

# Methods for the synthesis and purification of polycycloalkane candidates for photolithography immersion fluids at 193 nm: requirements for removal of oxygen

**Juan López-Gejo**  
Columbia University  
Department of Chemistry  
3000 Broadway  
New York, New York 10027

**Joy T. Kunjappu**  
Brooklyn College of the City University of  
New York  
Chemistry Department  
2900 Bedford Avenue  
Brooklyn, New York 11210

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

**Paul Zimmerman**  
SEMATECH  
Austin, Texas 78741

**Nicholas J. Turro**  
Columbia University  
Department of Chemistry  
3000 Broadway  
New York, New York 10027

## 1 Introduction

In optical lithography, there is a need to develop novel materials and processes so as to push the limit of resist features toward dimensions less than 32 nm. The expected limit for the dimension of a photoresist feature that can be created with an optical lithography system is given<sup>1</sup> by the Rayleigh equation:

$$hp = \frac{k_1\lambda}{NA}, \quad (1)$$

where  $hp$  is the 1:1 half-pitch feature size,  $\lambda$  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.  $NA$  is defined by Eq. (2):

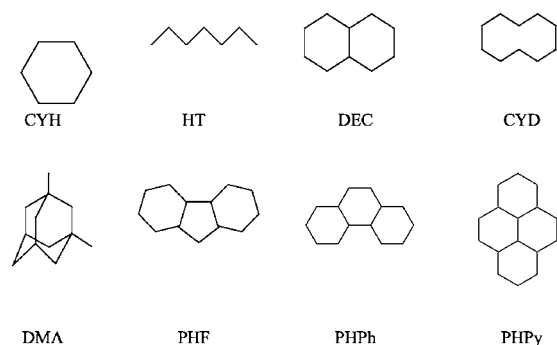
**Abstract.** Cycloalkanes are candidates for immersion fluids because of their potential for low absorption in the 193-nm region and for a high refractive index (RI). We have developed an empirical correlation between refractive index and density of alkanes, which allows a prediction of the best candidates for immersion fluids based on the alkane structure. In particular, the correlation reveals that polycycloalkanes such as perhydrophenanthrene (PPh) and perhydrodopyrene (PPhy), which have a higher RI than linear or cyclic alkanes, will be excellent candidates for immersion fluids at 193 nm. Therefore, PPh and PPhy were synthesized by exhaustive hydrogenation of phenanthrene and pyrene. However, methods for the purification of the synthesized and commercial alkanes such as cyclodecane (CYD), cyclohexane (CYX), pentane (PNT), and decalin (DEC) are required in order to determine the actual absorption of candidates at 193 nm. The presence of an absorbing impurity at 193 nm can cause the premature elimination of otherwise excellent potential candidates. A rather subtle impurity is molecular oxygen, which does not itself absorb at 193 nm, but which forms complexes with alkanes that do absorb at 193 nm. In this case, the "impurity" is readily eliminated by simple purging with nitrogen or argon gas. © 2007 Society of Photo-Optical Instrumentation Engineers. [DOI: 10.1117/1.2778641]

Subject terms: 193-nm immersion microlithography; second-generation immersion fluids; polycycloalkanes; purification; VUV solvents; oxygen complex.

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$$NA = n_{IF} \sin \theta_{\max}, \quad (2)$$

where  $n_{IF}$  is the immersion fluid's index of refraction at the lithographic wavelength (193 nm), and  $\theta$  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 the value of the wavelength  $\lambda$  or by increasing the value of the index of refraction  $n_{IF}$ . Attempts to decrease  $hp$  by decreasing  $\lambda$  to 157 nm have not proven successful, so new approaches are required and the design of new and optimized immersion-based lithography systems becomes more critical.<sup>2</sup> According to Eq. (1), this means maximizing  $NA$ . From a chemist's point of view, the challenge is to increase  $n_{IF}$  by synthesizing or developing high-refractive-index fluid materials. This investigation addresses the critical need to develop new immersion fluids that have a higher refractive index than water (the first-generation immersion fluid currently in use) and acceptable transparency at 193 nm. Thus, water is the benchmark for improvements in the generation



**Fig. 1** Chemical structures of alkanes investigated as immersion fluids in this work.

of immersion fluid: water possesses an index of refraction  $n_{IF}$  of 1.44 and an absorbance of  $<0.01 \text{ cm}^{-1}$  at 193 nm (Ref. 3). Recently, “second-generation” immersion fluids with a  $n_{IF}$  of  $\sim 1.6$  at 193 nm have been reported.<sup>4–8</sup> Typically, these fluids are saturated hydrocarbon, i.e., alkanes or cycloalkanes. In a previous publication, we presented perhydrophenanthrene (PHPh) as a possible immersion fluid because of its refractive index (RI) value. The RI of PHPh was measured along the spectra with a variable-angle spectroscopic ellipsometer, and a value of 1.7014 at 193 nm was obtained with an accuracy of  $10^{-3}$ , which shows the potential of this compound as immersion fluid.<sup>4</sup> From the standpoint of absorption at 193 nm, alkanes are good candidates for immersion fluids, since generally only highly energetic  $\sigma\text{-}\sigma^*$  electronic transitions are possible for alkanes. Therefore, methods for the identification of alkanes with high RI and transparency at 193 nm is of great importance for the photolithographic industry.

We have been able to identify candidates for high RI alkanes through an excellent direct linear correlation between the refractive index (at both 589 nm and 193 nm) of linear and cyclic alkanes and their densities.<sup>4</sup> Importantly, the correlation reveals that for comparable molecular weight, cycloalkanes and polycycloalkanes have higher RI at 193 nm than their linear analogs. Thus, from the correlation we selected based on density, there were two target polycycloalkanes for synthesis, purification and testing as candidates for immersion fluids: perhydrophenanthrene (PHPh) and perhydropyrene (PHPy). The goals of the research, which were to develop purification procedures that would produce liquid perhydrocycloalkanes with a high refractive index and an absorption at 193 nm, were limited by the inherent absorption of the pure material and impurities carried over from the synthesis (e.g., a C=C bond that resisted exhaustive hydrogenation) or through adventitious impurities (e.g., oxygen).

In addition to the investigation of the purification of PHPh and PHPy and their absorption and refractive index at 193 nm, some alkanes were selected for comparison: cyclohexane (CYH), cyclodecane (CYD), decalin (DEC), heptane (HT), perhydrofluorene (PHF), and 1,3-dimethyladamantane (DMA). In addition, two nonalkanes, acetonitrile and perfluoropentane, were investigated. The structures of all of the fluids investigated in this report are shown in Fig. 1.

## 2 Experimental Section

### 2.1 Chemicals

Cyclohexane [CHROMASOLV Plus, for HPLC,  $\geq 99.9\%$  (Aldrich)], cyclodecane [purum,  $\geq 99.0\%$  (GC) (Fluka)], decalin [purum, (cis+trans),  $\geq 98.0\%$  (GC)], heptane [CHROMASOLV Plus, for HPLC, 99% (Aldrich)], 1,3-dimethyladamantane [ $\geq 99\%$  (Aldrich)], acetonitrile [CHROMASOLV Plus, for HPLC,  $\geq 99.9\%$  (Sigma-Aldrich)], and perfluoropentane [97% (Aldrich)] were purchased in the highest purity available. Pyrene [crystalline, 95% (Aldrich)], phenanthrene [98% (Aldrich)], and Raney-nickel catalyst [W.R. Grace and Co., Raney 2400, slurry, in  $\text{H}_2\text{O}$ , active catalyst (Aldrich)] were purchased from Aldrich (Milwaukee, WI).

### 2.2 Synthesis of Perhydrophenanthrene and Perhydropyrene

Perhydropyrene was synthesized following a modification of a preparation described in the literature for polycyclic hydrocarbons,<sup>9</sup> and 12 g of pyrene was ground and partially dissolved in 75 mL cyclohexane. The Raney-nickel catalyst used for hydrogen of phenanthrene and pyrene was suspended in water. The catalyst was filtered and first washed with methanol to remove residual water and then washed with cyclohexane. The catalyst was stored suspended in cyclohexane. About 5 to 6 g of the catalyst was added to the pyrene solution. The hydrogenation was performed in a stainless steel reactor at an initial pressure of 120 atm of hydrogen and a temperature of  $100^\circ\text{C}$ . The hydrogenation was allowed to proceed for 24 h, at which point, the hydrogen pressure dropped down to 40 to 50 atm. After the first hydrogenation, the reaction solution was filtered to eliminate the old catalyst. Another 5 g of fresh catalyst was added to the filtrated solution. Another hydrogenation was carried out under the same conditions.

After the second hydrogenation, the reaction solution was filtered to eliminate the catalyst. Cyclohexane was removed in a rotovaporator. Approximately 10 mL of perhydropyrene was obtained as the final product. Absorption spectroscopy was employed to determine the purity of the product. A large absorption was detected in the UV region below 300 nm and was assigned to incomplete hydrogenation of the pyrene. After the second hydrogenation was carried out with fresh catalyst, traces of partially hydrogenated pyrene were reduced but not totally eliminated (Fig. 2).

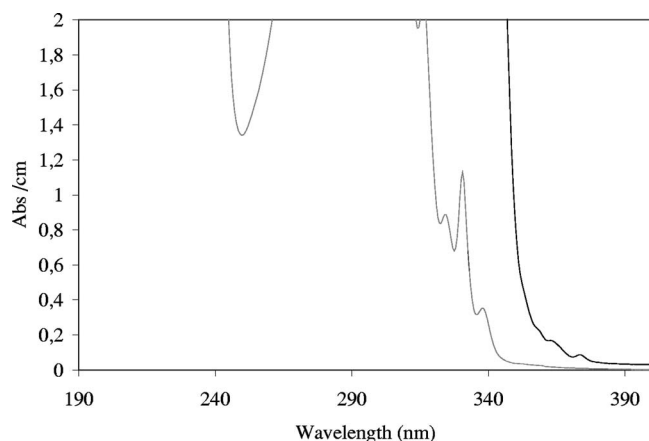
Similar reaction conditions were employed for the hydrogenation of phenanthrene to perhydrophenanthrene. In the latter case, reaction times of about 48 h were necessary for complete hydrogenation, presumably due to resistance to hydrogenation of the last double bond of phenanthrene.<sup>10</sup>

## 3 Purification

### 3.1 Oxidation Products and Elimination of Impurities from Commercial Alkanes

It was found that an exhaustive purification is required to minimize absorption at 193 nm, even for alkanes purchased in spectral purity grade. Two main methods were developed for the purification of commercial or synthesized fluids:

- Procedure 1: Silica gel was activated at  $500^\circ\text{C}$  for 5 h. The alkane was then passed through the silica gel col-

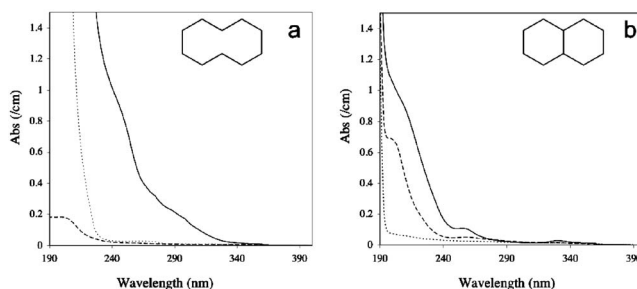


**Fig. 2** Absorption spectra of PHPy after first hydrogenation (black line) and second hydrogenation (gray line).

umn. The column was prepared in a Pasteur pipette, and the fluid was passed through the column by applying argon pressure on the top of the column. This method proved to be very effective for the elimination of highly polar impurities such as oxidation products. After the chromatographic purification, the fluid was collected in a UV-Vis quartz cuvette with a screw cap with a Teflon septum. The cuvette was purged with argon or nitrogen in order to eliminate the oxygen dissolved in the fluid. The purging process was absolutely necessary to minimize absorption at 193 nm of all alkanes studied because of the formation of oxygen-alkane complexes, as described below.

- Procedure 2: The alkane was treated with concentrated  $H_2SO_4$  for 12 h. The two nonmiscible phases were stirred vigorously during this period. The  $H_2SO_4$  treatment eliminates unsaturated impurities (isolated, conjugated, or aromatic double bonds) or impurities containing aromatic rings present in the fluid. After the treatment, the sulfuric acid phase was yellow in color. The sulfuric acid phase was separated by decanting, and the alkane layer was neutralized by treatment with NaOH pellets for 30 min and dried. A chromatography filtration through an activated carbon column was then performed to eliminate any remaining polar impurities.<sup>11</sup> As mentioned earlier, bubbling with nitrogen or argon was needed to eliminate the oxygen complex formed with the alkane.

The purification method needs to take into account the nature of the potential impurities present in the fluid. Procedure 1 is generally effective for the elimination of polar impurities such as inevitable oxidation products. However, if the impurity is nonpolar (i.e., contains a  $C=C$  double bond or aromatic system arising from the partially hydrogenated reactant), it may not be effectively separated through the silica gel chromatography, since the polarities and, therefore, the retention times of the impurities and the alkanes will be similar. Thus, a treatment with sulfuric acid is needed, and procedure 2 is more effective. The importance of the initial selection of the purification method is shown in Fig. 3. Figure 3(a) shows the absorption spectra of commercial and purified cyclodecane using both, proce-



**Fig. 3** Absorption spectra of cyclodane (a) and decalin (b) commercial sample (—), after purification with procedure 1(···) and procedure 2(---).

dures; Fig. 3(b) shows the absorption spectra of commercial and purified decalin using both procedures.

From Fig. 3, it is clear that the purification of cyclodecane is more effective by procedure 2, while for decalin, procedure 1 is more effective. Impurities of decalin are probably oxidation products resulting from the reaction of oxygen with highly reactive tertiary hydrogens to form peroxides, which then decompose to a family of “oxidation impurities.” The latter will generally possess a polar character and can be separated readily from the nonpolar alkane by silica gel chromatography. Cyclodecane is more stable against oxidation than decalin (cyclodecane does not possess any tertiary hydrogens), and the major impurities are probably residual  $C=C$  bonds, which cannot be separated using the silica gel column from the cyclodecane because of its similar polarity. This hypothesis is consistent with the observation that treatment with sulfuric acid is required to react with the  $C=C$  bonds and to eliminate the double-bond species. Oxidation products resulting from the reaction of these double-bond systems with sulfuric acid are retained in the active carbon column.

### 3.2 Reversible Formation of Oxygen-Alkane Complexes

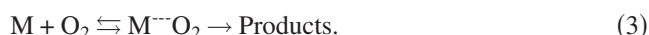
The goal of the purification methods was to achieve the highest possible degree of transmission at 193 nm, the working wavelength for current state-of-the-art microlithography systems. The last purification step is the elimination of the molecular oxygen from the solution by a simple purging with an inert gas (argon or nitrogen). This is a critical step, since we have found that for all of the alkanes investigated, the presence of oxygen results in the production of an intense absorption band in the region of 193 nm or longer wavelength. Purging with argon or nitrogen caused the removal of the absorption. Addition of air causes the reappearance of the absorption. Thus, the formation and elimination of the absorption is reversible. We conclude that oxygen forms complexes absorbing in the region of 193 nm. Evans investigated the formation of complexes of oxygen and organic molecules by UV absorption spectroscopy, employing a high pressure of oxygen in order to observe the complexes.<sup>12</sup> Most of the molecules studied had an aromatic character; however, it was noted that oxygen elimination was required to obtain transparency in the UV region for the alkanes hexane and cyclohexane. Tsubomura et al. studied the appearance of a new absorption band as a consequence of the interaction be-

**Table 1** Absorbance of air- and argon-saturated alkanes at 193 nm.

Compound	Absorbance at 193 nm (/cm)	Absorbance at 193 nm (/cm)
	Air saturated	Argon saturated
Pentane	0.6211	0.19
Cyclohexane	1.2531	0.03
Methyl-cyclohexane	>2	0.26
Heptane	1.37	0.04
Cyclodecane	1.1995	0.18
Decalin	1.1792	0.24
Perhydrofluorene	>2	>2
Perhydrophenanthrene	>2	>2
Perhydropyrene	>2	>2

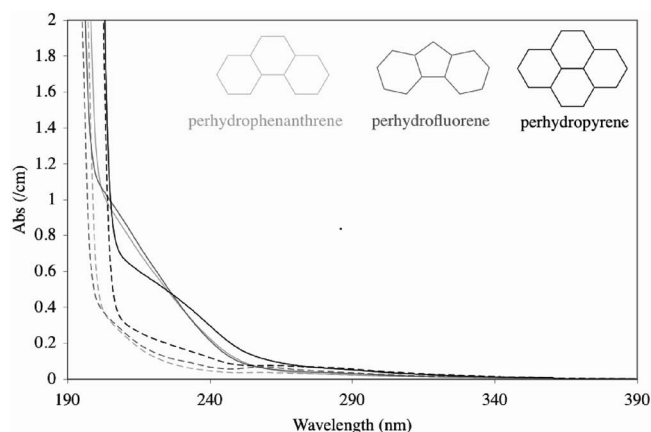
tween molecular oxygen and organic molecules such as ethyl alcohol, dioxane, n-butylamine, benzene, mesitylene, pyrrole, triethylamine, aniline, and N.N-dimethylaniline, but no alkanes were investigated.<sup>13</sup>

The oxygen sensitive absorption bands were readily eliminated by bubbling nitrogen or argon gas through the solution, demonstrating the very weak bonding of oxygen and the organic molecules. These results were hypothesized [Eq. (3)] to result from the formation of complexes resulting from charge transfer interactions between oxygen (charge acceptor) and the organic molecule (charge donor). This hypothesis was supported by the observation of a linear relationship between the ionization potential of the organic molecule and the absorption maximum and the reversibility of formation of the absorption. More recently, a theoretical study has been reported on the formation of a complex between molecular oxygen and cyclohexane.<sup>14</sup> This work was concerned with the dissociation of the complex after excitation. Scurlock et al.<sup>15</sup> have observed similar complex formation in their studies of singlet oxygen quenching by organic molecules:



## 4 Results

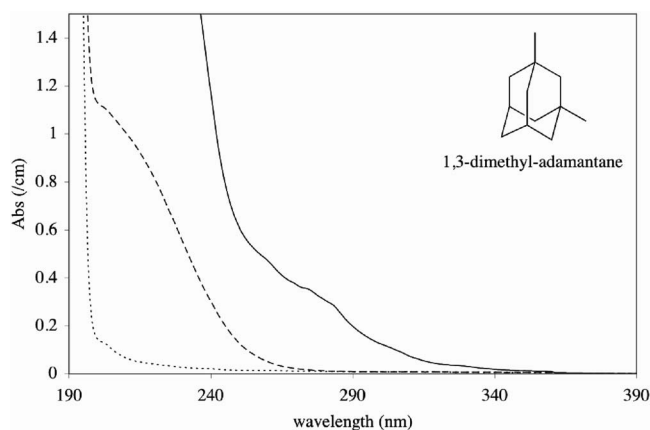
In the present work, the interaction between molecular oxygen and linear alkanes (pentane, heptane), cycloalkanes (cyclohexane, methyl-cyclohexane, cyclodecane), and polycycloalkanes (decalin, 1,3-dimethyladamantane, perhydrofluorene, perhydrophenanthrene, perhydropyrene) has been investigated in an attempt to delineate the origin of the far UV absorption band. In all cases, a strong absorption band has been found in the region of 193 nm when oxygen is present; the absorption is absent or decreases when oxygen is absent. Table 1 summarizes the absorbance values for all the alkanes at 193 nm in the presence and absence of oxygen. A substantial decrease in the absorbance at 193 nm can be observed for most of the compounds studied when oxygen is eliminated from the media. Nevertheless, some of the candidates still have an absorbance greater than 0.15/cm, which is the target value given by the microelectronic industry. For a more detailed discussion, see Ref. 4.

**Fig. 4** Absorption spectra of air-saturated (---) and argon-saturated (—) polycycloalkanes.

In the case of the synthesized polycycloalkanes (perhydrofluorene, perhydrophenanthrene, and perhydropyrene), there is no significant decrease in absorbance at 193 nm upon removal of oxygen, because the absorbance of these compounds is already high at 193 nm. Nevertheless, the formation of the oxygen complex can still be observed by the formation of an absorption shoulder between 210 and 250 nm in the presence of oxygen (Fig. 4).

Hypothetically, oxygen itself, not an alkane-oxygen complex, might be responsible for the new absorption when oxygen is present. To test this hypothesis, the absorption spectra of two nonpurified perfluoroalkanes, perfluoro-15-crown-5-ether and perfluoropentane, were measured in the presence and absence of oxygen. No difference could be found between the argon- and oxygen-saturated spectra. The result could be interpreted as being due to a lower solubility of oxygen in perfluoroalkanes. However, the solubility of oxygen in perfluoroalkanes is two times higher than in normal alkanes.<sup>16</sup> (Molar fractions of oxygen in heptane and perfluoroheptane are  $2.15 \times 10^{-3}$  and  $5.5 \times 10^{-3}$ .) Thus, oxygen itself is not responsible for the absorption at 193 nm observed with alkanes. This clearly supports the hypothesis that the new absorption at 193 nm created by the addition of oxygen to alkanes is due to the formation of a charge transfer complex between the molecular oxygen and alkanes. Evidently, the ionization potential of perfluorocarbons (perfluorocyclopentane 11.7 eV, perfluorocyclohexane 13.2 eV, and perfluorocarbon) is too high for significant electron transfer to molecular oxygen.<sup>17</sup> Therefore, no complex is formed between oxygen and perfluorocarbons and no absorption at 193 nm is observed upon addition of oxygen to the perfluorocarbons.

Since both linear and cyclic alkanes form an oxygen complex, the latter probably possesses a nonspecific or "loose" molecular geometry. Even with more complex alkanes like 1,3-dimethyladamantane (Fig. 5) a larger absorption band due to the formation of the oxygen complex at 193 nm was found. We suggest that the ionization potential of alkanes, although relatively high, is still a major factor in determining complex formation; a charge transfer contribution from the alkane to oxygen [Eq. (3)] contributes to the stability of the complex and, therefore, the absorption at 193 nm. Most alkanes and cycloalkanes possess<sup>18</sup> a similar

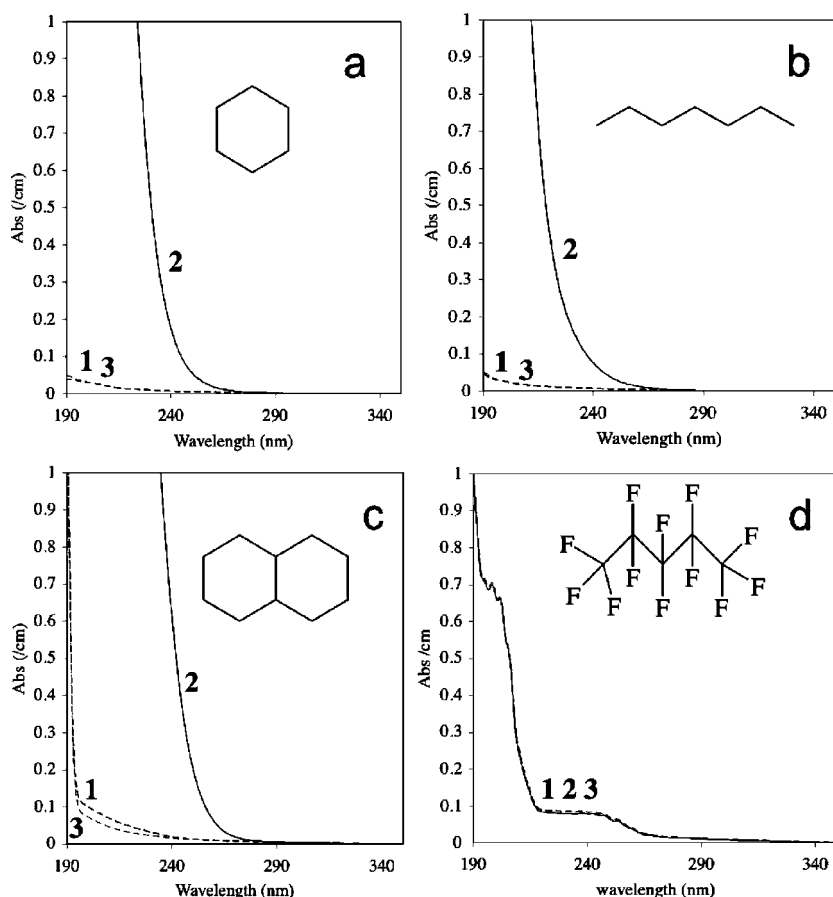


**Fig. 5** Absorption spectra of commercial (\_\_\_), purified (---), and argon-saturated (.-.) 1,3-dimethyl-adamantane.

ionization potential (9 to 10 eV); the effect due to the absorption of the molecular oxygen complex is expected to be crucial for all alkanes that are to be considered as viable candidates for immersion fluids.

The reversibility of this complex formation was studied with several alkanes. Fortunately, for all the alkanes investigated, the oxygen in the samples could be removed by purging with Ar or N<sub>2</sub> so that the issue of the absorption of

the alkane-oxygen complex can be overcome in working systems by purging the fluid. As can be seen in Figs. 6(a)–6(c) as examples, the absorption due to the oxygen complex can be readily eliminated by bubbling argon through the liquid; the absorption reappears by bubbling molecular oxygen for a couple of minutes. Bubbling again with argon reduces the absorption to the lower initial values. These experiments confirm that the binding of the complex is due to weak interactions between oxygen and the alkane, and that the formation of the complex is a perfectly reversible process. From Fig. 6, it can be seen that this reversibility has been observed for all types of alkanes: exemplars, linear (heptane), cyclic (cyclohexane), and polycyclic (decalin). Also, the lack of complex formation is shown in Fig. 6(d) for perfluoropentane for which the absorption spectrum is unchanged in the presence and absence of oxygen. As a final example, unpurified acetonitrile was found to possess a surprisingly low absorbance at 193 nm ( $\approx 0.25 \text{ cm}^{-1}$ ). Furthermore, no differences were found between air- and argon-saturated acetonitrile, which indicates that oxygen-acetonitrile complex formation does not take place. The ionization potential of acetonitrile<sup>19</sup> is 12.2 eV, a higher value than that for alkanes, which are in the range from 9 to 10 eV. Since the oxygen complex is a charge transfer complex with oxygen as an electron acceptor, the ionization potential of the organic molecule in the complex will define the extent of complex formation and



**Fig. 6** Absorption spectra of argon-saturated (dotted black line, 1), oxygen saturated (black line, 2), and argon-saturated again (dotted gray line, 3) of cyclohexane (a), heptane (b), decalin (c), and perfluoropentane (d).

the complex absorption wavelength. It should be mentioned that oxygen solubility in acetonitrile<sup>20</sup> is smaller than in alkanes (oxygen molar fraction  $\approx 4.5 \times 10^{-4}$ ), which will be another factor in limiting the absorption due to any charge transfer complex.

## 5 Conclusions

Two simple alkane purification methods were developed and standardized, which led to low absorption in the region 193 nm. Based on an excellent correlation between density and refractive index, the polycyclic alkanes, perhydro-pyrene, perhydrofluorene, and perhydrophenanthrene, were selected as potential high RI fluids, synthesized and purified. Although these synthesized fluids had high RIs (PHPy  $n_{193 \text{ nm}} = 1.7014$ , PHF  $n_{193 \text{ nm}} = 1.6684$ ), even after extensive purification, they all showed absorbance (in the absence of oxygen) of  $> 2 \text{ cm}^{-1}$  at 193 nm. Apparently, this high absorption is intrinsic to the compound itself, since it could not be reduced after several purification cycles. Further discussion can be found in Ref. 4. Commercially available alkanes (heptane) and cycloalkanes (decalin, cyclohexane, cyclodecane, 1,3-dimethyladamantane) were also purified; the purified liquids (in the absence of oxygen) showed absorbance  $< 0.26 \text{ cm}^{-1}$  at 193 nm. The research reported here demonstrates that purification is a critical feature in the practical application of alkanes as immersion fluids for photolithography at 193 nm. Even "spectral-grade" commercially available alkanes require extensive purification.

A second important feature revealed by this study is the requirement of the elimination of oxygen from alkanes, since an alkane-oxygen complex is formed and results in significant absorption at 193 nm. Fortunately, simple bubbling of argon or nitrogen through the fluid thoroughly removes the absorption due to the complex. Removal of the oxygen is important not only from the standpoint of minimizing the absorption of the fluids at 193 nm, but also because the excitation of the complex can cause the formation of reactive oxygen species capable of degrading the immersion fluids and producing over time significantly absorbing products.<sup>15</sup>

## Acknowledgments

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**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. After his post-doctoral research in organic photochemistry at Columbia University, USA, developing high refractive index and low absorbance immersion fluids in collaboration with SEMATECH, he is now developing prediction

models for industrial process control at the University of Sao Paulo, Brazil.



**Joy T. Kunjappu** holds two doctoral degrees from the University of Bombay, India (PhD, 1985 and DSc, 1996). His postdoctoral training was at Columbia University, USA, where he researched spectroscopic characterization of surfactant aggregates. Currently, he is in 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 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 the book *Essays in Ink Chemistry: For Paints and Coatings Too*.



**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- $\mu\text{m}$  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, CA, 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- $\mu\text{m}$  and sub-0.18- $\mu\text{m}$  photolithography processes until early in 1997. He has been in the semiconductor industry for over 19 years, holds over 30 patents, and has published over 100 papers in the area of lithographic materials and processes. He is the former chair of the SPIE Conference on Resist Technology, is a member of the ACS and SPIE, and is an associate editor for the *Journal of Micro/Nanolithography, MEMS and MOEMS*.



**Paul Zimmerman** is an Intel assignee to SEMATECH where he is currently the project manager for high-index fluids and resists. Paul received his PhD from the University of Pittsburgh and an MBA from Arizona State University. He has worked for Intel Corporation since 1994, first spending nearly three years as a surface chemist in Portland Technology Development. He spent two years working in assembly test development in Chandler, Arizona. From 2001–2004 he was on assignment at International SEMATECH de-

veloping advanced materials for 157-nm and 193-nm immersion and EUV lithography. While on assignment at International SEMATECH, he had over 30 publications and three patents. Prior to his current assignment he was on assignment at IMEC to aid in the development of high-*k* dielectrics for the 32-nm node and beyond. He is also focused on development of non-Si nanotechnologies for low-power, high-performance logic applications, including Ge for pMOS and III/V materials for nMOS.



**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 mentored 200 postdocs. Over 100 undergraduates have been trained in research under his supervision. He is the author of two textbooks on organic photochemistry used by several generations of organic photochemists since 1965. He has published over 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.