Polycycloalkanes as Potential Third-Generation Immersion Fluids for Photolithography at 193 nm

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In a search for alkane candidates for 193 nm immersion fluids, several alkanes and cycloalkanes were synthesized, purified, and screened to ascertain their absorption at 193 nm, refractive index, and temperature dispersion coefficient in the context of the actual application. In general, cycloalkanes, and more specifically polycycloalkanes, possess a higher refractive index than do linear alkanes. Decalin, cyclodecane, perhydrophenanthrene (PHP), perhydrofluorene (PHF), and perhydropyrene (PHPY) are examined as potential second- and third-generation immersion fluids. The use of perhydropyrene, which possesses a high refractive index of 1.7014 at 193 nm, may be limited as an immersion fluid because of high absorption at 193 nm. Mixtures of cycloalkanes can lead to a higher enhancement of the refractive index together with a decrease of the viscosity. Exhaustive purification of the fluids is a critical step in determining the real absorption of the different fluids at 193 nm. Even very small traces of impurities possessing a high absorption coefficient at 193 nm can lead to an unacceptably high level absorption at 193 nm, previously incorrectly attributed to the alkane instead of the absorbing impurities.

1. Introduction

A current holy grail in optical lithography is the development of novel materials and processes so as to push it toward dimensions < 32 nm. The minimum feature that can eventually be printed with an optical lithography system is determined by the Rayleigh expression, eq 1.[1]

$$\mathrm{hp} = \frac{k_1\lambda}{\mathrm{NA}} \tag{1}$$

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 given by eq 2

$$NA = n_{\mathrm{IF}} \sin \theta_{\max} \tag{2}$$

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, half pitch (hp) can be decreased by decreasing λ or increasing the n_{IF}. As the challenges of shorter wavelength (157 nm) became increasingly difficult, usage of immersion-based 193 nm lithography systems became more attractive.[2] Therefore, for current 193 nm photolithography systems, there is a need to develop new immersion fluids that have a higher refractive index than that of water, $n = 1.44$.[3] In addition, candidates must have an acceptable transparency at 193 nm. Recently, second-generation fluids with a refractive index of ∼1.6 at 193 nm have been prepared, driven by the growing interest in this area.[4] In those studies, absorbance and viscosity have been identified as the critical and limiting issues that must be considered to obtain a valid second-generation immersion fluids. However, newer systems have been emerging with lower absorption coefficient and high refractive index values, too.

In previous publications, we have suggested the combination of inorganic salts ($BaCl_2$), surfactants, and crown ethers as plausible methods of increasing the refractive index of water to be used as an immersion fluid.[5] In most cases,

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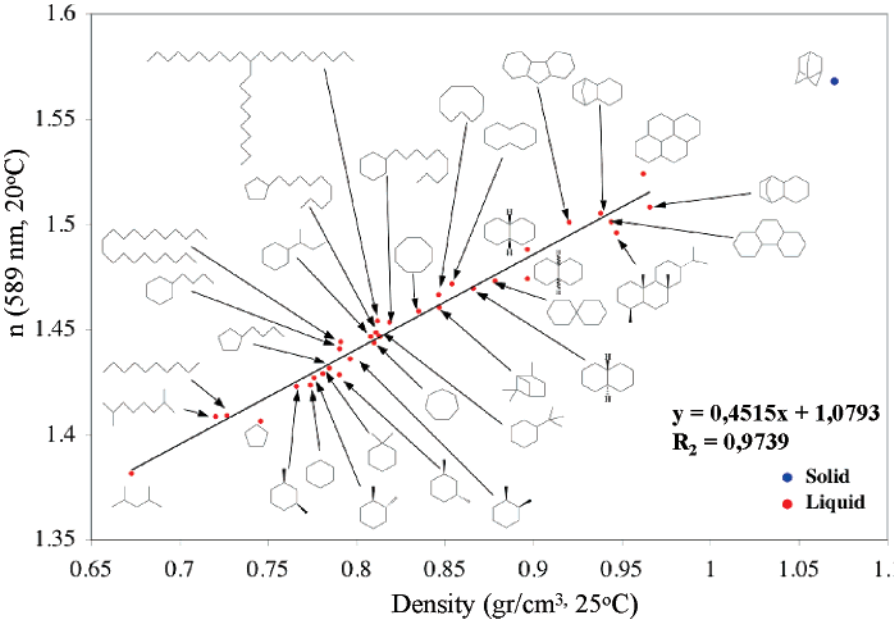

Figure 1. Refractive index (d line) vs density of alkanes and cycloalkanes at room temperature.

limitations due to the high absorption of the fluid were identified, eliminating the acceptability of the candidates.

In order to avoid absorption at 193 nm, π and n orbitals should be avoided in the molecular structure. From this point of view, alkanes and cycloalkanes are the most promising candidates in terms of potential low absorption at 193 nm, since, for saturated hydrocarbons, only high energy $\sigma-\sigma^*$ electronic transitions are possible. $\sigma-\sigma^*$ Transitions require a higher energy than n$-\sigma^*$, n$-\pi^*$, and $\pi-\pi^*$ transitions, and the corresponding absorption band appears, in general, near or below 193 nm.[6]

Given that alkanes and cycloalkanes are promising candidates for transparency at 193 nm, we now turn to the issue of how to select the most promising alkane and cycloalkane candidates with the highest index of refraction. A major focus is the exact experimental determination of the values of the refractive index of selected candidates, i.e., cycloalkanes at 193 nm, and whether the value can be maximized to an acceptable level required for an immersion fluid at 193 nm. To systematically address this issue, we have employed the well-established physical organic chemistry principle of chemical structure−material property correlations.

From a search of the literature,[7] we have discovered an excellent linear correlation between the index of refraction (at 589 nm) of pure liquid alkanes and liquid cycloalkanes and their densities (Figure 1). The first important conclusion from the correlation is that the higher the density of the alkane or cycloalkane, the higher the refractive index at 589 nm. We assume that knowledge of the value of the refractive index at 589 nm can reliably be extrapolated to the value at 193 nm. We start with the working hypothesis that "electron density" and "free volume" will be useful concepts for a theoretical understanding of the correlation of chemical structure and refractive index. When the molecules are well-packed, there is less free volume in the liquid, and the same number of molecules occupies less volume; therefore, there is less "free volume" or space between molecules. When this is the case, the "electron density", which is the effective number of electrons per unit of volume, increases. This high number of electrons per volume unit affects the light when it passes through the fluid with a corresponding change in the refractive index. The hypothesis interprets the correlation, shown in Figure 1, to mean that liquids with small free volume, corresponding to high liquid density, will correlate with a high electronic density and high refractive index.

The second important conclusion from the correlation of Figure 1 is that, for comparable molecular weight, cycloalkanes possess a higher refractive index than the corresponding linear alkanes (e.g., cyclodecane and decane). Our working hypothesis interprets this feature of the correlation to mean that the supramolecular (intermolecular) organization of the cycloalkanes results in better packing and in a higher density and, therefore, a higher refractive index than the equivalent molecular weight linear alkane.

A third important conclusion from the correlation of Figure 1 is that, for comparable molecular weight, the refractive index increases by increasing the number of connected rings (e.g., cyclodecane and decalin). The working hypothesis interprets this feature of the correlation to mean that polycycloalkanes are better able to minimize free volume than monocycloalkane or linear alkanes. Finally, a fourth important conclusion of Figure 1 is that this linear relationshop between density and refractive index is not lost by changing from liquid to solid phase (Figure 1, adamantine solid).

But is the extrapolation of the refractive index at 589 nm to the refractive index at 193 nm valid? With limited literature data available,[8] we have constructed a graph of refractive index of hydrocarbons at 193 nm *versus* density

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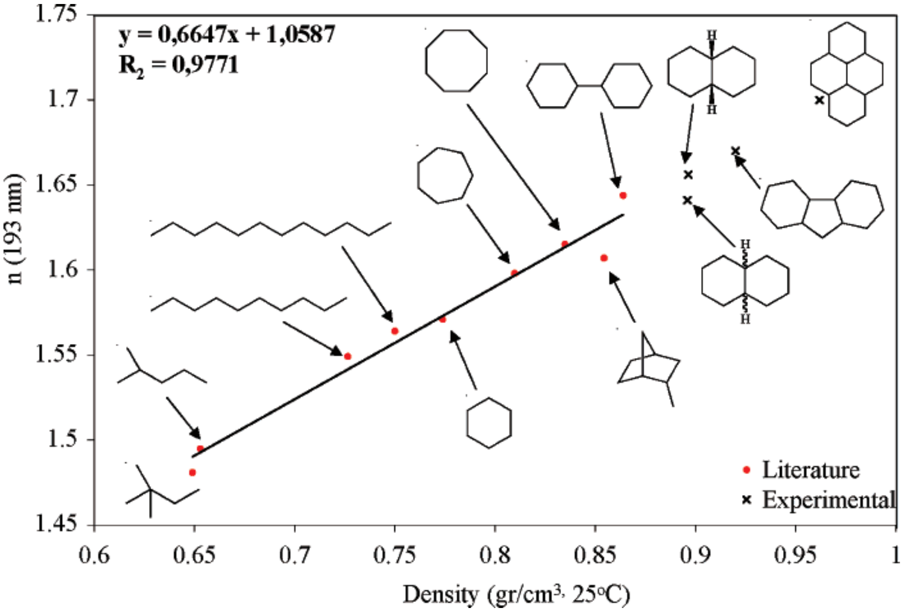

Figure 2. Refractive index (193 nm) of cycloalkenes and noncycloalkenes as a function of the density.

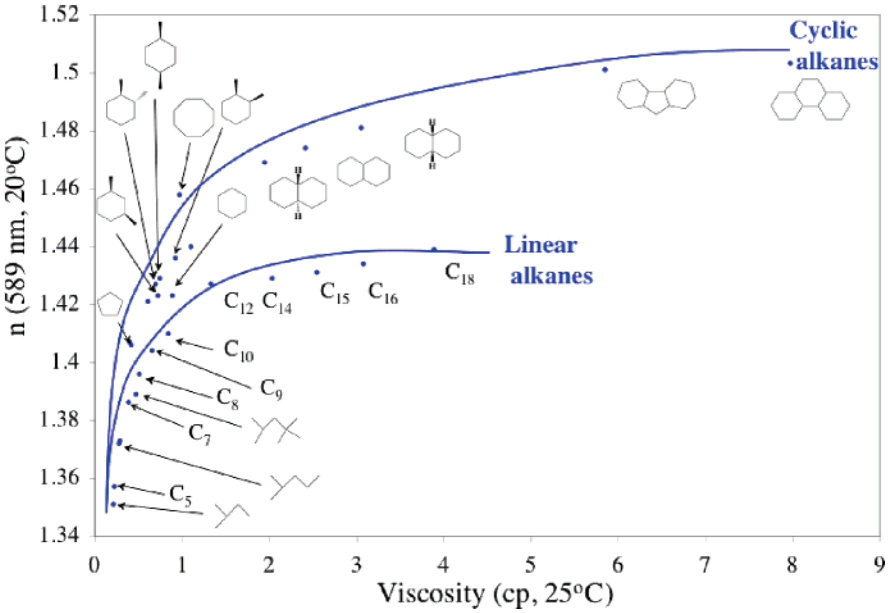

Figure 3. Refractive index (d line) vs viscosity of liquid alkanes and cycloalkanes at room temperature.

(Figure 2) for comparison with the correlation of Figure 1. The linearity of the plot completely validates our hypothesis that the extrapolation of values of the refractive index at 589 nm are useful for predicting the values of the refractive index at 193 nm. The excellent linear relation between density and refractive index at 193 nm provides confidence to extrapolate to higher densities in order to find the highest refractive index possible. Several polycycloalkanes (×'s in Figure 2) have been synthesized or purified based on extrapolation of Figure 1, and our measurements at 193 nm indicate that the extrapolation is justified.

Another issue to be addressed is the relationship between viscosity of the candidates for high refractive liquids and index of refraction. From a literature survey, the refractive index of alkanes and cycloalkanes generally increases with increasing viscosity, but not in a linear fashion (Figure 3), except at viscosities < 1 cP. At viscosities > 1 cP, there are two clear trends: one for linear alkanes and another for cycloalkanes. In general, for the same viscosity value, cycloalkanes present a higher refractive index than do linear alkanes. Interestingly, the viscosities of alkane mixtures have been observed to be smaller than those of the pure components.[9] This finding suggests the possibility that, by appropriately mixing polycycloalkanes, a fluid with low viscosity and high refractive index could be obtained.

In summary, from an analysis of refractive index values of alkanes and cycloalkanes at 589 nm, it is concluded that polycycloalkanes are promising candidates for both attaining a high refractive index at 193 nm and a high transparency at 193 nm. From this analysis, the following cycloalkanes were selected for initial synthesis and exhaustive purification: decalin, cyclodecane, perhydrofluorene, perhydropyrene, and perhydrophenanthrene.

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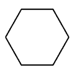
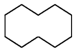
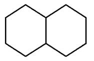
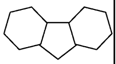
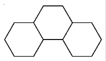
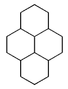
[9] (a) Triphati, N. *Int. J. Thermophys.* **2005**, *26*, 693. (b) Korsten, H. *AIChE J.* **2001**, *47*, 453.

Table 1. Structure and Physical Chemical Properties of the Cycloalkanes Used in This Study

	**Name:** Cyclohexane MW: 84.09 Formula C_6H_{12} Bp. 80.7 ºC Density 0.779 g/ml at 25ºC		**Name:** cyclodecane MW: 140.27 Formula $C_{10}H_{20}$ Bp. 201 ºC Density 0.871 g/ml at 25ºC
	**Name:** Decalin MW: 138.25 Formula $C_{10}H_{18}$ Bp. 189-191 ºC Density 0.896 g/ml at 25ºC		**Name:** PHF MW: 178.31 Formula $C_{13}H_{22}$ Bp. 253 ºC Density 0.92 g/ml at 25ºC
	**Name:** PHP MW: 193.35 Formula $C_{14}H_{24}$ Bp. 270 ºC Density 0.944 grml at 25ºC		**Name:** PHPY MW: 218.38 Formula $C_{16}H_{26}$ Bp. 318 ºC Density 0.96 g/ml at 25ºC

Except for decalin, cyclodecane, and perhydrofluorene, the most promising candidates, perhydropyrene and perhydrophenanthrene, are not commercially available and had to be synthesized. We note that small impurities, resulting from alkane oxidation and possessing a high extinction coefficient at 193 nm, are commonly found in commercial cycloalkanes. For example, commercially available decalin contains impurities, presumably oxidation products, that absorb strongly at 193. Thus, even commercial alkanes claiming to be “highly purified” need to be subjected to exhaustive purification in order to minimize the absorption at 193 nm. Purification techniques were developed to obtain highly pure compounds.

2. Experimental Section

2.1. Refractive Index. For the exploratory work in the visible region, an Abbe refractometer (Bausch & Lomb) coupled with a thermostatic bath were used. All measurements presented in this work were made at 20 °C. To characterize the refractive indices at 193 nm, a Variable Angle Spectroscopic Ellipsometer (VASE, by J. A. Woollam Inc., U.S.A.) was modified. The instrument was originally designed to measure optical constants of thin films. It also provides the ability to measure transmission. The ellipsometer has precise (0.044 mRad) goniometers, resulting in an accuracy of 10^{-3}. A prism fluid cell with nominal apex angle of 45° was mounted onto the sample stage. The light came into the prism cell from a monochromator. The incident angle could be adjusted by turning the sample stage. The outgoing light was collected by the detector. Additional details can be found elsewhere.[4b]

2.2. UV Spectra. Absorption measurements were performed 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 was used as reference.

2.3. Materials. Decalin (decahydronaphthalene (a cis−trans mixture) >98%, 250 mL) was purchased from Fluka, while perhydrofluorene (97%, 150517, 10 g) was purchased from Aldrich. Perhydropyrene and perhydrophenanthrene were synthesized by hydrogenation of pyrene and phenanthrene, respectively. Details of the synthesis and purification are reported in another publication.[10] The basic physico-chemical data of the cycloalkanes and polycycloalkanes used in this work are listed in Table 1.

3. Results and Discussion

3.1. Refractive Index. The experimental refractive index of the polycycloalkanes as a function of wavelength is presented in Figure 4. As can be observed, the eventual value of refractive index at 193 nm follows the same trend as the value at 589 nm. Perhydropyrene (PHPY) is the compound with the higher refractive index at 193 nm (n193 nm = 1.7014), followed by perhydrofluorene (PHF) (n193 nm = 1.6684), decalin (n193 nm = 1.6238), cyclodecane (n193 nm = 1.6211), and cyclohexane (n193 nm = 1.5618). French et al. measured similar values,[8b] 1.571 and 1.641, for cyclohexane and decalin, respectively. This result confirms the validity of our hypothesis on the basis of literature data at 589 nm.[7] Perhydropyrene has 14 stereoisomers, the most stable of which is the trans, trans, anti, trans, *trans*-perhydropyrene, (1, 2, 3, −3ar, 4, 5, 5at, 6, 7, 8, 8at, 9, 10, 10ac, 10bt, 10 cm^3)-hexadecahydropyrene, which is a needle-shaped crystal and, therefore, not useful as an immersion liquid.[11] Most probably, the mixture of the steroisomers gives liquid character to the perhydropyrene.

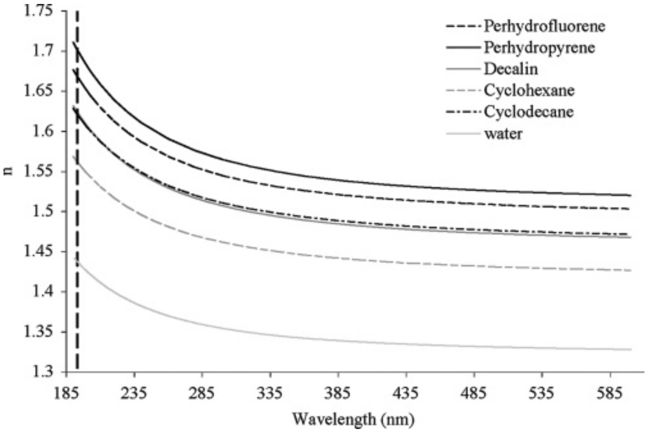


Figure 4. Refractive index vs wavelength of polycycloalkanes.

3.2. Temperature Dispersion (d*n*/d*T*). The change of refractive index as a function of the temperature is an important parameter for the immersion fluids. A low d*n*/d*T* (<250 ppm/K) is required for acceptable industrial application of a candidate immersion fluid, since small changes in temperature are expected during the exposure, and these variations should not cause changes in the refractive index of the fluid. Studies of the temperature dispersion (d*n*/d*T*) of cycloalkanes were performed at 589 nm (Figure 5). The absolute values of d*n*/d*T* obtained at this wavelength cannot be extrapolated to 193 nm, but again, trends and relations between the structure and variation of d*n*/d*T* can be obtained. At 589 nm, the temperature dispersion of the refractive index of cycloalkanes has values between 250 and 500 ppm/K. A similar, slightly higher value may be expected at 193 nm and, therefore, over the specification limit of 250 ppm/K. This means that special temperature-control devices have to be developed in order to apply these fluids. However, PHPY has an acceptable value of 277 ppm/K at 589 nm. The temperature dispersion decreases with an increase in the molecular weight; thus, the fluids with a higher refractive index are actually those with lower dispersion.

Since there is a direct relation between density and refractive index, a major change in the density of the material

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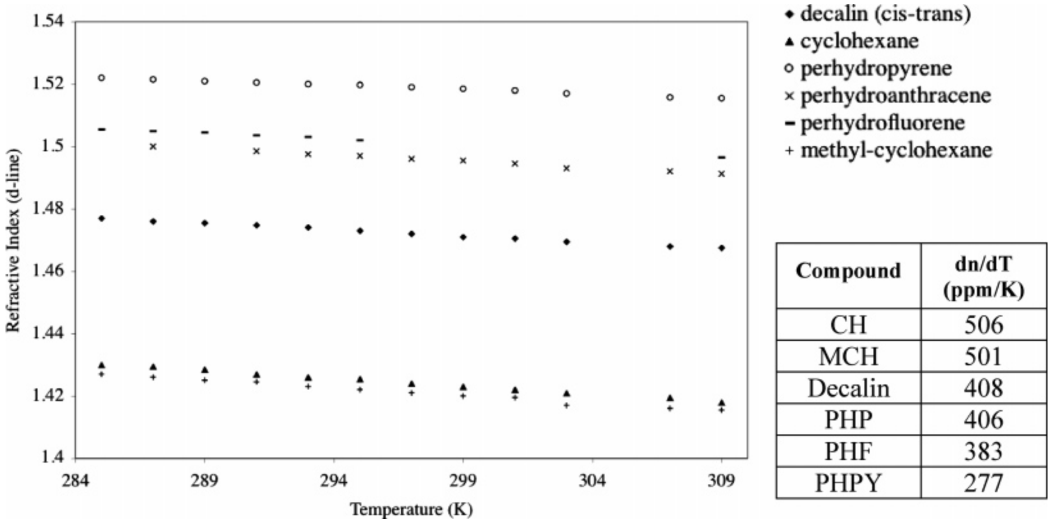


Compound	dn/dT (ppm/K)
CH	506
MCH	501
Decalin	408
PHP	406
PHF	383
PHPY	277

Figure 5. Temperature dispersion (d*n*/d*T*) of cycloalkanes.

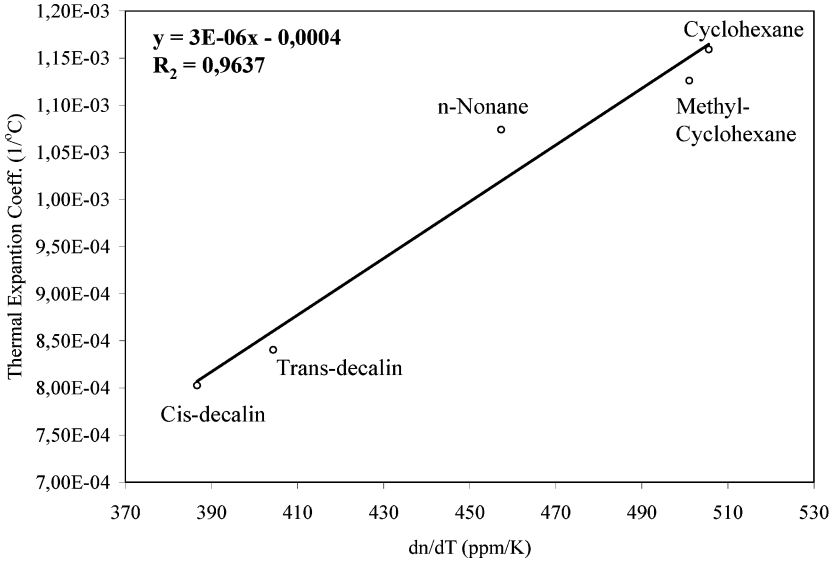


Figure 6. Relationship between thermal expansion coefficient and the temperature dispersion of the refractive index at 589 nm of some cycloalkanes.

with the temperature should give a major change in the refractive index. The temperature dispersion of the refractive index should be related to the thermal expansion coefficient of the materials. In Figure 6, the correlation between thermal expansion coefficients and temperature dispersion of the refractive index is shown. A perfectly linear correlation is observed for alkanes and cycloalkanes between these two physical parameters.

PHPY, PHF, and perhydrophenanthrene (PHP) are fluids with a high density, i.e., these molecules can be packed very well and there is little free volume in the bulk of the fluid. This packing effect affects the thermal expansion coefficient and, therefore, the temperature dispersion of the refractive index.

In summary, though an absolute value of the temperature dispersion for 193 nm has not been obtained, on the basis of the results at 589 nm, we may infer that PHPY, PHP, and PHF are the fluids that promise to have the lower dispersion at the wavelength of interest.

3.3. Absorption Spectra. An absorbance < 0.15/cm is specified as a requierement for second and third generations of immersions fluids. Alkanes were selected as candidates for immersion fluids because of their low absorption due to the absence of n and π molecular orbitals and, therefore, the corresponding low-energy electronic transitions in the deep UV. Absorption spectra of commercial alkanes and cycloalkanes were measured, and an unexpected strong absorption was observed in all cases, showing the need for purification. In addition, strong contribution to the absorption has been attributed to the formation of a reversible charge-transfer complex between the cycloalkane and the molecular oxygen.

The absorption spectra of all candidates after purification and purging with argon or nitrogen are shown in Figure 7. As can be observed, some of the candidates present a high absorption at 193 nm even after removal of the dissolved oxygen. Cyclohexane does not present almost any absorption at 193 nm. However, decalin and cyclodecane have an acceptable absorbance < 0.2/cm at 193 nm, while PHPY, PHP, and PHF have an unacceptable high absorption at 193 nm. In spite of several purification processes, some impurities may be present in the fluids. The small absorption band with a maximum at 260 nm may be attributed to impurities that have made it through the exhaustive purification process.

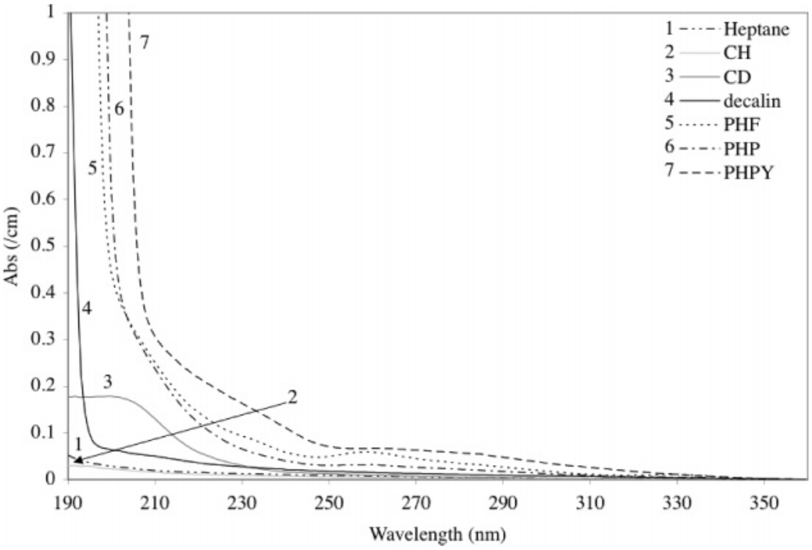
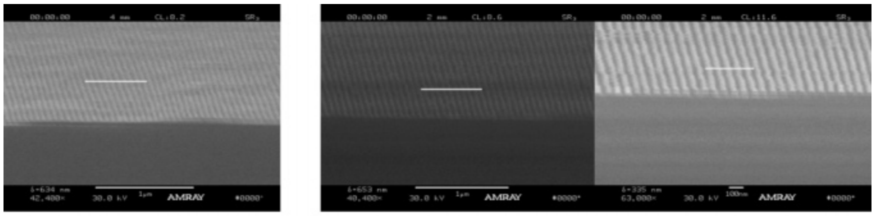


Figure 7. Absorption spectra of cycloalkanes and polycycloalkanes used in this study.



1.5 NA. 32 nm half pitch 1.45 NA. 33 nm half pitch

Figure 8. Imaging with decalin.

These traces of some absorbing compound can contribute to the higher absorption at 193 nm. Therefore, it is still possible that further purification and elimination of those traces may decrease the absorption at the wavelength of interest (193 nm).

Heilbronner et al. studied the photoelectron spectrum of several polycyclic alkanes.[12] They calculated an increase of the total energy of the two highest occupied canonical molecular orbitals (HOMOs) with increasing number of *transoid*-connected cyclohexane rings in the structure. They suggested that the calculated energy gap Δ between these two highest occupied canonical molecular orbital (HOMO and HOMO-1) and the rest of the orbitals increases from $\Delta = 0.40$ eV for cyclohexane to $\Delta = 0.79$ eV for perhydropyrene with an increasing number of *transoid*-connected cyclohexane rings. A higher energy of the HOMO and HOMO-1 does not necessarily imply a lower energy gap between the HOMO and lowest unoccupied molecular orbital (LUMO), which is the electron transition that determines the longest wavelength absorption of the alkane. In our case, the appearance and shifting of a band to longer wavelengths that show the absorption spectra in the series cyclohexane, decalin, perhydrophenanthrene, and perhydropyrene may indicate that the increasing number of *transoid*-connected cyclohexane rings from 1 to 4 (1, cyclohexane; 2, decalin; 3, perhydrophenanthrene; and 4, perhydropyrene) implies an increase in the HOMO energy but not an increase in the LUMO. Therefore, the energy gap between HOMO and LUMO seems to decrease as the number of *transoid*-connected cyclohexane rings is increased in the molecule. To confirm this decrease in the HOMO−LUMO gap, calculations should be done at the level of density functional theory where it has been shown that the gap is a reasonable approximation to the first transition energy.

In conclusion, increasing the number of *transoid*-connected cyclohexane rings has been demonstrated to be a valid strategy for increasing the density and, therefore, increasing the refractive index. However, these attractive features are offset by a corresponding increase in an absorption around 193 nm, which can be attributed to a decrease in the HOMO−LUMO gap with *transoid*-connected rings. At the same time, the viscosity of the fluids seems to increase by increasing the number of rings. This viscosity increase can be attributed to an increase in the surface of the molecule; this surface increase within increases the Van der Waals forces between molecules and causes an increase in viscosity.

3.4. Exposure Results and Analysis. A JSR2928 resist (54 nm) was used for exposure, coated over an anti-reflective (AR) layer (AR29-A bottom anti-reflective coating (BARC) 39 nm) with a JSR TCX041 topcoat (40 nm). The film stack was optimized by using IL-SIM software.[13] Decalin and cyclodecane were chosen as immersion fluids because of their high refractive index (decalin n_{193} nm = 1.6238) and acceptable transparency at 193 nm. The scanning electron microscopy (SEM) pictures are shown in Figures 8 and 9. Resolutions of 33 and 32 nm have been demonstrated using an effective NA of 1.45 and 1.50 when decalin was used as

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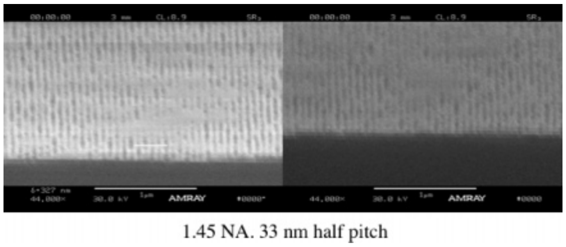

Figure 9. Imaging with cyclodecane.

an immersion fluid (Figure 8). The modulation is high, and the photoresist is not degraded by the fluids.

In the case of the cyclodecane, a low modulation was found, probably because of the high absorption of the fluid. Some chemical interaction between the photoresist and the cyclodecane cannot be excluded. Further studies on this issue will be performed.

4. Conclusion

Cycloalkanes and polycycloalkanes have been studied as possible candidates for immersion fluids at 193 nm. The refractive indexes of cycloalkanes and polycycloalkanes increase with increasing density of the fluid. In terms of structure, the refractive index of the fluid has been observed to increase by increasing the number of *transoid*-connected cyclohexane rings.

The temperature dispersion has been observed to be directly related to the thermal expansion coefficient of the fluid. If the fluid has a high thermal expansion coefficient, the density decreases significantly with small changes in temperature. A decrease in density is going to directly affect the refractive index.

In terms of absorption, the increasing number of *transoid*-connected cyclohexane rings has been observed to lower the energy gap between the HOMO and LUMO, which causes longer wavelengths in the absorption band.

However, decalin and cyclodecane bear the potential to function acceptably as a second-generation fluid (n_{193} nm $>$1.6 nm, absorption $<$ 0.15 cm). The resolution of 193 nm immersion lithography has been pushed down to 32 nm using decalin and cyclodecane as immersion fluids. With the latter, low modulation problems were found during exposure because of high absorption or possible chemical interaction between the photoresist and the fluid.

For the development of a third-generation fluid based on cycloalkanes, new strategies must be developed. The increase in the number of connected rings in the structure is a valid strategy for increasing the refractive index but has the limitation of increasing the absorption. Another possible strategy is that solid cycloalkanes with high refractive index can be dissolved in the decalin or cyclodecane.

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