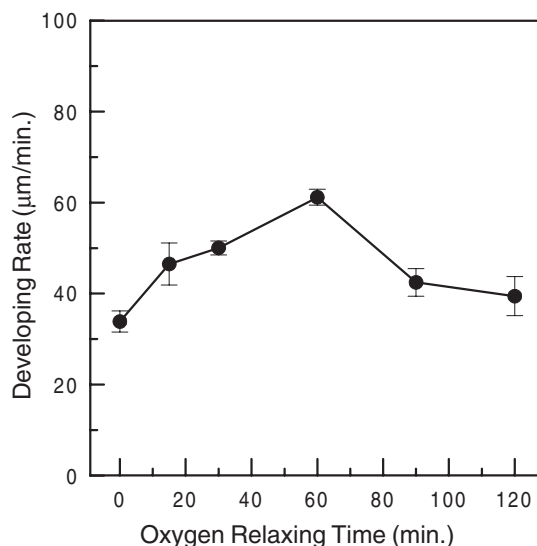
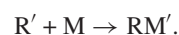


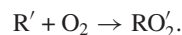
Figure 4. Development rate of the SU-8 resists relaxed in oxygen atmosphere for various times.

The prepared resists were also exposed to a low dose and developed for a short time (3 min) to study the effect of dissolved oxygen on the lithographic behavior of the SU-8 resist. The development rates were then measured and plotted against the oxygen-relaxing time. As plotted in figure 4, the development rate initially increased with relaxing time, but then decreased, probably because the resist was too dry to develop after such extended relaxation. From the figure, the maximum rate of development of the oxygen-relaxed resist is almost twice that obtained without oxygen relaxation. These results imply that the trapped oxygen restrains the cross-linking of the SU-8 resist and then accelerates the development rate.

Similar results were also observed for UV-cured epoxy coating [15]. Normally, the photo initiator in the epoxy generates a free radical (R') under UV irradiation. The radical reacts with the monomer (M) and thus initiates cross-linking:



However, the surface layer of the epoxy coating always remains uncured and tacky after UV irradiation. The dissolved oxygen is believed to suppress the curing reaction of the epoxy because oxygen is a strong free radical scavenger:



Consequently, the dissolved oxygen kills the free radical and then 'quenches' the cross-linking reaction of the epoxy molecules [15]. This effect is especially obvious with high oxygen concentration or low irradiating dosage.

4. Oxygen quenching effect in the DXL SU-8 process

From the above results and discussion, this study proposes a possible mechanism explaining the effects of oxygen atmosphere on the lithographic quality of the DXL SU-8 process. As illustrated in figure 5(a), high-energy x-rays induce fluorescence on penetrating the resist. The fluorescence initiates excessive cross-linking and blurs the pattern transfer in the DXL SU-8 resist process.

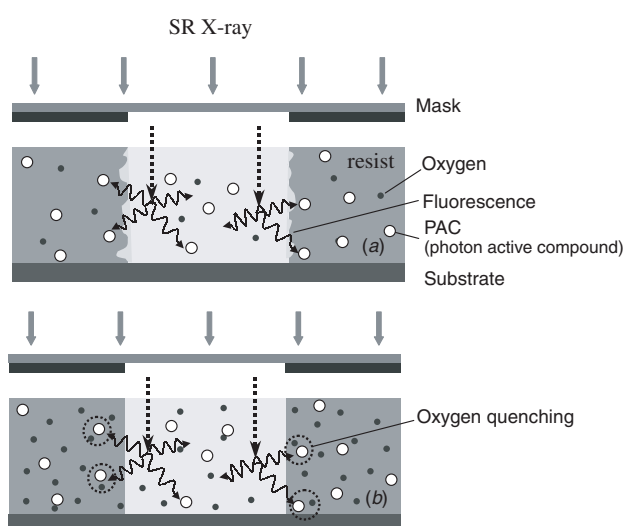


Figure 5. Schematic diagram illustrating the effects of dissolved oxygen on the pattern-transfer quality under x-ray irradiation, (a) low oxygen concentration (b) high oxygen concentration.

If the unbaked resists were exposed to the air for sufficient time, the oxygen slowly diffused into the resist. In the masked area, where a very low dose was deposited, the trapped oxygen effectively suppressed the excess cross-linking reaction induced by fluorescence. However, in the unmasked area, high flux x-rays dominated the results, despite the presence of dissolved oxygen. Accordingly, the oxygen quenching effect helps ensure accurate pattern transfer in the DXL SU-8 process.

5. Ultra-deep x-ray lithography of SU-8 resists

An ultra-thick SU-8 resist (1.5 mm) was prepared and patterned via synchrotron x-rays to evaluate its lithographic quality. The resist processes were as described in section 2, except that all the resists were held in an oxygen atmosphere for 6 h before soft baking. The resists were exposed to synchrotron x-rays to achieve a minimum dose of 25 J cm^{-3} . Aluminum foils of various thicknesses were inserted into the beamline to modify the top dose in the resist. After development, the resists were released from the substrate, and the dimensions of specific resist structures were measured and plotted against the top/bottom dose ratio.

According to figure 6, the lithographic precision of the DXL SU-8 process was approximately $2 \mu\text{m}$. No obvious change in the resist dimensions was observed with changing dose ratio. Since the thickness of the resist is $1500 \mu\text{m}$, the sidewall of the patterned SU-8 resist is quite vertical in relation to the substrate. Our previous studies also showed that the average surface roughness of the DXL SU-8 resist is around 12 nm [12]. These results indicate that the DXL quality of the SU-8 resist is as good as that obtained using a PMMA resist. However, the sensitivity of the SU-8 resist significantly exceeds that of PMMA, meaning the required exposure time can be markedly reduced. For example, only half an hour was required to pattern a 1.5 mm-thick SU-8 resist using the aforementioned light source. However, over 20 h are required to pattern a PMMA resist of the same thickness. This time

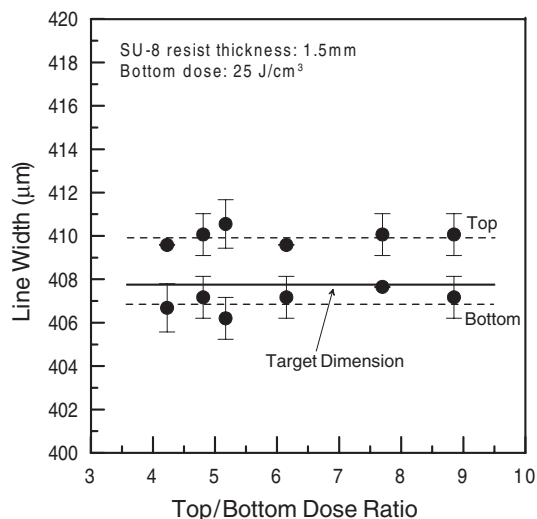


Figure 6. Line width of a specific resist microstructure with various top/bottom dose ratios. All the resists were held in an oxygen atmosphere for 6 h before soft baking.

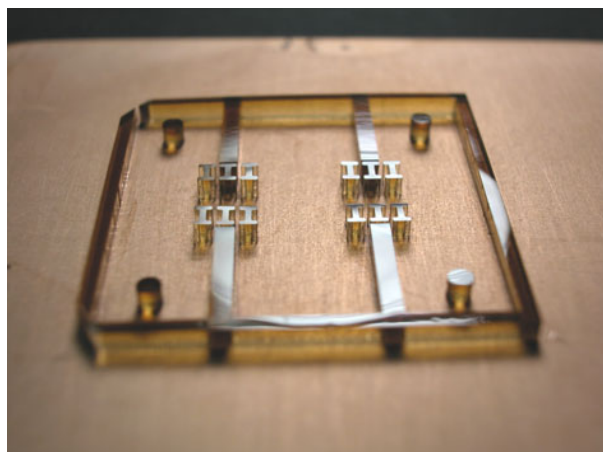


Figure 7. Photograph of a DXL SU-8 resist structure on a copper substrate. The resist is used as a master to electroplate $\text{Cu}/\text{Al}_2\text{O}_3$ for fabricating mm-wave RF cavities.

difference represents a significant advantage since synchrotron radiation is very precious. Figure 7 shows a photograph of a DXL SU-8 resist structure (1.5 mm thick) on a copper substrate. The resist was then used as a master for plating $\text{Cu}/\text{Al}_2\text{O}_3$ composite to create the RF cavities of an mm-wave klystron. Although the cross-linked SU-8 resist is difficult to strip chemically, in this case, the resists may be burnt away by thermal pyrolysis because the cavity is electroplated with a refractory composite material.

6. Summary

This work used deep x-ray lithography to fabricate ultra-thick (1.5 mm), high-precision RF cavities for mm-wave klystron application. Highly sensitive SU-8 resist, rather than conventional PMMA resist, was used to reduce exposure time. However, preliminary results show that the transferred pattern becomes blurred when the traditional resist process is

implemented. The x-ray-induced fluorescence seems to cause this poor pattern definition.

The lithographic quality improved significantly if the resist was relaxed in an oxygen atmosphere before soft baking. Additional absorption peaks, corresponding to the C=O chemical bond, were observed in the FTIR spectrum of the oxygen-relaxed resists. Oxygen treatment also increased the development rate of the low-dosed resist, implying that the trapped oxygen suppresses the cross-linking reaction of the SU-8 resist. Consequently, if the SU-8 resist is oxygen-relaxed, trapped oxygen might quench the excess photochemical reaction induced by fluorescence, yielding a clear pattern defined by x-ray irradiation. This oxygen quenching effect was applied to improve the lithographic quality of the DXL SU-8 process in this study. The lithography results show that the maximum dimension error is only around 2 μm when a 1.5 mm-thick SU-8 resist is patterned, meeting the critical micromachining tolerance requirements for the mm-wave klystron application.

Acknowledgments

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