

Supercritical drying for water-rinsed resist systems

Hideo Namatsu^{a)}

NTT Basic Research Laboratories, 3-1 Morinosato Wakamiya, Atsugi-shi, Kanagawa 243-0198, Japan

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Two methods of supercritical resist drying (SRD) using CO₂ have been developed for water-rinsed resist patterns. The key to their effectiveness is the use of a surfactant. In indirect SRD, a solution of *n*-hexane, a CO₂-philic liquid, and a surfactant, sorbitan fatty acid ether, first replaces the water, and is in turn replaced with liquid CO₂ before SRD is performed. The addition of a compound with a high hydrophilic-lipophilic balance to the surfactant compensates for the poor miscibility of water in a solution of *n*-hexane and sorbitan fatty acid ether. In direct SRD, which does not require a CO₂-philic liquid, the water is replaced directly with liquid CO₂ containing a surfactant, fluoroether carboxylate, which makes water miscible in CO₂; and then SRD is performed. The excellent results obtained by both methods demonstrate that there is no inherent barrier to the use of SRD on water-rinsed resist patterns. © 2000 American Vacuum Society. [S0734-211X(00)01406-2]

I. INTRODUCTION

To fabricate nanodevices with dimensions less than 100 nm, we need fabrication techniques with increased resolution capabilities. However, increased resolution results in the formation of patterns with a high aspect ratio, which is the ratio of line height to linewidth. One reason for this is that a resist requires a certain thickness when used as an etching mask; and this thickness, which determines the line height, cannot be reduced nearly as much as the linewidth. When the aspect ratio is very high, patterns tend to collapse, primarily because of the capillary force¹ generated when the rinse solution used to wash patterns after development is dried. This force results from the difference between the pressure exerted by the rinse solution remaining between lines and the air pressure that arises during drying. One way to suppress pattern collapse is to reduce the surface tension of the rinse solution, which determines the pressure difference.

Supercritical resist drying (SRD), which is the use of a supercritical fluid to dry resist patterns after rinsing, in principle should not generate any surface tension. This is because, in the phase diagram for the drying process, the phase does not cross the liquid-vapor equilibrium curve; and consequently, there is no liquid-gas interface where surface tension could be generated.^{2,3} The advantages of using carbon dioxide (CO₂) for the supercritical fluid are that the critical point is relatively low and it is very safe.

The conventional supercritical drying process commonly employs alcohol, such as ethanol, for rinsing, which is replaced by CO₂. Alcohol is used because it readily dissolves in CO₂⁴ and is easy to handle. It has been used with good effect to dry fine silicon patterns without any collapse.² But when drying resist patterns, there is an additional consideration, namely, water contamination.³ Moisture in the chamber can cause the acrylate-type resist to swell, because H₂O molecules become seeds for the release of gases from inside the resist film. This results in pattern deformation. By preventing water contamination, resist patterns rinsed with alcohol can be dried without any collapse or deformation.

Thus, we have found that good results can be obtained by drying resist patterns rinsed with alcohol in supercritical CO₂, provided that water contamination is prevented. However, for some resist systems, water itself is used for rinsing, for example, after development in an alkaline solution such as an aqueous solution of tetramethyl ammonium hydroxide (TMAH). This presents a huge problem because water, which causes pattern deformation, is present in great quantities in the drying chamber. The rinse water cannot simply be replaced with CO₂, because water hardly dissolves in CO₂. Furthermore, the water cannot first be replaced with alcohol because most resists requiring a water rinse, like polyvinylphenol-based resists such as NEB-31 and novolac-based resists such as SAL-601, quickly dissolve in alcohol. New techniques are, therefore, required to dry water-rinsed resist patterns in a supercritical fluid.

This article describes two SRD techniques for water-rinsed resists; indirect SRD and direct SRD. The key to their effectiveness is the use of a surfactant, which enables rinse water to be replaced with CO₂. When the proper surfactant is used, both methods can dry water-rinsed resist patterns without any collapse.

II. EXPERIMENT

The samples consisted of a layer of the chemically amplified negative resist NEB-31 (Sumitomo Chemical, Inc.) on a Si wafer. They were prebaked at 105 °C for 4 min, exposed to an electron beam, and postexposure baked at 90 °C for 2 min. Then, they were developed in a 2.38% aqueous solution of TMAH and rinsed with deionized water.

The SRD apparatus is illustrated in Fig. 1. The liquid CO₂ in the cylinder has a purity of 99.99 vol % and a water content of less than 0.005 vol %. The basic SRD process is as follows: First, a wet sample that has just been rinsed is placed in the chamber. Next, the rinse solution is replaced with liquid CO₂. This involves sending CO₂ into the chamber at a pressure of 7.5 MPa, which is the pressure used for supercritical drying, while keeping the temperature at 23 °C. At this temperature, CO₂ is completely liquid at pressures above 6.3 MPa. Then, the temperature is raised to 35 °C

^{a)}Electronic mail: nam@aecl.ntt.co.jp

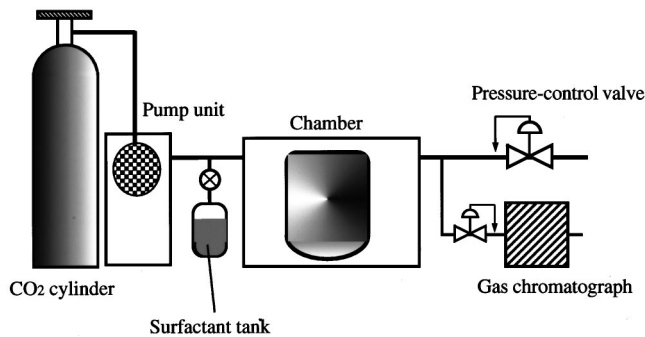


FIG. 1. Apparatus used for SRD studies.

while the pressure is maintained at 7.5 MPa with a pressure-control valve. At this point, the condition becomes supercritical. Finally, the CO₂ is slowly released at a constant rate, and the process is completed when the pressure reaches atmospheric pressure.

The surfactants tested for indirect SRD were obtained from the Kao Corporation. The surfactant used in direct SRD, fluoroether carboxylate, is Kritox-157 from Dupont. The surfactant tank in Fig. 1 was used only for direct SRD.

Gas chromatography was carried out by feeding CO₂ into a hydrogen flame ionization detector through a fused silica capillary column with a nonpolar inner wall. The oven, injector, and detector were kept at a temperature of 150 °C. The detector, which is sensitive to organic compounds but not to CO₂, was used to determine whether or not the CO₂ released contained any organic compounds.

III. RESULTS AND DISCUSSION

A. Effect of H₂O in supercritical resist drying

In SRD, it is important to suppress water contamination, which causes pattern deformation.^{2,3} The contamination results from the condensation of the moisture normally present in the chamber. And the film thickness increases with the amount of H₂O in the chamber. This increase can lead to pattern deformation due to film swelling. There is significant water contamination when the pressure is high.³

However, water contamination was found to be a problem only when the CO₂ was in the supercritical state. Figure 2 shows how the film thickness varies with CO₂ pressure. For CO₂ in the supercritical state (a), the film thickness increases dramatically; while for liquid CO₂ (b), there is hardly any change at all. The increase results from swelling as H₂O molecules become associated with supercritical CO₂ and diffuse into the resist film.^{2,3} The associated molecules do not diffuse into the film when CO₂ is a liquid; but they diffuse easily in the supercritical state because their diffusion rate is very high, like that of a gas. In addition, in the supercritical state, the density of CO₂, which is related to the solubility of H₂O in CO₂, increases with pressure. As a result, supercritical CO₂ under high pressure causes water contamination. Figure 3 shows resist patterns rinsed with alcohol and dried by SRD. Though the sample was covered with alcohol, not water, high-pressure SRD has caused the resist to swell due

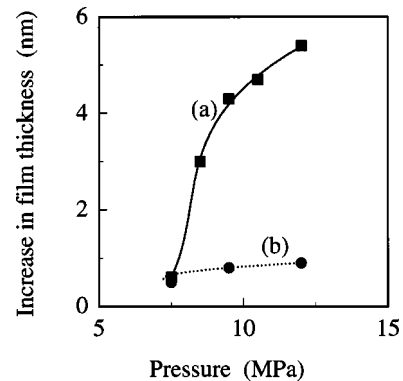


FIG. 2. Relationship between increase in film thickness and pressure of (a) supercritical CO₂ and (b) liquid CO₂. The resist is a 150-nm-thick layer of ZEP-7000B (Nippon Zeon).

to water contamination from moisture in the atmosphere. By suppressing the dissolution of moisture into supercritical CO₂, drying can be carried out without resist swelling.

B. SRD for water-rinsed resist patterns

Since the presence of water strongly affects the results obtained with SRD, as explained above, it is essential to prevent water contamination. However, when water itself is

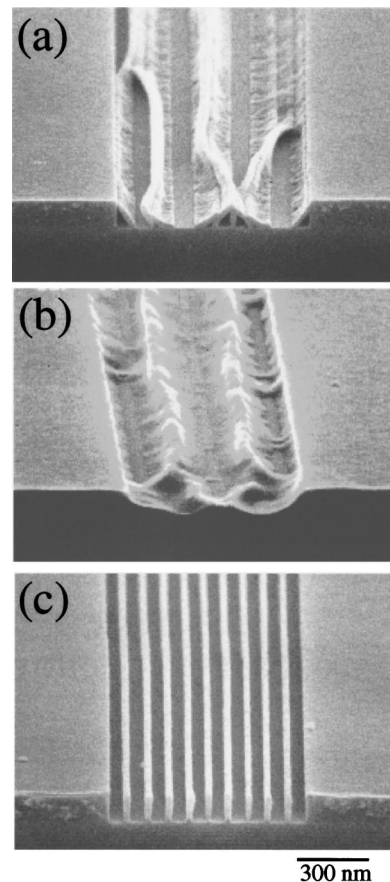


FIG. 3. Resist patterns rinsed with ethanol after drying using (a) nitrogen blow, (b) supercritical CO₂ at 12 MPa, and (c) supercritical CO₂ at 7.5 MPa. The resist is a 150-nm-thick layer of ZEP-7000B.

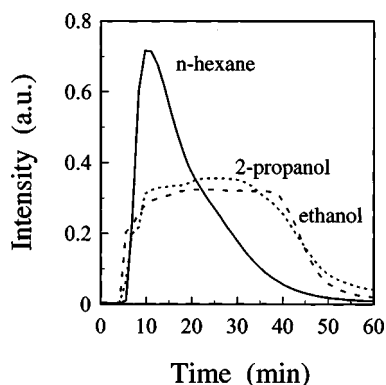


FIG. 4. Efficiency with which various compounds are replaced with liquid CO_2 .

used for rinsing, such as for chemically amplified resists developed in an aqueous solution of TMAH, the presence of large quantities of water cannot be avoided. The hint for solving this problem comes from the data in Fig. 2, which shows that water contamination occurs in supercritical CO_2 , not in liquid CO_2 . So, if CO_2 is introduced in liquid form and the water is removed before the CO_2 is converted to the supercritical state, no water contamination should occur. In this study, two methods of removing the rinse water were developed.

1. Indirect SRD

In order to eliminate water contamination in SRD, an attempt was made to replace the rinse water with another liquid before introducing the CO_2 . The replacement liquid requires the following properties: It should not dissolve resist materials, and it should be miscible in liquid CO_2 . Though polar organic compounds, such as ethanol, are commonly used in supercritical drying, they cannot be used to dry water-rinsed resists because they dissolve the resist. In contrast, nonpolar compounds do not dissolve water-rinsed re-

sists. On the other hand, CO_2 is a relatively nonpolar molecule because it has no dipole moment; so it should be very miscible in nonpolar liquids, but not polar liquids. Small hydrocarbons dissolve especially easily in liquid CO_2 . Figure 4 shows how efficiently various compounds are replaced with liquid CO_2 . The data were obtained by putting a fixed volume of a compound in the chamber at 23°C , injecting liquid CO_2 under a pressure of 7.5 MPa, and feeding the gas released to a gas chromatograph. As can be seen in Fig. 4, *n*-hexane, a small nonpolar compound, is released faster than alcohol; that is, liquid CO_2 replaces *n*-hexane very quickly. The *n*-heptane, which is larger than *n*-hexane, is replaced more slowly than *n*-hexane. So, *n*-hexane is an excellent liquid to use for replacement with liquid CO_2 .

As mentioned above, *n*-hexane does not dissolve water-rinsed resists, such as NEB-31; and it dissolves readily in liquid CO_2 . The one remaining problem is that water is not completely miscible in *n*-hexane. The solution is to use a surfactant, in particular, a nonionic surfactant, which dissolves readily in an organic liquid. The surfactants tested, all of which dissolve in *n*-hexane, are listed in Table I. The hydrophilic-lipophilic balance (HLB) indicates the proportion of hydrophilic groups in a surfactant molecule. When the HLB is large, the surfactant easily emulsifies a mixture of *n*-hexane and water. The maximum HLB obtainable is 20.⁵ Though polyethylene derivatives, such as polyoxyethylene sorbitan monolaurate and polyethylene glycol mono-4-nonylphenyl ether, have a large HLB, they dissolve resists like NEB-31. One type of surfactant that does not dissolve such resists is sorbitan fatty acid ether. Among the ethers in this group, sorbitan monolaurate (SPAN20) has the highest HLB, which makes it the most suitable.

Next, the appropriate concentration of surfactant was examined. To obtain a uniform emulsion, enough micelles must form to enable all the water to disperse in the *n*-hexane. That is, the concentration of sorbitan monolaurate should be the critical micelle concentration (CMC), since excess sur-

TABLE I. Surfactants tested for indirect SRD.

Surfactant	HLB	Solubility in hexane (1%)	Damage to NEB-31 resist
Polyethylenealkylalylether			
Polyethyleneglycol mono-4-nonylphenyl ether (NPE-5)	10.8	good	Dissolved in hexane/water solution
Sorbitan fatty acid ether			
Sorbitan trioleate (SPAN 85)	1.8	good	none
Sorbitan sesquioleate (ARLACEL 83)	3.7	good	none
Sorbitan monolaurate (SPAN 20)	8.6	good	none
Polyoxyethylene sorbitan fatty acid ether			
Polyoxyethylene sorbitan trioleate	11	good	Dissolved in hexane solution
Polyoxyethylene sorbitan monolaurate	13.3	good	Swelled in hexane solution

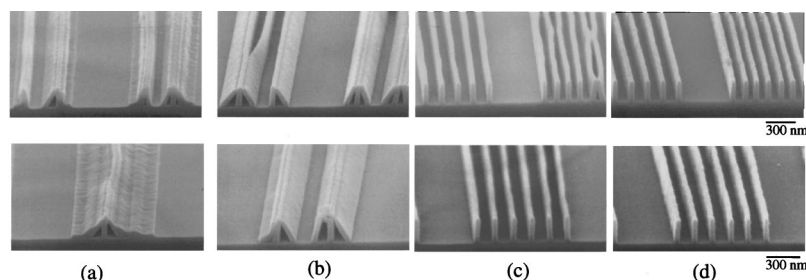


FIG. 5. Resist patterns after drying using (a) a nitrogen blow and (b)–(d) supercritical CO_2 at 7.5 MPa. The resist is a 300-nm-thick layer of NEB-31. The liquid used to replace the rinse water is a solution of *n*-hexane, and sorbitan monolaurate (SL) and polyethylene glycol mono-4-nonylphenyl ether (NPE-5) in several ratios: (b) SL:NPE-5=0.7:0; (c) SL:NPE-5=0.7:0.05; and (d) SL:NPE-5=0.7:0.1. The widths of the lines/spaces are 60/120 and 60/70 nm (top images), and 50/120 nm (bottom images).

factant leaves a residue on the surface of the resist. The CMC was determined by measuring the transmittance of a solution of surfactant and *n*-hexane at a wavelength of 360 nm for various concentrations of surfactant.⁶ The results indicated that the CMC of sorbitan monolaurate was about 0.7 g/100 ml. In subsequent experiments, this concentration of sorbitan monolaurate was used. The relatively small HLB of sorbitan monolaurate was compensated for by using a small amount of polyethylene glycol mono-4-nonylphenyl ether (NPE-5), which does not significantly damage NEB-31 resist patterns.

Figure 5 shows some NEB-31 resist patterns after drying. The patterns were formed by e-beam exposure, development, and rinsing in water. Then, the samples were dipped in *n*-hexane containing sorbitan monolaurate and NPE-5, and subjected to SRD. Various ratios of sorbitan monolaurate to NPE-5 from 1:0 to 7:1 were tested. The figure shows that pattern collapse diminished and finally disappeared as the amount of NPE-5 increased. So, the addition of about 10% NPE-5 to the sorbitan monolaurate sufficiently boosts the miscibility of water in *n*-hexane. These results demonstrate that indirect SRD, which involves treatment with a solution of *n*-hexane and a surfactant, prevents pattern collapse due to the surface tension of rinse water.

2. Direct SRD

The second method is the direct replacement of rinse water with CO_2 , and it also employs a surfactant. In this case, the surfactant molecules must have CO_2 -philic chains and hydrophilic groups. Two well-known types of CO_2 -philic material are fluorinated compounds^{7,8} and methyl silicone compounds.⁹ For example, CO_2 can dissolve more than 5 wt % of fluoroether.¹⁰ So, an appropriate surfactant is a fluorinated or methyl silicone compound with a hydrophilic tail. In this study, fluoroether carboxylate ($\text{F}-(\text{CF}_2\text{CF}_2)_n\text{CF}_2\text{CF}_2-\text{COOH}$) was selected. It is known to form micelles, and the CMC is 3×10^{-5} mol/l.⁷ The ammonium salt of fluoroether carboxylate, which exhibits less interfacial tension in water, could not be used because it damages resist patterns.

The surfactant is supplied from a tank between the pump and the chamber (cf., Fig. 1), and liquid CO_2 with surfactant dissolved in it is fed into the chamber, which contains a water-rinsed sample. After the water is replaced with the liquid CO_2 /surfactant, the chamber is filled with just liquid CO_2 by cutting off the supply of surfactant. Then the chamber is heated to the critical point of CO_2 .

Figure 6 shows NEB-31 resist patterns after drying by this method. Fine resist patterns without any collapse were obtained by treating samples with a solution of liquid CO_2 and surfactant before converting the CO_2 to the supercritical state. In addition, it was found that fluoroether carboxylate did not damage the resist. So, direct SRD is just as effective as indirect SRD in drying water-rinsed resist patterns.

IV. CONCLUSION

Two methods of supercritical resist drying (SRD) that can be used on water-rinsed resist patterns have been developed. The key to their effectiveness is the use of a surfactant, which enables rinse water to be replaced with liquid CO_2 before the actual drying procedure is carried out. One method is indirect SRD, in which rinse water is first replaced with *n*-hexane, a CO_2 -philic compound, containing a surfactant. The surfactant improves the miscibility of water in *n*-hexane; and the best one discovered so far is a mixture of sorbitan monolaurate and a small amount of polyethylene glycol mono-4-nonylphenyl ether. After the solution of *n*-hexane and surfactant replaces the rinse water, it in turn is replaced with liquid CO_2 , and SRD is carried out. In direct SRD, liquid CO_2 containing the surfactant fluoroether carboxylate directly replaces the water, and is in turn replaced with pure liquid CO_2 , which is then turned supercritical for drying. Both methods enable the drying of very fine resist patterns without pattern collapse; and they demonstrate the suitability of SRD for water-rinsed resist systems, which are promising candidates for the next-generation lithography.

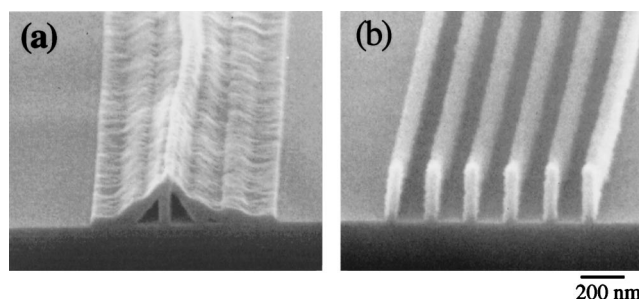


FIG. 6. Resist patterns after drying using (a) nitrogen blow and (b) supercritical CO_2 at 7.5 MPa. The resist is a 300-nm-thick layer of NEB-31. Supercritical drying was carried out after the samples were treated with liquid CO_2 containing the surfactant fluoroether carboxylate. The width of the lines is 50 nm.

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