Amplification of the index of refraction of aqueous immersion fluids with crown ethers

Juan López-Gejo
Joy T. Kunjappu
Nicholas J. Turro
Columbia University
Department of Chemistry
New York, New York 10027

Will Conley
Freescale Semiconductor
Centre de Recherche
870 rue Jean Monnet
Crolles, France

Abstract. There is a current need for high refractive index (RI) materials that can be used in aqueous systems for improving 193-nm immersion photolithography. Although heavy metal salts such as Ca^{2+} and Ba^{2+} have the potential to substantially increase the RI of aqueous solutions, the water solubility of these salts with common anions is often too low to achieve concentrations that significantly increase the RI to the desired values. We therefore investigate the use of crown ethers to enhance the solubility of these cations. Most of crown ethers are soluble in water, are inexpensive materials, and are available commercially. 15-crown-5-ether and 12-crown-4-ether are liquids at room temperature and therefore can be used as neat immersion fluids without dilution in water. Saturation of crown ethers with inorganic salts do not lead to any increase in the refractive index due to their low solubility in such an apolar medium. Thus, the use of inorganic salts as refractive index enhancement agents does not seem to be a desirable proposition in the present case. Instead, the use of crown ethers or their derivatives can be an alternative system, since these compounds have properties such as density, viscosity, and boiling point similar to aqueous media. *© 2007 Society of Photo-Optical Instrumentation Engineers.* [DOI: 10.1117/1.2435730]

Subject terms: second-generation immersion fluids; 193-nm immersion microlithography; refractive index; crown ethers.

Paper 06038R received Jun. 3, 2006; revised manuscript received Sep. 25, 2006; accepted for publication Oct. 4, 2006; published online Mar. 9, 2007. This paper is a revision of a paper presented at the SPIE Conference on Advances in Resist Technology and Processing XXIII, San Jose, California, Feb. 2006. The paper presented there appears (unrefereed) in SPIE Proceedings Vol. 6153.

1 Introduction

The holy grail in optical lithography has been the development of novel materials and processes to push it toward dimensions less than 45 nm. The minimum feature that can eventually be printed with an optical lithography system is determined by the Rayleigh equation.[1]

$$hp = \frac{k_1 \lambda}{\mathrm{NA}},$$

where hp is the 1:1 half-pitch feature size, λ is the lithography wavelength (193 nm), k_1 is a measure of the lithography process capability, and NA is the numerical aperture of the stepper's lens. NA can be defined as

$$\mathrm{NA} = n_{IF} \sin \theta_{\max},$$

where n_{IF} is the immersion fluid's index of refraction at the lithographic wavelength (193 nm) and θ is the aperture angle, which is the angle sustained by the ray of the largest spatial frequency permitted by the optical system. Therefore, hp can be decreased by decreasing λ or by increasing the n_{IF}. As the challenges of shorter wavelength (157 nm) become increasingly difficult, use of immersion-based lithography systems becomes more highlighted.[2] Therefore, in current 193-nm photolithography systems, there is a need to develop new immersion fluids that have a refractive index higher than water with acceptable transparency at 193 nm, since water ($n_{IF}=1.44$) is known as the best fluid for 193-nm immersion systems so far.[3] Recently, second-generation fluids with a refractive index of $\sim$1.6 at 193 nm have been presented, which demonstrated growing interest in this area.[4–6] Some of the developed fluids present some limitations such as high absorbance ($>0.4/\mathrm{cm}$) at the working wavelength[4] or high viscosity.[5]

In previous publications, we have presented the combination of inorganic salts (6-M $CdCl_2$) and surfactants (8.2-mM SDS) as a plausible method of increasing the refractive index of water to be used as an immersion fluid.[7] Following the strategy of adding surfactants to increase the solubility of inorganic salts, a fluid with a refractive index close to 1.6 was identified. Nevertheless, inherent limitations, due to the toxicity of the salt at its high concentration, were found and this limitation is being addressed by us.

In spite of the limitations, the strategy of adding inorganic salts has some positive attributes. For example, the addition of inorganic salts increased the refractive index of the water in an effective manner, maintaining other important physical properties such as density, and viscosity almost intact, but the final value is limited by the solubility of the salt. In this work, a combination of $BaCl_2$ and crown ether was studied as a possible candidate to increase the refractive index of aqueous immersion fluids. Large cations

1537-1646/2007/$25.00 © 2007 SPIE

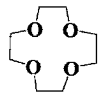
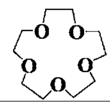
12-Crown-4-ether (12C4) 	15-Crown-5-ether (15C5) 
Physical Data	
FW = 176.21 Boiling Point = 255 °C Flash point = 120±30 °C Density = 1.089 g/ml at 25 °C Melting point = 16 °C	FW = 220.26 Boiling Point ≈ 350 °C (cal. value) Flash point = 139 °C Density = 1.109 g/ml at 25 °C

Fig. 1 Structure and physical properties of 12C4 and 15C5.

such as Ba^{2+} or Cs^{1+} are more polarizable than smaller ones on the top of the group in the Periodic Table. Thus, at equal concentrations of inorganic salt, the increase in the refractive index is higher for $Ba^{2+} > Sr^{2+} > Ca^{2+}$. Nevertheless, the solubility decreases with the size of the ions. The goal of this study is to increase the solubility of $BaCl_2$ and therefore increase the refractive index with the minimum amount of salt.

Large anions are more effective in increasing the refractive index than are small ones, but at the same time they present a high absorption. Therefore, Cl^- was chosen as the cation, though it is not effective in increasing the refractive index.

Crown ethers are well-known complexation agents[8] used for the selective elimination of cations from water. In particular, 15-crown-5-ether (15C5) forms a very stable complex with the Ba^{2+} in aqueous solutions[9,10] and organic solvents.[11–13] In addition, 15C5 and 12C4 are liquids at room temperature with similar densities as that of water and viscosities (Fig. 1).

Here, advantage is taken of the fact that $BaCl_2$ is nontoxic compared to the elevated toxic levels of $CdCl_2$.

2 Analytical Techniques

2.1 *Refractive Index*

For exploratory work in the visible region, an Abbe refractometer (Bausch and Lomb) coupled with a thermostatic bath was used. All measurements presented in this work were made at 20 °C. For the refractive index measurements along the whole spectral region of potential candidates selected after the preliminary screening, a spectroscopic ellipsometric technique was used in a Woollam M-2000 variable angle spectroscopic ellipsometer. The ellipsometric parameters Ψ and Δ were fit to a Cauchy model using the Woollam WVASE32 software. The fluids were measured by filling a 2-in.-diam Fluoroware cup until a flat surface was obtained, and then leveling the base of the ellipsometer. This ensured that only reflections from the top surface of the fluid were collected and analyzed.

2.2 *Contact Angle*

Surfaces for contact angle measurements were prepared by spincoat techniques. A silicon wafer was used as a substrate and polymethyl methacrylate (PMMA) was deposited as the polymer model. A solution of 0.02 g of PMMA (75,000 MW) in 0.6 g of THF was prepared, and 10 μL of this solution was deposited by spincoat at 3000 rpm.

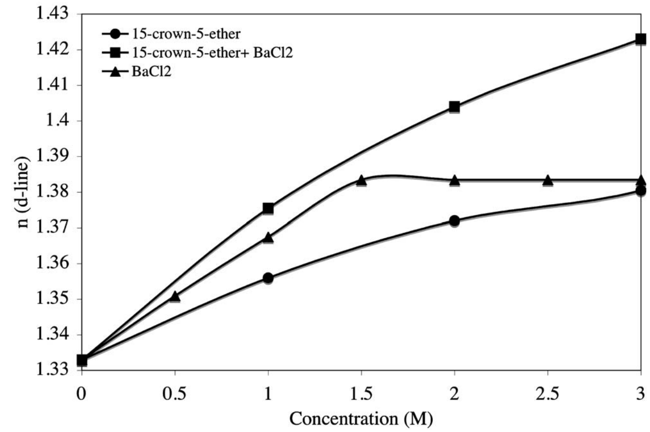


Fig. 2 Increase of refractive index at 589 nm by addition of $BaCl_2$ (▲), 15C5 (●), and $BaCl_2$ and 15C5 (■).

For the contact angle measurements, 2 μL of the immersion fluid was deposited with a micropipette over the PMMA surfaces, and its contact angle measured with a Rame-Hart 100-00 contact angle goniometer.

2.3 *Ultraviolet Spectra*

Absorption measurements were made in a UV-spectrometer (Shimadzu, UV-2401PC, software UVPC 3.9) on a 1-mm optical path cuvette. Air was used as background and ultrapure water as reference.

3 Experimental Results

3.1 *Refractive Index*

The refractive index of the fluid can be increased by adding $BaCl_2$ up to the solubility limit of the inorganic salt in the solvent, until a "plateau" is reached (Fig. 2), while the increase due to the introduction of the crown ether is linear, since no solubility limit is reached. The combination of both compounds gives the best result in terms of refractive index enhancement. A linear behavior is obtained as in the case of the crown ether alone, revealing that the solubility limit of the inorganic salt has been overcome. Therefore, it is clear that the introduction of crown ethers is a good strategy to increase the solubility of the inorganic salt in the solvent.

As has been shown, the addition of the crown ether increases the refractive index in a very effective manner without causing any solubility problem. Since the 15-crown-5-ether and 12-crown-4-ether are liquids, miscible with water at room temperature, different solutions with volume fraction can be prepared and the refractive index measured (Fig. 3).

As expected, the highest refractive index corresponded to the crown ether alone, and there is a linear increase in the refractive index with an increase in the concentration of the crown ether. The next question is: can the refractive index be increased by saturating the solutions with the inorganic salt ($BaCl_2$)? In all cases, except for pure crown ether, the final refractive index can be increased for both crown ether (12C4 and 15C5) solutions by saturating the

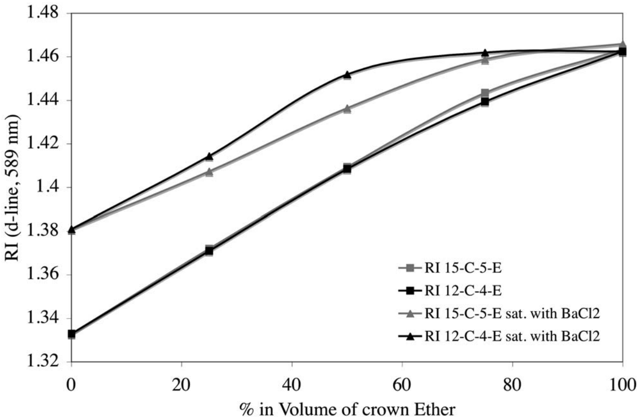


Fig. 3 Increase of the refractive index by addition of 12C4 (black line), 15C5 (gray line), alone (■), and saturated with $BaCl_2$ (▲).

solutions with $BaCl_2$. No $BaCl_2$ can be solubilized in pure crown ether, most probably because of the low polar character of the solvent. A high polar solvent such as water may be needed to solubilize the inorganic salt, but the dilution of the crown ether with this amount of water reduces the total refractive index of the solution, and no improvement in the refractive index is obtained. Therefore, the use of crown ether alone is proposed and it eliminates the need for the addition of the inorganic salt, which avoided several technical problems associated with the possible contamination of the wafer by the remaining inorganic salts during the production process.

The refractive index measurements of 15C5 and 12C4 as a function of wavelength are presented in Fig. 4. A value of 1.68 is obtained for 193 nm, which is clearly higher than the 1.44 of water, while the d-line index of the crown ethers is 1.463 compared to water's index of 1.33. Therefore, the dispersion for the crown ether is 0.22, which is double the value of water ($\Delta n = 0.11$).

3.2 *Ultraviolet Absorption*

An accurate determination of the UV extinction coefficient of crown ethers at 193 nm implies some difficulties because of the presence of some impurities in the commercial samples. In the synthesis of 15C5, an alkali metal hydroxide is used as the condensing agent[14] (Fig. 5) and 1-4-dioxane as solvent. Both compounds have a high absorption in the UV region. Molar extinction coefficient of 1,4-dioxane (Sigma-Aldrich, spectrophotometric grade, >99%) at 193 nm has been found to be 1.2 L cm^{-1} mol^{-1}. Even a high pure 15C5 (98%) with small traces of alkali metal hydroxide, or some crown ether derivative with a double bond, will absorb in the UV region. The high boiling point of the 15C5, close to 350°C, together with its low flash point (147°C) implies serious difficulties in purifying the crown ether by distillation. Nevertheless, some absorption of the crown ether itself must be assumed. The open question is: which is the extinction coefficient that can be accepted for its success in an industrial application?

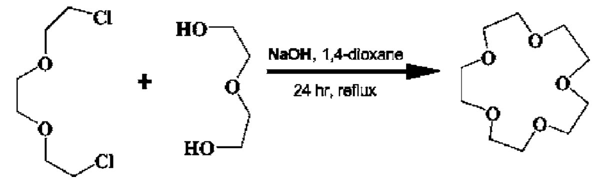


Fig. 5 Scheme for the synthesis of 15C5 ether and the origin of the alkali impurity.

Modification of the crown ether structure may lead to a shift of the absorption band and a reduction of the extinction coefficient at the desired wavelength (193 nm). The main absorption of cyclic ethers should be assigned to the transition of the oxygen electrons located in the molecular orbital n to the σ^*.[15] This transition, which is present in most of the cyclic ethers, is missing in the ethylene oxide (C_2H_2O).[16] There is the possibility of some symmetry forbidden transition A_1-A_2 caused by the excitation of an electron from b_1 to b_2 orbital in ethylene oxide, where a comparable transition in the other molecules would be allowed. The addition of functional groups may introduce a similar strained or symmetry change in the crown ether that may shift the absorption to shorter wavelengths. This new functionalized crown ether should maintain its properties of low melting point, density, and viscosity. Therefore, the crown ether itself can be considered to be a good starting model for the development of a future immersion liquid.

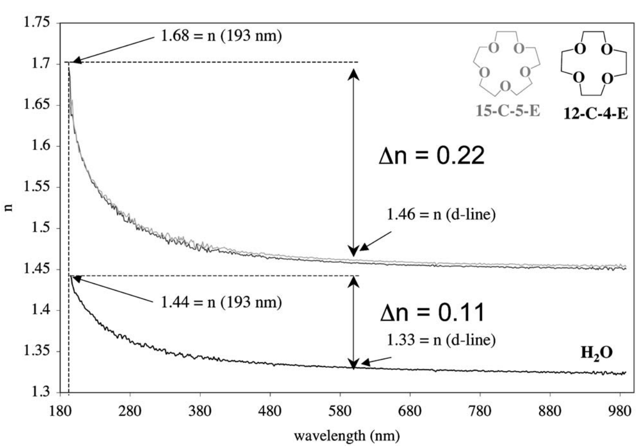


Fig. 4 Refractive index along the spectra for the 15C5, 12C4, and water.

3.3 *Contact Angle*

The flow dynamics of immersion fluids can be characterized by their wetting properties on photoresist surfaces. The effective wetting of the surfaces of the photoresist by the immersion fluid is crucial to minimize voids or cavities, which may lead to bubbles or splashing.[4] Typically, the photoresists used in microlithography are acrylic-based polymers. The static contact angle of the crown ether and water over a surface of PMMA is presented in Table 1.

As expected, water (polar) has a relative large contact angle with an apolar surface like PMMA. Crown ethers are low polar solvents with a very small contact angle with the polymer surface. Possible chemical interactions between the photoresists used for 193 nm and the crown ether, as well as fluid dynamic studies, should be performed to delineate the effect of wetability.

Table 1 Contact angle of the different fluids with PMMA surfaces.

Compound	Contact angle (deg)
Water	67
12-crown-4-ether	5
15-crown-5-ether	7

4 Conclusion

The use of crown ethers to increase the solubility of inorganic salts and, therefore, to enhance the refractive index of aqueous fluids, is studied. The solubility limit inherent in the inorganic salt $(BaCl_2)$ is overcome by adding an equal amount of crown ether to the aqueous solution. The fact that 15C5 and 12C4 are liquids at room temperature presents the chance to use them as pure immersion fluids for immersion microlithography at 193 nm. Increase in the crown ether refractive index by adding an inorganic salt has not been achieved because of the low solubility in the pure crown ether. Nevertheless, the use of pure crown ether is found to be the best fluid in terms of refractive index that helps to eliminate the use of inorganic salts and avoid possible deposits during the printing process. Measurement of the refractive index at 193 nm gives a value of 1.68 for the 15C5, which is over the desired value for the second-generation fluids. Absorption of the fluid should be precisely determined and reduced by purification. Further development in the crown ether structure may allow reduction of the absorption at the desired region and increase in the refractive index, but this structural change and addition of functional groups should not increase the melting point. Fluorination of crown ether leads to reduction of absorbance, but the refractive index also decreases. The 18-crown-6-ether, a solid at room temperature, can be functionalized by introducing a long aliphatic chain in the structure and therefore reducing the melting point below room temperature. The product, 2-decyl-18-crown-6-ether, is a liquid with a refractive index at 589 nm of 1.4605. Similar functionalization opens a broad window of possibilities to develop and optimize an immersion fluid with the appropriate physical properties, based on the crown ether structure.

Further studies of the photostability of the fluid and the compatibility with the photoresist should be carried out.

Acknowledgment

The authors thank James Christopher Taylor and Grant Willson of the University of Texas, Austin, for the measurements of the refractive index at 193 nm. They also gratefully acknowledge the funding received from SEMATECH.

References

1. S. Owa and H. Nagasaka, "Advantage and feasibility of immersion lithography," *J. Microlithogr., Microfabr., Microsyst.* **3**(1), 97–103 (2004).
2. J. Mulkens, D. G. Flagello, B. Streefkerk, and P. Graupner, "Benefits and limitations of immersion lithography," *J. Microlithogr., Microfabr., Microsyst.* **3**(1), 104–114 (2004).
3. B. W. Smith, A. Bourov, H. Kang, F. Cropanese, Y. Fan, N. Lafferty, and L. Zavyalova, "Water immersion optical lithography at 193 nm," *J. Microlithogr., Microfabr., Microsyst.* **3**(1), 44–51 (2004).
4. B. Budhlall, G. Parris, P. Zhang, X. Gao, Z. Zarkov, and B. Ross, "High refractive index immersion fluids for 193 nm immersion lithography," *Proc. SPIE* **5754**, 622–629 (2005).
5. J. Zhou, Y. Fan, A. Bourov, N. Lafferty, F. Cropanese, L. Zavyalova, A. Estroff, and B. W. Smith, "Immersion lithography fluids for high NA 193 nm lithography," *Proc. SPIE* **5754**, 630–637 (2005).
6. S. Pemg, R. H. French, W. Qiu, R. C. Wheland, M. Yang, M. F. Lemon, and M. K. Crawford, "Second generation fluids for 193 nm immersion lithography," *Proc. SPIE* **5754**, 427–434 (2005).
7. K. Lee, J. Kunjappu, S. Jaockusch, N. J. Turro, J. Lopez-Gejo, T. Widerschpan, J. Zhou, B. W. Smith, P. Zimmerman, and W. Conley, "Investigation of the index of refraction of aqueous immersion photolithography: The effect of ionic surfactants and inorganic salts on the index of refraction of aqueous solutions," (submitted for publication).
8. F. Arnaud-Neu, R. Delgado, and S. Chaves, "Critical evaluation of stability constants and thermodynamic functions of metal complexes of crown ethers," *Pure Appl. Chem.* **75**(1), 71–102 (2003).
9. R. M. Izatt, R. E. Terry, B. L. Haymore, L. D. Hansen, N. K. Dalley, A. G. Ayondet, and J. J. Christensen, "Calorimetric titration study of the interaction of several uni- and bivalent cations with 15-crown-5, 18-crown-6, and two isomers of dicyclohexo-18-crown-6 in aqueous solution at 25°C and μ=0.1," *J. Am. Chem. Soc.* **98**, 7620–7626 (1976).
10. V. P. Vasil'ev, M. N. Goncharova, and T. D. Orlova, "Thermochemistry of complexation between 15-crown-5 and Ba^{2+} ion in aqueous solution," *Russ. J. Coord. Chem.* **26**, 170–171 (2000).
11. G. Wenz, H. J. Buschmann, and E. Schollmeyer, "Thermodynamics of complexation of some monovalent and bivalent cations by crown ethers, benzo crown ethers and cryptands in N, N-dimethylformamide," *J. Coord. Chem.* **48**(4), 465–476 (1999).
12. H. J. Buschmann and E. Schollmeyer, "Complexation of alkaline earth (Group 2A) cations by non-cyclic, macrocyclic, and macrobicyclic ligands in propylene carbonate solutions," *Thermochim. Acta* **207**, 329–336 (1992).
13. H. J. Buschmann, "The influence of acetonitrile on complex formation of crown ethers containing different donor atoms," *J. Solution Chem.* **17**(3), 277–286 (1988).
14. B. R. Bowsher, "The use of alkali hydroxides in the template synthesis of 15-crown-5," *Inorg. Chim. Acta* **45** L5–L6 (1980).
15. G. Fleming, M. M. Anderson, A. J. Harrison, and L. W. Pickett, "Effect of ring size on the far ultraviolet absorption and photolysis of cyclic ethers," *J. Chem. Phys.* **30**(2), 351–354 (1959).
16. NIST data base, see http://webbook.nist.gov/chemistry/.

Juan López Gejo received his degree in chemistry at the University of Burgos (Spain). His PhD thesis was in environmental photochemistry, completed in the chemical engineering department at the University of Karlsruhe (Germany) in 2005. He is presently doing postdoctoral research in organic photochemistry at Columbia University, developing high refractive index and low absorbance immersion fluids in collaboration with SEMATECH.

Joy T. Kunjappu holds two earned doctoral degrees from University of Bombay, India, a PhD in 1985 and a DSc in 1996. His postdoctoral training was at Columbia University, where he researched on the spectroscopic characterization of surfactant aggregates. Currently, he is on the faculty of the chemistry department of Brooklyn College of the City University of New York. Previously he taught at Columbia University and Yeshiva University, and worked for ink and sterilization industries. Over a span of 35 years in research and teaching, his areas of interest have included radiation chemistry, photochemistry, surfactants, laser dyes, DNA-molecule interactions, inks, sterilization, materials science, and synthesis of polymers. He is the author of about 90 scientific publications and a book, "Essays in Ink Chemistry: For Paints and Coatings Too."

Nicholas J. Turro is the William P. Schweitzer Professor of Chemistry at Columbia University, where he has been since 1964. He also holds professorships at the Department of Chemical Engineering and the Department of Earth and Environmental Engineering. He has been widely recognized by national and international awards as a leader and pioneer in the area of supramolecular chemistry, organic photochemistry, molecular spectroscopy, host-guest chemistry, and magnetic effects on photochemical reactions. He has sponsored the PhD thesis of 70 students, and has mentored 200 postdocs. More than 100 undergraduates have been trained in research under his supervision. He is the author of two textbooks on organic photochemistry, which is considered the "bible" of the field for several generations by organic photochemists since 1965. He has published more than 760 research papers and has been selected as one of the most highly cited chemists for the past two decades. He is a member of the National Academy of Sciences and the American Academy of Arts and Sciences.

Will Conley is in the advanced optical lithography group at Freescale Semiconductor, where his main focus is advanced imaging strategies and solutions for sub-0.050-μm lithography at the Crolles 2 Alliance in Crolles, France. Prior to joining Freescale, he was with National Semiconductor's advanced technology group in Santa Clara, California, in the advanced optical lithography group, developing process solutions for the Cyrix microprocessor program until the divestiture. Prior to joining National Semiconductor, he was with IBM at the Semiconductor Research and Development Center in East Fishkill, New York. He was involved in the development of 0.18 μm and sub-0.18-μm photolithography processes until early in 1997. He has been in the semiconductor industry for more than 19 years; holds more than 30 patents, and has published more than 100 papers in the area of lithographic materials and processes. He is the former chair of the SPIE conference on resist technology and is a member of the ACS, SPIE, and an associate editor for the *Journal of Micro/Nanolithography, MEMS, and MOEMS*.