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Degradation of Hydrocarbon Fluids in the Immersion Lithography at 193 nm

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The search for successful generation 3 immersion lithography fluids is focused on high refractive index fluids which are transparent to 193 nm light. This search has led to saturated hydrocarbons which have been shown potential in this field. This paper discusses our observations that many immersion fluid candidates (saturated hydrocarbons and acetonitrile) were observed to polymerize upon irradiation with 193 nm light.

Keyword: immersion lithography, hydrocarbon polymerization, refractive index

1. Introduction

In 1965 the visionary Intel cofounder Gordon Moore made the prediction that the number of transistors on a chip will double about every two years. Over the past 40 years the industry has kept pace with that prediction. They have mainly achieved this by incrementally extending optical lithography to meet the needs of the semiconductor industry. The current development node for the industry seeks to achieve feature sizes with dimensions of less than 32 nm.[1] The resolution for optical lithography is determined by the wavelength of the imaging light (λ) and the numerical aperture (NA) of the projection lens according to the Rayleigh criterion[2]:

$$R = k_1 \frac{\lambda}{NA} \qquad (1)$$

According to this relationship, the resolution can be decreased by either decreasing the wavelength or increasing the numerical aperture. The k_1 factor depends on the specific process latitude. The numerical aperture (NA) is defined by the relationship:

$$NA = n \cdot \sin\theta \qquad (2)$$

where n is the refractive index of the surrounding medium and θ is the aperture angle, which is the angle sustained by the ray of the largest spatial frequency permitted by the optical system. Traditional systems which are imaged in air have a numerical aperture approaching 1. However, when air is replaced by a fluid with a higher refractive index this allows for a decrease in the feature sizes.

The wavelength in lithographic imaging systems has steadily decreased over decades to today's high resolution wavelength of 193 nm. A further reduction to 157 nm has proven challenging with a variety of complications.[3] Recently 157 nm lithography was abandoned, leaving the main hope for continued scaling using lithography as extreme ultra violet (EUV). However, EUV lithography is unlikely to be ready for even limited production before 2015 which will be far too late for the 32 and possibly 22nm nodes.

Given this state of events, immersion lithography at 193 nm seems the most likely candidate to extend optical lithography for the foreseeable future. The criterion for these immersion fluids are that they be transparent to the imaging light with a required absorbance ≤0.05/cm and possess refractive indices significantly greater

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than water.[4] Additionally, the fluid should be unreactive and have a viscosity no more than five times that of water. A few respective candidates for immersion lithography are displayed in table 1. Already in limited production, water based immersion has shown great utility imaging at the 45nm node. The need for liquids of even higher refractive indices is now urgent as the only other lithography that can be implemented for the 32 nm node is double patterning which is expensive and has overlay limitations. Recent efforts are underway to exploit higher-index hydrocarbon fluids. This paper evaluates a variety of organic fluids for immersion lithography at 193 nm. Imaging experiments with some select hydrocarbons was shown to result in decomposition of the fluid to products which increased the absorption of the fluid at 193 nm. The details of these experiments are discussed below.

Table 1. Refractive indices of 193 nm transparent fluids.[5, 6]

Fluid	Refractive Index (193 nm at 21.5°C)
Water	1.456
Dodecane	1.557
Cyclohexane	1.566
Decalin	1.641
Bicyclohexyl	1.644

2. Experimental

2.1 Fluid Purification and Handling

Details of fluid purification were described in a previous publication.[7] Complexes formed between oxygen and these organic fluids increases absorption and reactive and are thus undesirable. Prior to use all fluids are degassed by nitrogen purging to reduce the oxygen content to low ppm values (> 1 ppm).

2.2 Laser Irradiations

Our irradiation setup was adapted from previous water immersion experiments.[8] Irradiation at 193nm is obtained with a Lambda Physik 4030 NovaLine laser operating a repetition rate of up to 4000 Hz. An ML2100 variable dielectric attenuator from Metrolux Corporation is used to attenuate in-situ the laser fluence to a final fluence incident on the fluid cell of 0.2 mJ/cm^2/pulse. The beam spot at the front of the cell, as measured by exposing a photosensitive film is 5 mm high and 1.5 mm wide.

2.3 Degradation Studies

The irradiated fluids were first analyzed by GC-MS for lower weight byproducts. The irradiated fluid samples were deposited on silicon wafers and the volatile components were driven off at 60°C under partial pressure. The sample residues were analyzed using a time-of-flight Secondary ion mass spectrometer (TOF-SIMS) The TOF-SIMS was an Ion-TOF IV (GmbH). Spectra were collected for 3 minutes on each sample for both positive and negative ions.

3. Results and Discussion

A stark increase in absorption of various fluids was observed when they were exposed to 193 nm irradiation. This is outlined in figure 1a, where all the fluids studied (decalin, bicyclohexyl, cyclohexane, *n*-heptane and acetonitrile) were shown to decompose with irradiation.

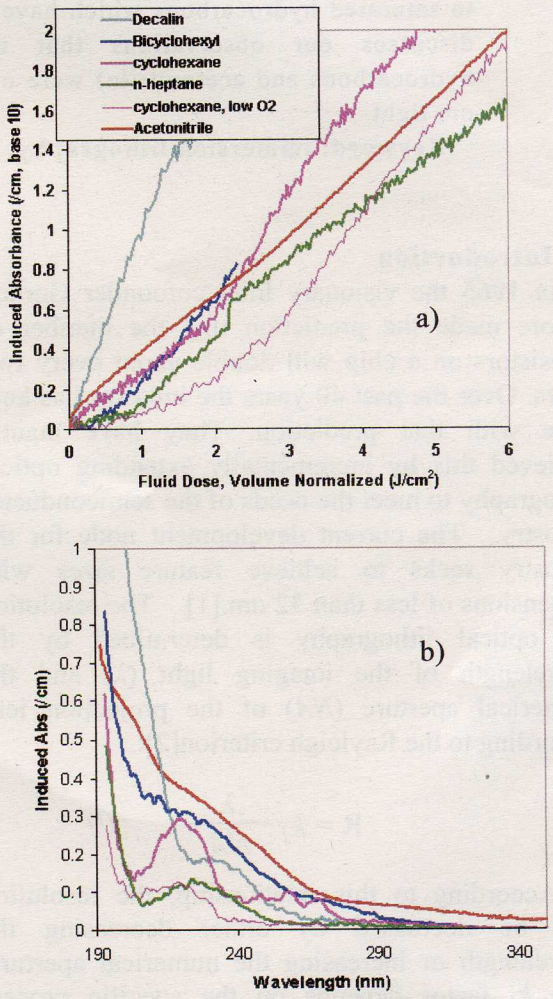

Fig. 1. Fluid degradation with irradiation at 193 nm; a) absorption increase and b) absorption spectra of liquids after 2 J/cm^2 irradiation.

The increase was constant for all fluids, with the greatest rate of increase in absorption occurring in decalin. A snapshot of the absorption of various fluids after 2 J/cm^2 is displayed in figure 1b. All the fluids develop consider absorption with characteristics indicating the creation of unsaturated products with π-π^* transistions.

A GC-MS analysis of these post-irradiation fluids showed a great number of byproducts. An analysis of the irradiation degraded cyclohexane in particular was shown to decompose a major extent to cyclohexanol, decalin and bicyclohexyl. Many of the other degradation products consisted of various bicyclohexyl derivatives of varying levels of saturation and oxidation.

Irradiation of saturated hydrocarbons in the presence of oxygen is known to create oxygenated hydrocarbon derivatives. In a study of the effect of 185 nm irradiation on cyclohexane Srinivasan and White showed cyclohexyl hydroperoxide to be the major product.[9] They noted that "irradiation of cyclohexane saturated with oxygen at 185 nm led to the rapid formation of cyclohexyl hydroperoxide and lesser amounts of cyclohexanol and cyclohexanone." Independent irradiation of pure cyclohexyl hydroperoxide resulted in the formation of cyclohexanol and cyclohexanone and it is believed that they are secondary products, formed from the decomposition of cyclohexyl hydroperoxide. The authors believe that these products are the result of direct reaction between oxygen and cyclohexane. No ozone was shown to be present during the photolysis. The authors believe that the products are a result of an excited O_2 with cyclohexane:

$$O_2 + h\nu \longrightarrow O_2^* \qquad (3)$$

$$O_2^* + RH \longrightarrow ROOH \qquad (4)$$

These results are seconded those of Kulevsky and coworkers, whose product accumulation studies show cyclohexyl hydroperoxide to be the primary product and the alcohol and ketone to be secondary products.[10] They argue the existence of a contact charge transfer complex between oxygen and cyclohexane, where the C-H bond is the donor site. Following an electron transfer to oxygen, hydrogen is abstracted from the hydrocarbon by oxygen. The hydroperoxide is then formed by combination of the alkyl radical and the hydrogen peroxide radical.

$$O_2 + RH \rightleftharpoons O_2\text{---}H\text{---}R \overset{h\nu}{\rightleftharpoons} R\bullet\ H^+\text{-----}O_2^- \qquad (5)$$

$$R\bullet H^+\text{-----}O_2^- \rightleftharpoons R\bullet + HO_2\bullet \qquad (6)$$

$$R\bullet + HO_2\bullet \rightleftharpoons RO_2H \qquad (7)$$

In an effort to reduce the effect of oxygen on degradation of the hydrocarbon fluids, care was taken to reduce the oxygen concentration to below 1 ppm (cyclohexane low O_2, Fig. 1). A decrease was observed in the rate of induced absorption of cyclohexane. Though an improvement, the increase in the absorption and thus degradation of the improved degassed cyclohexane was still significant. From this observation we surmised that the degradation of the fluids was caused by other processes.

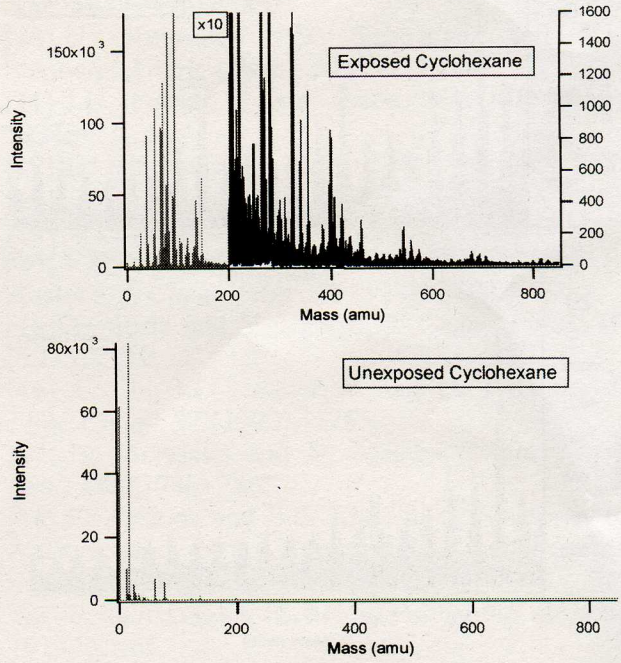

Fig. 2. Comparison of TOF-SIMS spectra for exposed and unexposed cyclohexane.

Further analysis was performed to deduce the other products and processes that were involved in fluid degradation. Fluids were initially analyzed via GC-MS but it was suspected that components were present that were too large for the gas chromatography. The fluids evaluated include acetonitrile, cyclohexane, bicyclohexyl and decalin. The exposed fluid samples were taken and drops were deposited on a Si wafer. The fluid was evaporated leaving a solid residue on the sample surface which was analyzed using TOF-SIMS. Unexposed fluids were also deposited on wafers and evaporated and analyzed as controls. Fig. 2 shows the comparison of results obtained from TOF-SIMS of the exposed and unexposed

cyclohexane. Unexpectedly large molecular products were observed with masses ranging up to 800 mass units. A repeating unit with molecular formula $C_{10}H_{14}$ was obtained from the mass spectrum, but it was difficult to discern the mechanism for this oligmer formation.

Irradiation with 193 nm light and evaluation of the other fluids, bicyclohexyl, decalin and acetonitrile also afforded large molecular weight products (Fig. 3). Repeating units with the molecular formula C_6H_{10} were observed for bicyclohexyl while no discernable repeating units could be obtained from the spectrum of decalin and acetonitrile.

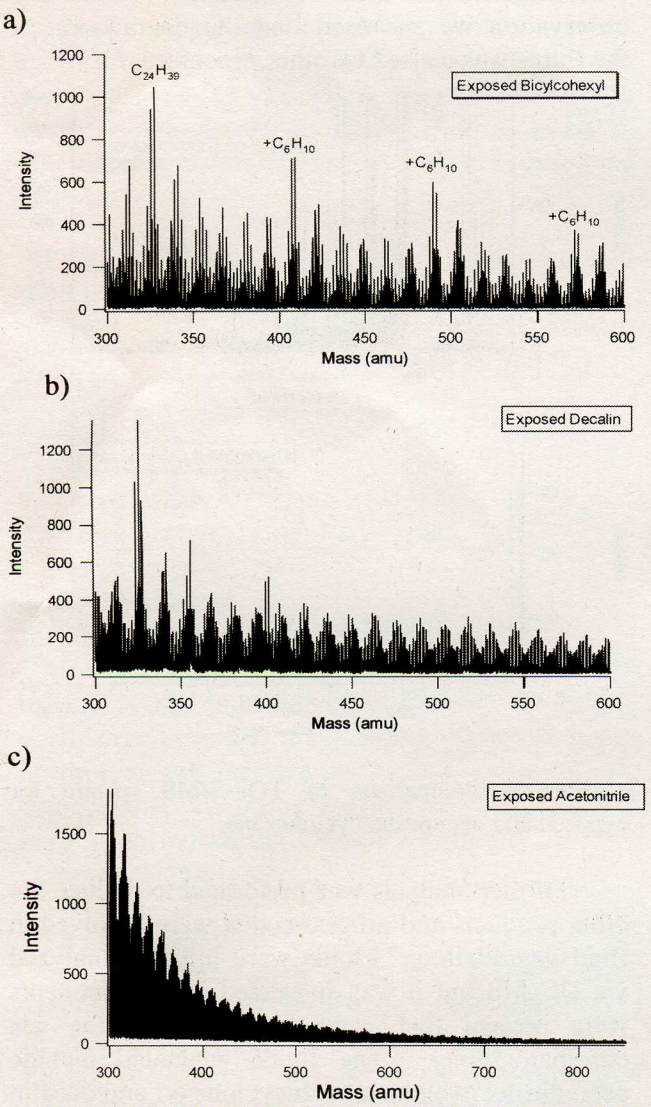

Fig. 3. Comparison of TOF-SIMS spectra for exposed a) bicyclohexyl, b) decalin, c) acetonitrile.

Evidence of polymerization of saturated hydrocarbons by photochemical means was not found in the literature. Precedence for polymer formation from saturated hydrocarbons was however found in the plasma and radiation chemistry literature.[11-13] A comparison of the decomposition of saturated hydrocarbons by photolysis and radiolysis however showed similarity in mechanism and fragmentation products.[14] When irradiated at far ultraviolet wavelengths beyond the ionization threshold (for most hydrocarbons approximately 150 nm, 8 eV) or a gamma source the formation of H_2 was observed as the most prevalent process.[14, 15] For both photolysis and radiolysis, the H_2 is formed from hydrogen being eliminated as a molecule from the excited hydrocarbon (Eqn. 9) and when H atoms undergo abstraction reactions with the hydrocarbon. For photolytic degradations the ratio in the mechanism of H_2 formation was found to be wavelength dependent, with higher rates of abstraction reactions occurring at shorter wavelengths. An analysis of the photolysis products of hydrocarbons showed other major products to be the alkene elimination product and the dimer.[15]

Even though the irradiation wavelength of 193 nm (6.42 eV) is below the ionization threshold of saturated hydrocarbons, multiphoton absorption of this light will place it well above the threshold. Multiphoton ionization of alkanes has been previously reported and it is plausible that nonlinear excitation is the basis of polymer formation.[16, 17] A plausible mechanism for polymer formation is laid out in Equations 8 through 12.

$$C_nH_{2n+2} \xrightarrow{nh\nu} C_nH_{2n+2}^* \quad (8)$$

$$C_nH_{2n+2}^* \longrightarrow C_nH_{2n} + H_2 \quad (9)$$

$$C_nH_{2n+2}^* \longrightarrow C_nH_{2n+2}^{\cdot+} + e^- \quad (10)$$

$$C_nH_{2n+2}^{\cdot+} \longrightarrow C_nH_{2n+1}^{+} + H \quad (11)$$

$$C_nH_{2n+1}^{+} + C_mH_{2m+2} \longrightarrow C_{n+m}H_{2(n+m)+1}^{+} + H_2 \quad (12)$$

Upon irradiation there is competition between eliminating molecular hydrogen and a hydrogen atom. The carbonium species that is produced when a hydrogen atom is eliminated is proposed to react with surrounding hydrocarbon (Eqn. 12).[13] This mechanism is proposed for radiation induced polymerization of saturated hydrocarbons and is plausible for the polymerization observed by photolysis. Our proposed mechanism does not exclude other likely mechanisms such as a radical pathway where carbon-carbon bond cleavage processes leading to the formation of two radicals are known as a primary process of far ultraviolet irradiation of alkanes.[18]

4. Conclusion

The search for the next generation of immersion fluids has led to saturated molecular weight hydrocarbons. These species possess both the required transparency at the imaging wavelength of 193 nm and higher refractive indices. This class of fluids however was shown to degrade upon irradiation to a wide variety of products all of which cause an increase in fluid absorption to unacceptable levels. This degradation occurred rapidly in spite of very low absorbance (≤0.03/cm) values for some liquids. High molecular weight products are proposed to be caused by multiphoton absorption by the fluids which is beyond the ionization threshold of hydrocarbons. Use of saturated hydrocarbons thus is limited in their ability to perform as effective immersion fluids at 193 nm without some manner of in-line repurification to remove the degradation products.

5. Acknowledgments

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