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Single-Step Optical Lift-Off Process

A process is described that allows the use of the lift-off metallization technique with ultraviolet exposure of a single layer of ®AZ-type photoresist. The process consists of soaking the resist layer for a predetermined time either in chlorobenzene or other aromatic solvents such as toluene and benzene before or after exposure. After development, resist profiles with overhangs suitable for lift-off metallization are obtained. It appears that removal of solvent and low-molecular-weight resin from the ®AZ resist may be responsible for the observed differential development rates. In addition, the soak time and temperature behavior indicate a diffusion-type process.

Introduction

Optical lithography is still used as the main tool in microcircuit fabrication, and very likely will continue to be used for at least the next ten years, even though the minimum linewidth that can be reproduced reliably is ≈ 2 μm. Even at this linewidth, metallic conductor patterns with metal thicknesses of ≈ 1 μm cannot be produced reliably by conventional wet-etching techniques. Reactive ion etching (RIE) methods may prove useful; however, additional process development is required before such methods can be introduced into the manufacturing environment.

An additive metallization technique, known as "lift-off" [1], was developed with the advent of electron-beam (e-beam) lithography in the late 1960s. This technique allows metallization *after* resist exposure and development, and utilizes the fact that electron scattering in the resist and backscattering from the substrate create a pear-shaped energy absorption profile in the resist. This absorption results in an undercut profile after resist development. With this undercut in the resist image, metal can be evaporated over the entire surface, and a discontinuity is maintained between the metal on the substrate and the metal over the resist, as illustrated in Fig. 1 (right-hand portion). During removal of resist in a suitable solvent, the metal over the resist is also removed and a clean and faithful reproduction of the image is obtained in the metal. This technique has been used in IBM and many other companies with polymethylmethacrylate (PMMA) electron resist for the fabrication of devices and circuits with minimum dimensions down to 0.07 μm [2–5]. An additional advantage of the lift-off technique is that multilevel metal structures can be formed and in fact any material or combination of materials that can be evaporated can be used.

• *Application of the lift-off process in optical lithography*

One of the main reasons for the success of the lift-off process in e-beam lithography is the fact that the energy absorption in the resist film during exposure is not linear, but reaches a maximum at about two-thirds of the beam penetration range [6, 7]. This ensures that, with proper exposure and development, undercut resist profiles can easily be obtained [8]. In optical (uv) exposure of photoresists, however, energy absorption is highest at the top of the resist film and lowest at the interface between the resist and substrate because of attenuation of uv light in the resist. In addition, standing-wave effects created by light reflected off the substrate further complicate the situation [9]. These exposure conditions make it impossible to obtain undercut or even vertical resist profiles with normal uv exposure of ®AZ-type positive photoresists [10].

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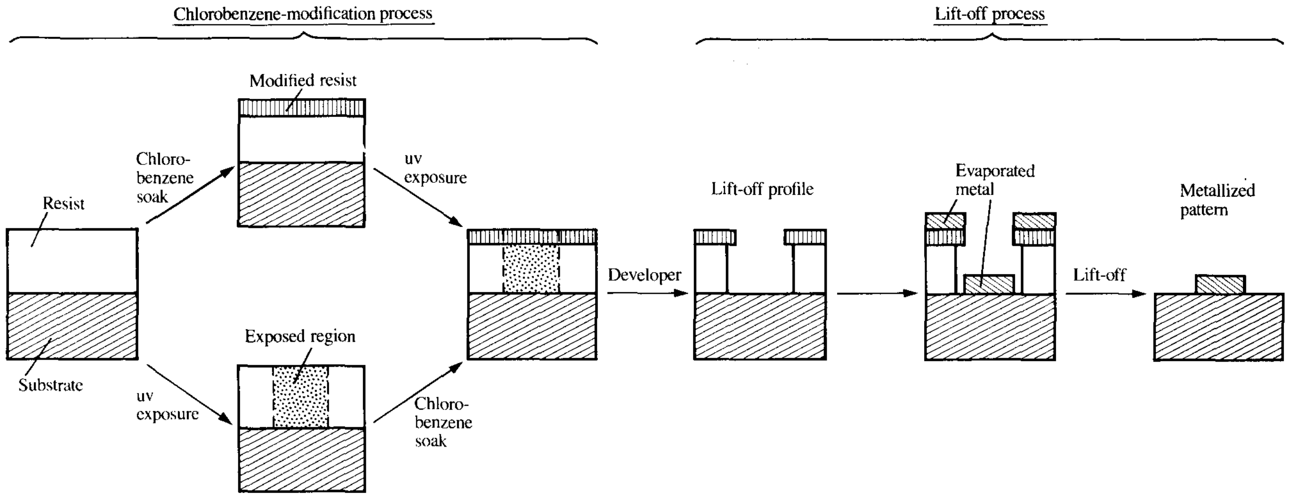


Figure 1 Schematic of the lift-off and chlorobenzene modification processes.

A technique that has been used successfully in e-beam lithography to increase resist sensitivity while maintaining the undercut feature of the developed resist consists of applying a coating of two or more resist layers with widely different solubilities. After e-beam exposure, a developer is chosen that develops the top layer at least ten times slower than the bottom layer. Alternatively, two mutually exclusive developers can be used for the successive development of the two layers [11]. Both of these approaches result in resist profiles suitable for lift-off metallization. With optical ®AZ-type resists, however, it is difficult to spin-coat two distinct layers without excessive mixing at the interface because of the low prebake temperatures these resists require between the coatings. The ®AZ resists should not be baked above 90°C. [This is in contrast to electron resists such as polymethylmethacrylate (PMMA), which can be baked at up to 170°C without deterioration.] The resist film, because it retains a large amount of solvent at this low temperature, can be easily redissolved by application of the second layer.

Recent work has concentrated on methods for obtaining undercut profiles using a single layer of uv-exposed ®AZ photoresist by means of surface modification before or after exposure; see Fig. 1. This work led to the development of a chlorobenzene-soak process with ®AZ-1350J photoresist (see for example Ref. [12]). For details of the basic process see Ref. [13]. The thickness of the top modified-resist layer depends on the prebake temperature of the resist and the soaking time in chlorobenzene. Wafers can be soaked in chlorobenzene *after* or *before* uv exposure. Although equally successful, exposure after soaking requires a longer soaking time.

Experimental procedures

In order to fully characterize the process and to determine its sensitivity to variations of such parameters as prebake temperature and time, soaking time, exposure density, developer concentration, etc., tests were run on silicon wafers using ®AZ-1350J photoresist.

The effect of the soaking time in chlorobenzene on the modified ®AZ-layer thickness was measured by coating silicon wafers with ®AZ-1350J resist to a thickness of 1-2 μm, prebaking at a certain temperature and time, and exposing a pattern in a contact printing system through a chrome mask. After exposure, the wafers were soaked in chlorobenzene for various time periods, developed for a fixed time, and prepared for observation by scanning electron microscope (SEM). The thickness of the modified layer (overhang) was measured in the SEM for every sample at the point where it joins the profile of the main resist layer.

Figure 2(a) shows the modified layer thickness for ®AZ-1350J prebaked at 70°C for 15 min developed in 1:1 ®AZ developer-water *vs* the chlorobenzene soaking time. The resist modification rate is almost linear with time with an approximate value of 80 nm/min. The modification rate was also verified in the Film Thickness Analyzer (FTA), which measures resist thickness as a function of time in the developer (solubility curves) [14], as shown in Fig. 2(b). Curve 1 shows the development characteristics of unsoaked resist exposed at 404.7 nm with a dose of 60 mJ/cm^2; Curve 2 is for a 5-min chlorobenzene soak; and Curve 3 is for a 10-min soak. These curves indicate that the development rate of the modified layer, even in the

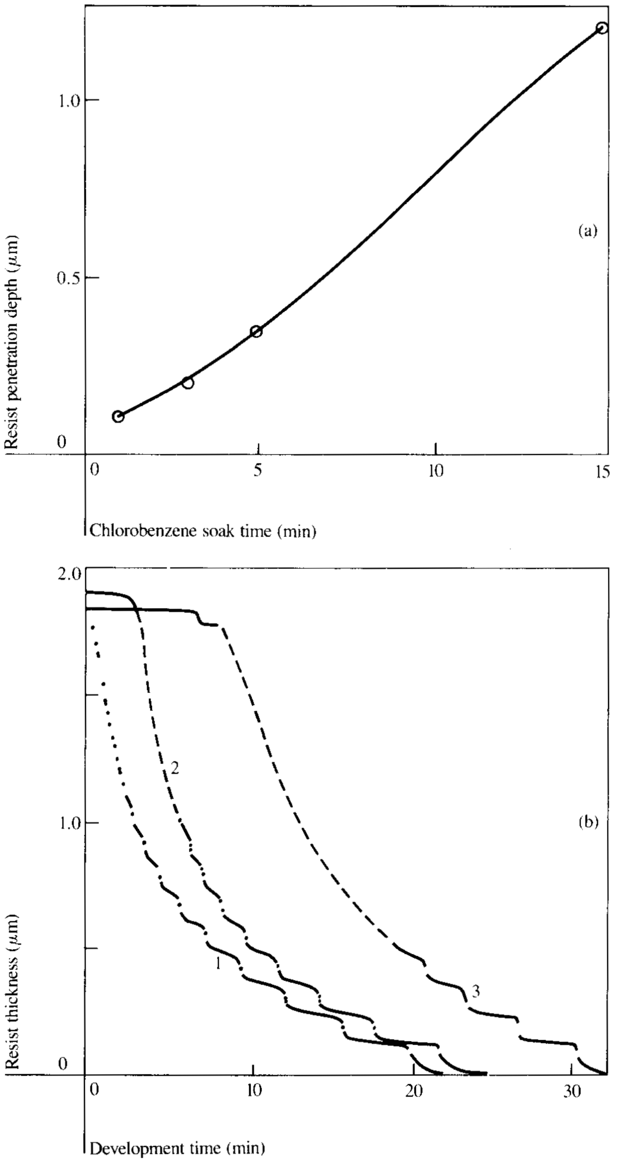


Figure 2 (a) Surface modification rate of ®AZ-1350J resist in chlorobenzene. (b) Development rates obtained in the Film Thickness Analyzer (FTA); 2-min exposure. Curves 1, 2, and 3 are for 0-, 5-, and 10-min chlorobenzene soaks.

exposed regions of the resist, is very slow until the interface between the unmodified and modified layers is reached. At this point, development proceeds at the normal rate of an unsoaked resist.

Figures 3(a–d) show examples of the precision obtainable for metallized structures using a 5-min chlorobenzene soak either before [Figs. 3(a, b)] or after [Figs. 3(c, d)] development. Figures 3(a, c) are before lift-off; Figs. 3(b, d) are after lift-off. In these examples, a 1.5-μm-thick film of ®AZ-1350J was baked at 70°C for 15 min, exposed for 1 min, and developed in a 1:1 solution of ®AZ developer-water. Finally, a 0.5-μm [Figs. 3(a, b)] or 1.0-μm [Figs. 3(c, d)] layer of aluminum was evaporated on top.

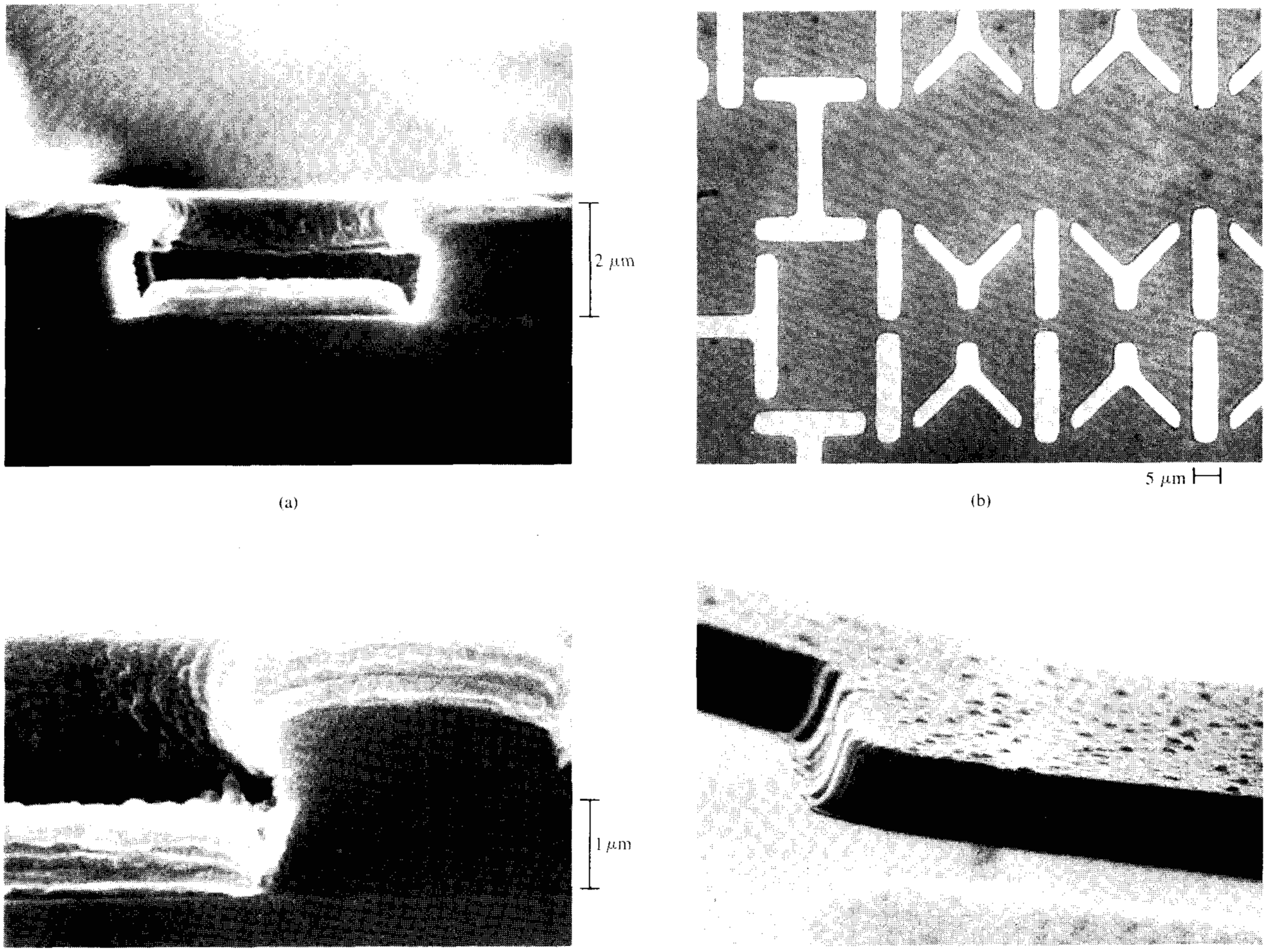
Figures 4(a–c) show the effect of exposure dosage on the shape of the chlorobenzene-soaked (5 min, after exposure) ®AZ-1350J profile. At higher exposure the main resist profile (the *foot* or bottom layer) becomes more vertical, whereas the overhang (top layer) is unaffected. The results with other solvents (5-min soak) are summarized in Table 1. Only toluene and benzene showed any effect, and the effects were not nearly as dramatic as that obtained with chlorobenzene.

Soaking in chlorobenzene prior to uv exposure was also tried with ®AZ-1350J and 1:1 ®AZ-1350 developer-water. Good overhangs could be obtained but the soaking times had to be doubled for the same overhang thickness obtainable by soaking after exposure. Better profiles could also be obtained for all soaking conditions in chlorobenzene if some Alnoval resin [15] was added to the ®AZ-1350J resist in amounts equal to approximately 10–20% of the amount present in the resist.

The chlorobenzene soak (or single-step optical lift-off process) has been practiced with the ®AZ-1350J, with or without resin added, in order to test the reproducibility of the process. The reproducibility appeared very good under these conditions, although no systematic study of linewidth tolerance was undertaken at this time. The chlorobenzene process with ®AZ-1350J resist has in fact been successfully used in IBM for the fabrication of Josephson test circuits [12].

Further investigation of the surface-modification process

The fact that the thickness of the modified ®AZ layer after soaking in chlorobenzene or other aromatic solvents depends on the soaking time tends to indicate that the process is controlled by the diffusion rate of the solvent in the ®AZ layer. This hypothesis is also supported by the fact that the modified-layer thickness depends on the resist prebake conditions. At higher prebake temperatures, the resist molecules are more tightly packed and the solvent diffusion rate is reduced. Figure 5 shows the modified-resist layer (overhang) thickness as a function of soaking time for three resist prebaking temperatures. For a 30-min 66°C prebake, the diffusion rate is three times higher than that for a 80°C bake for *any* soaking period. Figure 6(a) shows the overhang thickness as a function of prebake time at a constant temperature of 75°C and a constant soak time of 17 min. Figure 6(b) shows the same thickness as a function of the prebake temperature with a constant chlorobenzene soak time of 17 min. There is a linear



(a) (b) (c) (d)

Figure 3 Precision of metallized structure for optically exposed ®AZ-1350J resist, 1.5 μm thick, baked at 70°C for 15 min and exposed 1 min; 5-min chlorobenzene soak *prior to* development, 0.5 μm Al, (a) before and (b) after lift-off. (c) Chlorobenzene soak *after* development, 1.0 μm, before and (d) after lift-off.

dependence of the modified-resist layer thickness on soaking time, prebake temperature of the resist, and baking time. The very strong dependence on prebake temperature is illustrated by the steep slope in Fig. 6(b). In order to test the chlorobenzene-diffusion theory further, the assumption was made that if solvents similar to chlorobenzene but different in molecular size were used, the diffusion rate should be higher for the smaller-size solvent. Fluorobenzene, bromobenzene, toluene, and kerosene were tried. Surprisingly, the largest molecule (bromobenzene) produced a thicker overhang than the fluorobenzene (smallest molecule); see Fig. 7. For ®AZ-1350J and 1:1 ®AZ developer-water, toluene also produced an overhang, similar to that obtained for fluorobenzene. Figure 8 shows SEMs of ®AZ-1350J soaked in toluene for 10 min, developed in a 5% solution of 1:1 ®AZ developer-water at resist prebake temperatures varying from 65°-100°C for 10 min. Here, the length and thickness of the overhang decrease as the prebake temperature increases. These results are consistent with results from chlorobenzene soaking, except that the soaking times required to produce the same overhang thickness are longer for the toluene case. Also, in order to test one hypothesis that the chlorobenzene remains in the pores of the resist, thereby blocking developer attack, one wafer was processed as discussed previously, except that the resist was baked at 70°C for 15 min prior to development. If this hypothesis were true, baking should drive off the chlorobenzene and thus reverse the effect of soaking. The test, however, showed no deterioration of the overhang (*i.e.*, no increased solubility of the treated resist layer) after development and in fact indicated a slight improvement.

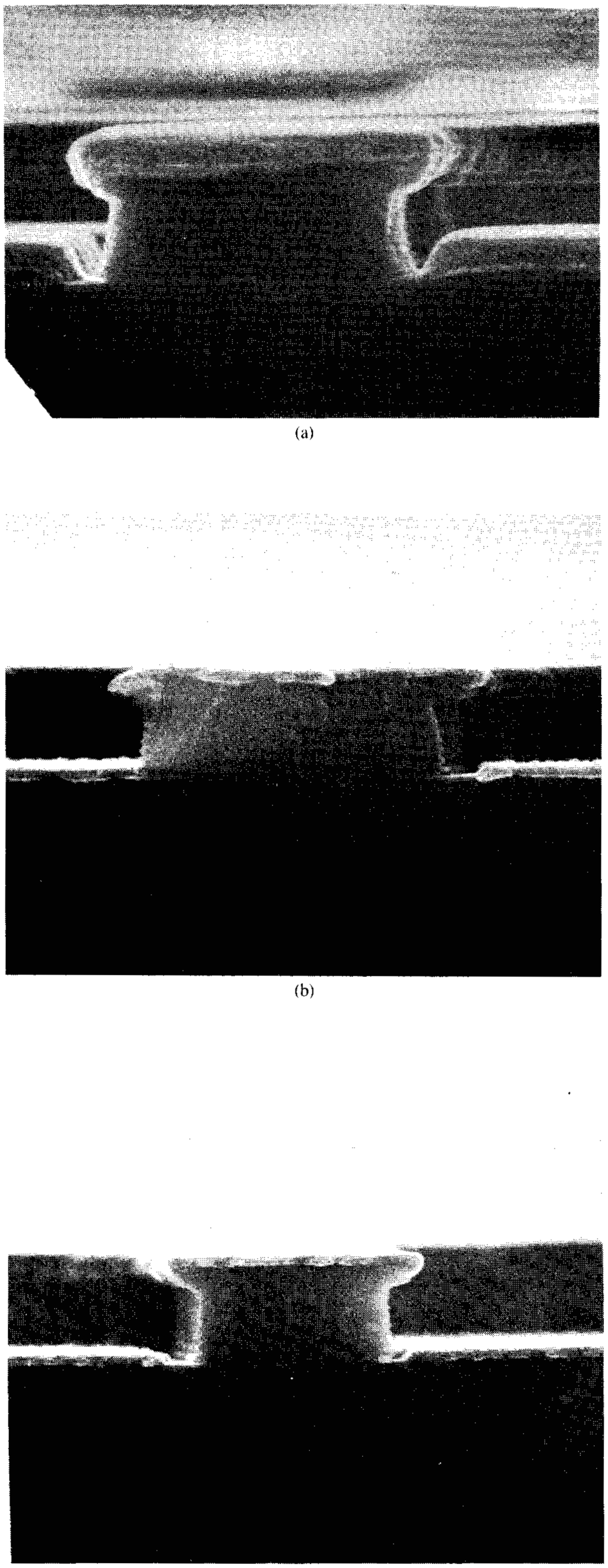


Figure 4 ®AZ-1350J resist (1.5-μm-thick) profiles prior to lift-off at exposures of (a) 0.5, (b) 1, and (c) 2 min, with constant soak (5 min) and development (2 min) times.

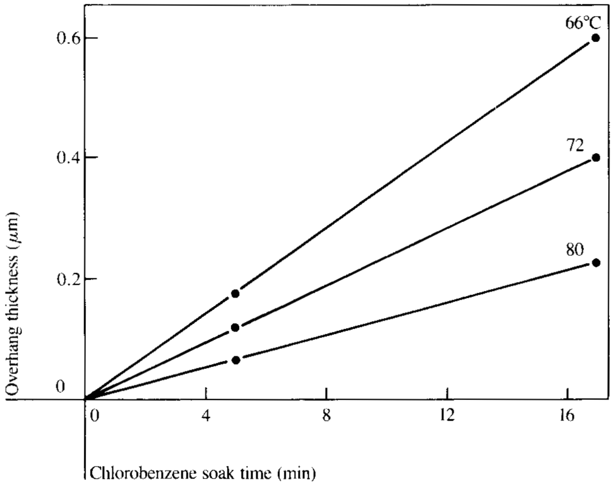


Figure 5 Modified ®AZ-1350J resist layer (overhang) thickness as a function of the chlorobenzene soaking time for three resist prebake temperatures; resist baked in air for 30 min.

Additional efforts to explain the phenomenon were undertaken by separately studying the two ®AZ resist components, the photoactive compound (PAC), a diazo oxide, and the Alnoval resin. Infrared and ultraviolet spectra of the two components were obtained separately before and after soaking in chlorobenzene for up to 16 h. No detectable differences were observed in any case, except for some residual chlorobenzene, indicating that there was no chemical reaction between chlorobenzene and the resist components. Similar tests with exposed and unexposed ®AZ-1350J resist produced the same results. In addition, we could not detect any significant shift or intensity change in the OH absorption in either the PAC or the resin due to possible hydrogen bonding of the resist components and the chlorobenzene.

In order to test the effects of soaking on the Novolak-type ®AZ resin without the PAC, solutions of both Alnoval and Varcum [16] resins were prepared with ®AZ thinner and other solvents. These polymeric solutions were coated on silicon wafers and developed in the FTA, using 1:1 ®AZ developer-water solutions. Another group of wafers was soaked prior to development in toluene for 15 min and then developed in the FTA. The normal development time for the unsoaked Alnoval resin in ®AZ thinner and ethyl-™Cellosolve-acetate (Cellosolve is a trademark, Union Carbide Corp.) was approximately 2 min for a 700-nm-thick film. When the same resin was soaked in toluene, there was no thickness loss during development for 7 min, at which time the film lifted off the surface of the wafer due to poor adhesion. The normal development time of the Varcum resin was slightly faster ($\approx$1.25 min). The toluene-soaked samples showed no thickness loss for 3.5 min of development (half of the time required

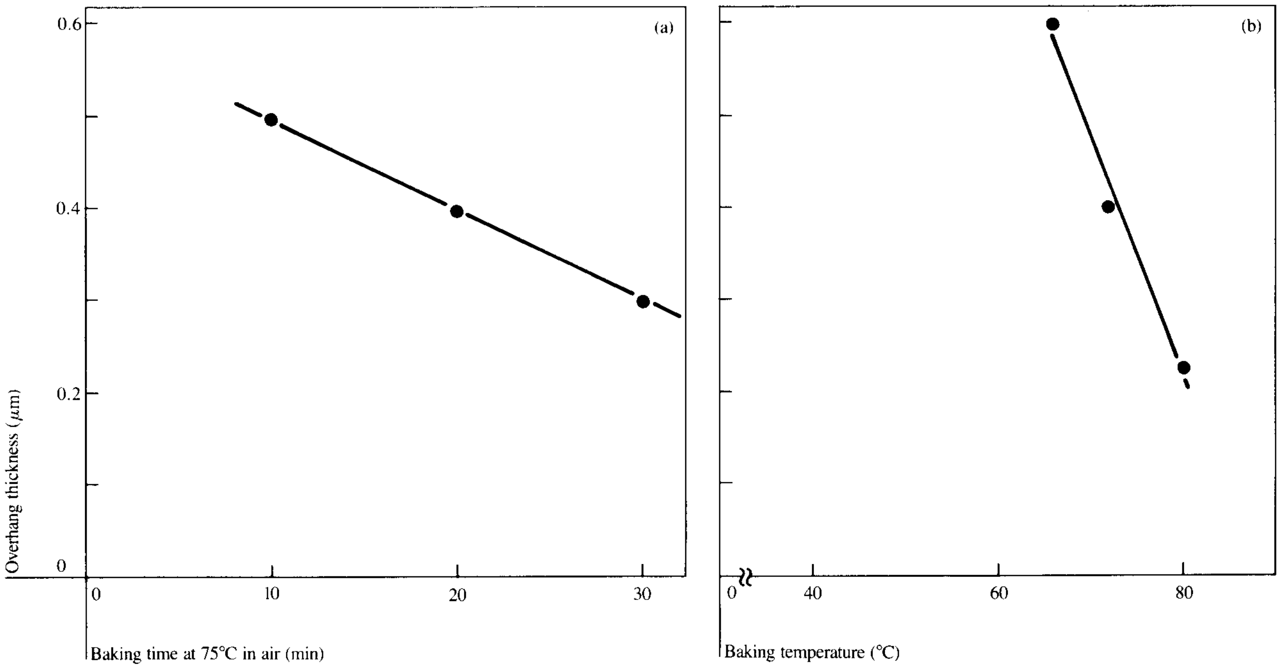


Figure 6 Overhang thickness as a function of resist prebake (a) time at 75°C and (b) temperature for 30-min bake. Chlorobenzene soaking for 17 min.

for ®AZ resin). These results indicate that the resin may be partially responsible for the effects of soaking ®AZ resists in chlorobenzene or other aromatic solvents.

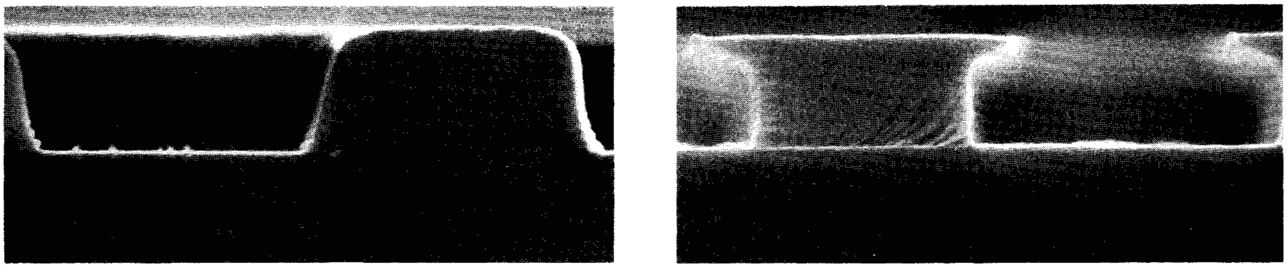
Mass spectrometry and gel permeation chromatography were used to study the effects of a solvent soak on the resin films. The mass analyses were performed on a computer-controlled high-temperature mass spectrometer system. A 1-μm film of Alnoval resin, coated on a silicon substrate and prebaked at 70°C for 30 min, was soaked in bromobenzene for 20 min. The sample was placed in the mass spectrometer and heated from 70° to 170°C at a rate of 1°C/min. Similar studies on unsoaked ®AZ-1350J [17] and Alnoval resin films indicated that for a 70°C prebake, the films contained 10% by weight cellosolve acetate as residual casting solvent. However, the results of the mass analysis of the bromobenzene-soaked resin films showed that all of the cellosolve acetate and 90% of the low-molecular-weight monomers and dimers (MW = 107 and 288) had been removed.

Gel permeation chromatography (Waters liquid chromatograph, Styrogel column [18]) also showed that the chlorobenzene-soluble fraction of the Varcum resin contained low-molecular-weight fractions, while the residue contained the high-molecular-weight species.

Table 1 Effect of alternate solvents on ®AZ-type resist profiles.

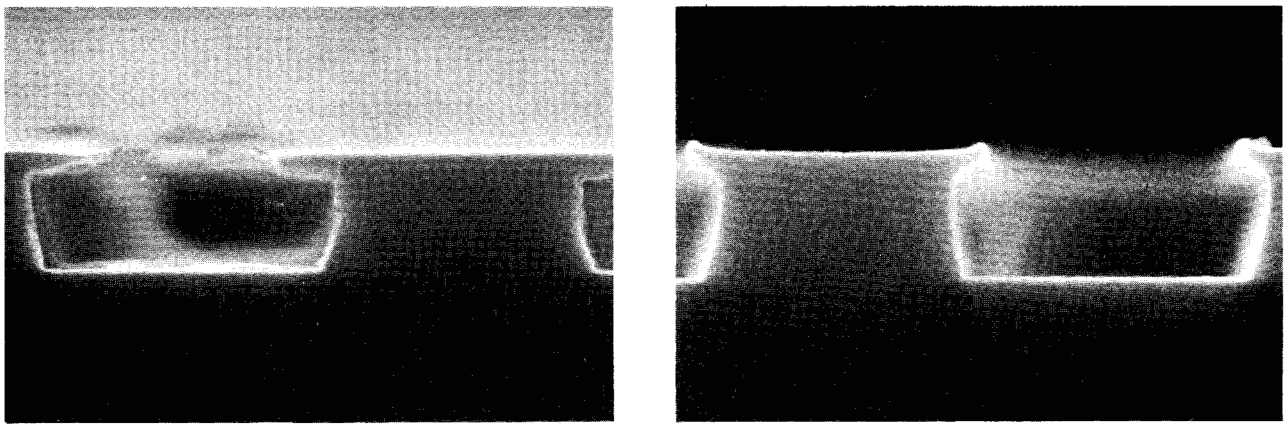
Solvent	*Observed effect*
Trichloroethylene	None
Benzene	Straight edges, no overhang
Toluene	Very small overhang
Methylcyclohexane	None
Ethylene glycol	None
Chloroform	No development possible
Cyclohexanone	Dissolves resist
Ethyl acetate	Dissolves resist
Kerosene	None

The amount of solvent and the molecular weight distribution of the resin affect the development properties of the photoresist film. It has been shown that removing solvent in resist films by increasing prebake temperatures decreases both the thicknesses and the development rates of the films [19]. It has also been shown, by using the FTA to monitor *in situ* development, that Varcum resin previously washed in chlorobenzene and spin-coated onto a Si wafer will develop at a rate that is 2.5 times slower than a film spun from resin that has not had low-molecular-



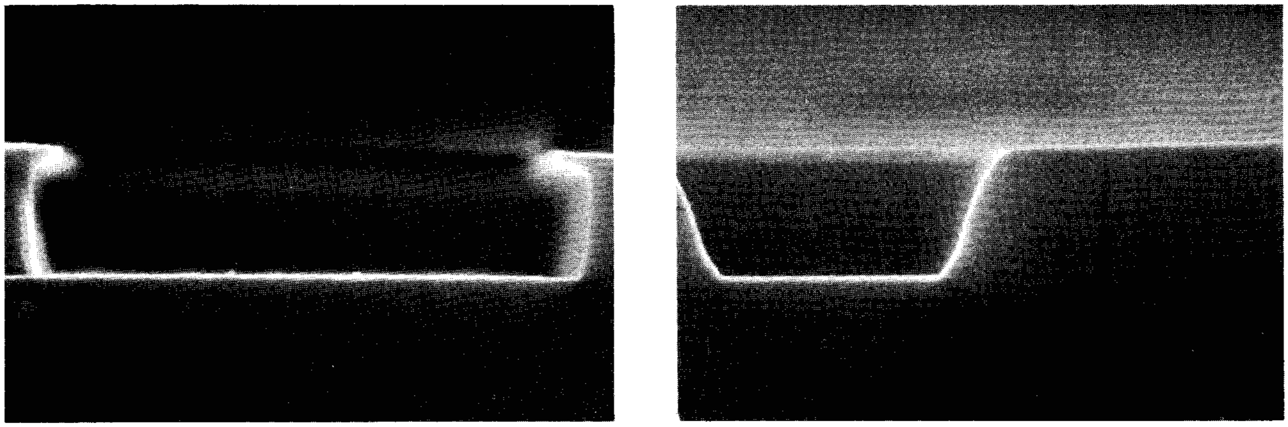
No soaking

Bromobenzene



Chlorobenzene

Toluene



Fluorobenzene

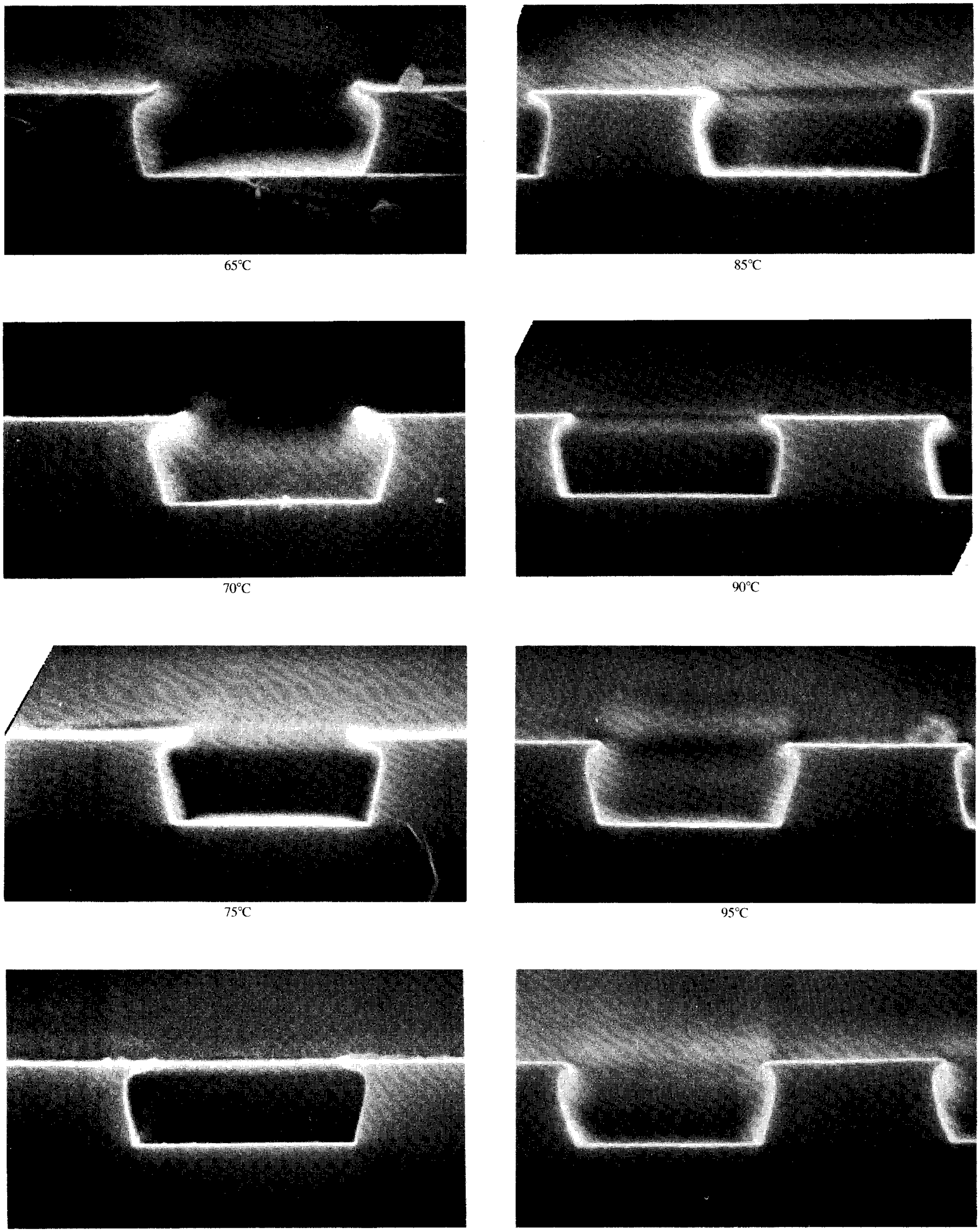
Kerosene

Figure 7 Profiles of ®AZ-1350J resist soaking in various aromatic solvents for 10 min and developed in 1:1 ®AZ developer-water.

weight species removed by solvent washing. It therefore seems likely that diffusion of the resist-developing solution and subsequent solubilization of the resist film are affected by removal of the solvent and low-molecular-weight resin. By removal of what in effect are plasticizers, the chlorobenzene soak creates a dense surface layer less susceptible to developer attack. The post-bake process causes further densification and improvement of the profile.

Conclusions

A new process has been proposed and tested for obtaining undercut profiles suitable for lift-off metallization with uv exposure systems and ®AZ-type photoresists. The process has been tested with ®AZ-1350J photoresist and a chlorobenzene soak, followed by development in 1:1 ®AZ developer-water. Two process variations include the use of a toluene presoak (instead of chlorobenzene) and soaking in chlorobenzene *before* (rather than after) uv ex-



65°C

85°C

70°C

90°C

75°C

95°C

80°C

100°C

Figure 8 Profiles of ®AZ-1350J resist (1.5 μm thick) prebaked at various temperatures for 10 min, soaked in toluene for 10 min, and developed in 1:1 ®AZ developer-water.

posure. This process has been practiced in IBM for Josephson device lithography. Studies conducted so far indicate that the chlorobenzene removes residual solvent and low-molecular-weight resin, thereby reducing the solubility of the modified layer in the developer solution.

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