

High Refractive Index Fluid for Next Generation ArF Immersion Lithography

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ArF immersion lithography using a high-refractive-index fluid (HIF) is considered to be one of the most promising candidates for hp38nm or below. We have developed JSR HIL-001 and HIL-002 as new immersion fluids, the refractive index and transmittance of which are 1.64, >98%/mm and 1.65, >99%/mm (193.4nm, 23°C), respectively. Using HIL-001 immersion and a two-beam interferometric exposure tool, hp30nm imaging has been demonstrated. However, despite the remarkable advances of recent HIF research, there is still a lot of issue about whether an organic fluid can be used in immersion lithography, since optical and photochemical behaviors of organic fluids at ArF wavelength have not been well understood so far. Besides, cost and disposal issues will be encountered when the organic immersion fluid is substituted for water. In this paper, we will address such problems by reporting our updated results on research of JSR HILs.

Keyword: high-refractive-index fluid, ArF immersion lithography, photo-decomposition, UV absorption, photoresist defects

1. Introduction

It is considered that high-refractive-index fluid (HIF) will be used as the immersion fluid in the next generation of 193nm Immersion lithography instead of water. By increasing the refractive index of the immersion fluid, both lithography resolution and DOF (depth of focus) would be improved. Thus, development of a suitable HIF has become one of the key technical challenges to be addressed in order to realize ArF immersion lithography. Recently a number of organic HIFs have been reported [1-5]. The optical properties for some of the HIF candidates, such as refractive indices (>1.6) and

transmittance (>98%/mm), are very promising. Successful imaging of hp32nm L/S has also been demonstrated by two-beam interferometric exposure tool [2, 3]. However, despite the remarkable advances of recent HIF research, there is still a lot of doubt about whether an organic fluid can be used in immersion lithography, since optical and photochemical behaviors of organic fluids at ArF wavelength have not been well understood so far. In this paper, we will address such problems by reporting our updated results on research of HILs, which are the current candidates of immersion fluids under development at JSR for the next generation

ArF immersion lithography.

2. Experimental

2.1. HIL samples

All samples were carefully deoxygenated and saturated with nitrogen by storing in a nitrogen glove box for at least 24h before use.

2.2. Computational Calculation of UV absorption

Absorption wavelength and oscillator strength f is calculated by time-dependent density theory. Calculated absorption spectra are given by Combination of Gaussian and Lorentzian functions.

2.3. UV Measurement

UV absorbance was measured using a JASCO V550 spectrometer and quartz cells with PTFE stoppers. The UV absorbances of fluids are evaluated by the cell reflection using the method described below. Thus, a fluid sample was measured independently in a 2cm-path cell and a 1cm-path cell. The subtraction of the two absorbances is used as the true absorbance per cm. However, the UV absorbance data measured in laser irradiation experiments are collected in this manner.

2.4. HIL Photo-decomposition by ArF Laser Irradiation

Cymer Nanolith7000-300 was used as the laser source. The same 1cm-path quartz cells in UV measurement were used.

2.5. Refractive Index Measurement

Refractive index was measured by prism-goniometric minimum deviation methods. The temperature of the prism was controlled within $\pm 0.05^\circ\text{C}$. The estimated measurement error is $< \pm 0.00002$.

2.6. Photoresist, Processing, and Defect Detecting

JSR ARX2014J, methacrylate base photoresist, was used in this study as a standard 193nm photoresist. ARC29A, supplied by Nissan Chemical Industries Ltd, was spin-coated on bare-Si substrate as a bottom anti-refractive coating (BARC). Aqueous tetramethyl, ammonium hydroxide (TMAH, 2.38 wt%) was used for developing the photoresist, and deionized water (DIW) was used in the water puddle experiment. Dry exposure was conducted by the following procedures. Photoresist coat, bake, and development were conducted using a Tokyo Electron Clean Track ACT8 coater developer. Nikon 193nm scanner NSR S306C (NA=0.78) was used for exposure. The defect inspection was performed by a defect inspection tool, KLA2351 (KLA-Tencor) on 90nm L/S pattern. The defect reviewing and the CD-measurement of each wafer were performed by CD-SEM, S9389 (Hitachi High-Tech.). HIL immersion exposure was performed in collaboration with IBM Almaden Research Center and Canon using a two-beam interferometric exposure tools.

3. Results and Discussion

3.1. A Novel High Transparent Immersion Fluid

High transmittance is required for HIF in order to obtain imaging with high quality. However, unlike water, organic fluids generally have strong or relatively strong inherent absorption at 193nm. They also tend to contain different organic impurities which are often opaque at 193nm, and are practically impossible to be fully removed. To distinguish the inherent absorption from that coming from impurities, theoretical calculations of UV absorption for HIL-001 and HIL-002 were carried out. Our calculation clearly shows HIL-002 has less absorption near the 193nm region compared with HIL-001. Thus, we prepared HIL-001 and HIL-002 and purified them extensively. Fig. 1 shows the UV spectra of purified

Table 1 Fundamental parameters for water, HIL-001 and HIL-002

	water	HIL-001	HIL-002
$n@193\text{nm}, 23^\circ\text{C}$	1.44	1.64	1.65
Absorbance[cm^{-1}] $@193\text{nm}$	0.036/cm	0.052/cm	0.032/cm
Solubility of Air [ppm]	7 (O_2), 13 (N_2)	70 (O_2), 115 (N_2)	55 (O_2), 91 (N_2)
Viscosity [mPas]	1	2.1	2.9
Heat of Evaporation [KJ/g]	2.3	0.33	0.35

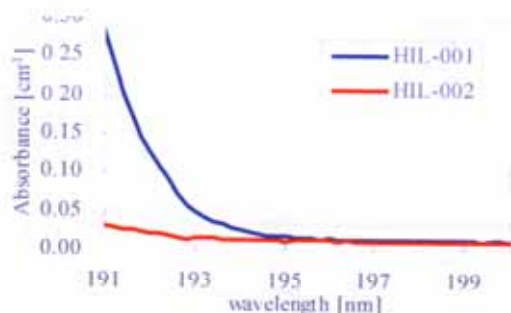


Fig. 1. Measured UV absorption spectra of HIL-001 and HIL-002

HIL-001 and HIL-002. These samples for both HIL-001 and HIL-002 are the most transparent samples which could be obtained by repeated purification, and are estimated as the limit to their inherent transmittances. As it can be seen, absorption of HIL-002 is lower than that of HIL-001 at 193nm, and the absorption curve for HIL-002 is flatter than that for HIL-001 near the region of 193nm, which is consistent with our theoretical calculation. The fundamental parameters for water, HIL-001 and HIL-002 are listed in Table 1. Both HIL-series have quite similar fundamental parameters.

3.2 ArF Laser Photo-Decomposition of HILs

ArF laser induced photo-decomposition is one of critical issues for HIF application, as photo-decomposition of HIF would deteriorate the optical properties, generate impurities which may further interact with photoresist films or be harmful to the lens of the exposure tool. Thus, we studied HIL's photo-decomposition by ArF laser irradiation. The experiments are described in Fig. 2. A number of HIL samples are filled into quartz UV cells. All the HIL samples have been fully deoxygenated, and saturated with nitrogen. The UV cells are sealed by PTFE stoppers to prevent

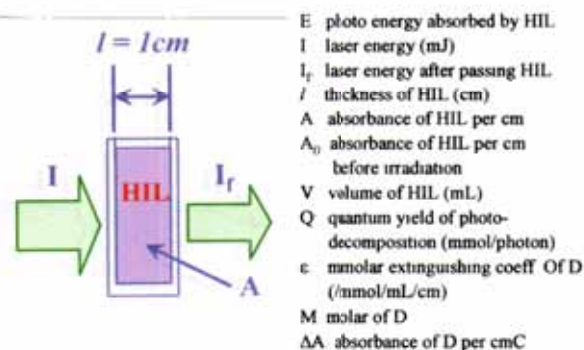
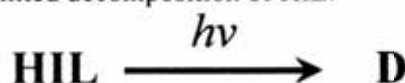


Fig. 2. Laser irradiation experimental for HILs

HIL from coming into contact with oxygen in the air during the experiment. After ArF laser irradiation with different dosages, the HIL samples were subjected to UV absorption measurements.

We have been trying to quantify photo-decomposition of HILs by establishing a physicochemical model (Fig. 3). In our model, HIL decomposes to D with quantum yield Q by photo irradiation. D could be a mixture whose average molar extinguishing coefficient is ϵ . We assumed Q and ϵ being constant, and D doesn't under go further decomposition or even if D photo-decomposes further ϵ doesn't change. This assumption is considered reasonable as the laser dose in our experiment is small enough to result in only limited decomposition of HIL.



Q : quantum yield of decomposition

ϵ : average molar extinguishing coefficient

Q and ϵ are assumed to be constants

$$E = I - I_r = I (1 - \exp(-A / \ln 10)) \sim I A_0 / \ln 10$$

$$M = Q E$$

$$\Delta A = \epsilon M / V, A = A_0 + \Delta A$$

$$A = k I / V + A_0 \quad (1)$$

$$k = \epsilon Q A_0 \ln 10 \quad (2)$$

Fig. 3. Physicochemical model of photo-decomposition for HIL

According to our model, k is a constant for a given HIL if ϵ and Q are constants (equation 2). Thus, the absorbance of HIL increases linearly with laser dose (equation 1). k represents the absorbance change of 1mL HIL when irradiated by 1mJ of ArF laser dose in 1cm-path cell. We defined k , the photodecomposition coefficient, which can be used to measure the tendency of photodecomposition for HIL. To make our model practically applicable, we don't consider separately HIL and the impurities it contains but take them as a whole (the HIL). The measured absorbance for

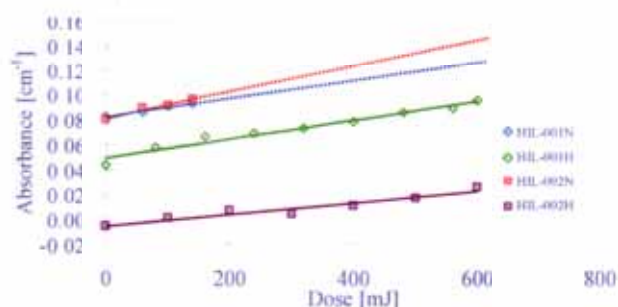


Fig. 4. Data of laser irradiation experiment. N and H denote normally and high transparent HIL. Dots are measured absorbances without reflection correction. Lines are calculated using equation 1.

Table 2 Summary of laser irradiation experiments

entry	sample	UV		Data fitting		Estimated UV change after exposure in a flow immersion tool	
		A_0 [cm^{-1}] (corrected)	T [%/mm]	r ; coefficient of linear correlation	$k \times 10^4$ [$\text{cm}^{-1}\text{mLmJ}^{-1}$]	ΔA [cm^{-1}]	$\Delta T/T$
1	HIL-001N	0.1091	97.52	0.98	2.31	4.62×10^{-4}	-0.0106
2	HIL-001H	0.0672	98.46	0.97	2.27	4.54×10^{-4}	-0.0105
3	HIL-002N	0.1040	97.63	0.96	3.30	6.60×10^{-4}	-0.0152
4	HIL-002H	0.0319	99.27	0.93	1.41	2.82×10^{-4}	-0.0065

HIL was used in the equations instead of its inherent absorbance. Thus, the absorbance data in laser irradiation experiments are plotted and fitted with equation 1 (Fig. 4). The calculation results are summarized in Table 2.

Both normally transparent (N) and high transparent (H) samples for HIL-001 and HIL-002 have been studied. The absorbance-dose shows good linear correlation for all the samples. The tendency for them to under go photodecomposition can be quantified by their k values, and is in the order HIL-002N > HIL-001N = HIL-001H > HIL-002H. Interestingly, HIL-001N and HIL-001H have almost identical k values but HIL-002H has much smaller k value than HIL-002N does. The reason for the difference between HIL-001 and HIL-002 is not clear at the present. By using k value and equation 1, we can estimate the change of transmittance of HILs after exposure when they are used in an immersion lithography system. The calculated absorbance change (ΔA) and transmittance change ($\Delta T/T$) are listed in Table 2 (We take the assumption; HIL flow rate = 0.5L/min, laser dose = 10000mJ/wafer, wafer processing rate = 1wafer/min, thickness of immersion fluid = 1mm

in the calculation). Our estimation shows the UV change of HILs will be very small before and after exposure when they are applied to an immersion lithography system.

3.3 Recycle of HIL

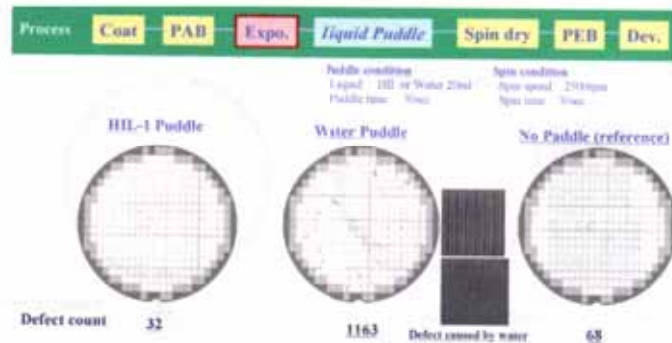
Water is disposed as a waste after immersion lithography process. However, that would not be the case for organic HIFs. In the viewpoint of environment protection and reduction of manufacturing cost, it is natural to consider recycling the HIF. Absorptions of both HIL-001H and HIL-002H, which have been deliberately degraded by applying over dosed irradiation (600,000mJ), were increased as shown in Table 3. By re-purification, both photo-degraded HILs were recovered to the initial level. Additionally, refractive index is one of the most important parameters for HIF, and must be held strictly constant during immersion photo-exposure. Thus refractive indices for HILs in laser irradiation experiment were measured and summarized in Table 3. Within the measurement error no refractive index variations were observed. It

Table 3 Summary of recycling of laser irradiation experiments

		before laser irradiation	after laser irradiation	after re-purification
HIL-001H	Abs. [cm^{-1}]	0.0682	0.5216	0.0663
	$\Delta n^{1)}$	-	0.00001	0.00001
	GC %	99.82	99.81	99.80
HIL-002H	Abs. [cm^{-1}]	0.0371	0.6126	0.0386
	$\Delta n^{1)}$	-	-0.00001	0.00000
	GC %	99.90	99.92	99.91

1) compared with sample before irradiation

is clear the refractive indices of HILs are stable enough for the purpose of immersion exposure. It is because the laser induced photodecompositions for HILs are quite limited within the laser dose we studied. In fact no new compounds could be detected in four laser irradiated HIL samples by GC analysis.



Substrate: TCX014(30nm)/ARX2014J(150nm)/ARC29A(77nm) Pattern size: 90nmLS

Fig. 5 "Fluid puddle" defect examination experiment

3.4 Immersion Defects

Water mark related defects and water leaching related defects are currently critical issues in immersion lithography. HILs are considered to be advantaged in defects compared with water, as HILs have much less leaching effect and much lower evaporation heat than water. We have compared the defect levels between water and HILs using "fluid puddle" method. The experimental methods and results are described in Fig. 5.

The reference wafer was processed in a standard photoresist procedure. In the fluid puddle tests, wafers were immersed in water or HIL-001 for 30sec after exposure. The wafers were spun at 2500rpm for 30sec to dry out the fluids before PEB and development. The defect inspection was performed by a defect inspection tool KLA2351 (KLA-Tencor) on 90nm L/S pattern. The defect reviewing and the CD-measurement of each wafer were performed by CD-SEM, S9380 (Hitachi High-Tech.). HIL-001 and water show 32 and 1163 defects counts, respectively, versus 68 counts for the reference. Our experiment suggests HIL-001 has less tendency to form immersion specific defects.

3.5 Hp30nm Imaging results

We have demonstrated imaging of hp32nm L/S with HIL immersion through use of a two-beam interferometric exposure tool. The resolution of an immersion lithography system is determined by the smallest refractive index among those of all the elements. Although HIL-001 has a refractive index of 1.64, the refractive index of the fused quartz prism we used is only 1.56. Thus, the prism is the critical factor which limits NA to around 1.5. To fully understand the potential of HIL immersion

and to extend NA up to 1.6, a new approach with a higher refractive index prism needs to be considered.

The approach we took takes the advantage of crystal quartz which has higher refractive index in e-axial direction, $n_e=1.674$ at 193.4nm. The experimental was considered with HIL-001 immersion (Fig. 6). The imaging results are shown in Fig. 7. Fine patterning of hp30nm L/S have been resolved. The estimated NA of this HIL-001 immersion system is higher than 1.6.

Route to a 30nm L/S litho

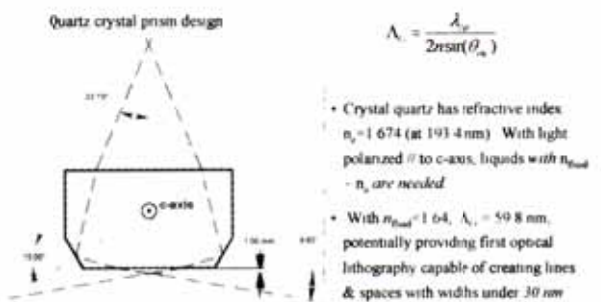


Fig. 6 Crystal quartz prism design

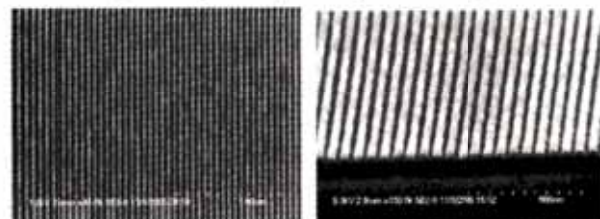
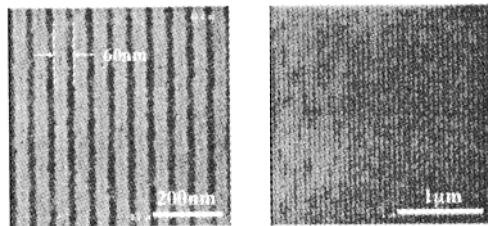


Fig. 7 hp30nm imaging result

Another approach we took takes use of fused quartz prism. However, the limitation of the refractive index of fused quartz was overcome

by a special design of the prism shape. This experiment was designed and carried out by Canon by using HIL-001 as the immersion fluid. The experimental conditions and results are shown in Fig. 8. Although it is still necessary to tune the experimental conditions to obtain more sophisticated image, hp30nm pattern has been successfully achieved. The estimated NA for this HIL immersion system is 1.61.



Condition
Exposure: Two Beams Interference(NA=1.61),
SEM: S-9300(Mag.=200k(left),50k(right)),
Substrate: Bare-Si, BARC(lower layer): ARC29A(100nm), BARC(upper layer):
NCA4938(80nm), Resist: ARX2014J(60nm), TARC: TCX015(90nm),
Immersion liquid: HIL-001(JSR, $n=1.64@193\text{nm}$)

Fig. 8 hp30nm imaging result

4. Conclusion

Our experiments show that HIL-series fluids are promising fluid candidates for the next generation of ArF immersion lithography. Their refractive indices and transmittance are larger than 1.60 and 98%/mm at 193.4 nm, respectively. High transmittance close to that of water has also been achieved. They are durable enough to ArF laser exposure and their refractive indices remain constant during exposure. Furthermore, they show less tendency to have immersion related photoresist defects than water. It has also

been demonstrated that with elaborate of prism design, NA of a two-beam interferometric exposure system based on HIL immersion can reach 1.6NA. Further studies which are expected to lead to practical application of HILs to immersion lithography are underway.

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