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Comparative Study of PMMA 120K and 996K for Electron Beam Lithography Application

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ABSTRACT

Photoresist is a photo-sensitive material applied to the substrate in a liquid state in small quantities.Photoresist is a radiation sensitive compound that is available both as positive and negative, depending on how it responds to radiation. In positive resists, the exposed regions of the material become soluble so that following development the exposed area are removed. In negative resists, the opposite happens where the resists becomes insoluble and exposed regions remain after development process. Poly(methyl methacrylate) (PMMA) was remained as selection resists in fabricating fine and high resolution patterns by electron beam lithography (EBL). Spin coating method is commonly used for the thin film formation with uniform thicknesses onto substrates. PMMA polymer with a molecular weight (MW) 120 K and 996K was dissolved in solvents which are anisole and chlorobenzene, 2% and 4% of solid content respectively. Then, the resist solution was spun coat at P-silicon for various spin speed and prebake to increase resists adhesion. This paper focused on influence of spin speed, PMMA molecular weight, type of solvent and percentage of resist solid content toward the resist thickness. The resist thickness are decreased when the spin speed increase, however the thickness of resist will increase when the percentage of solid content increase.As conclusion, thickness of the photoresist layer was dependent on the coated spin speed, molecular weight, solvent selection as well as solid content.

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INTRODUCTION

The resist thickness is depends on spinner rotational as well viscosity and solid content of diluted photoresist (Ruska, 1987). Thinner resist layers produce better electron beam resolution and alleviate some high-energy imaging problems since thicker resist causes resolution problems due to scattering of beam energy (Tolliver, 1988). Resist was dispensed either wafer at static or dynamic, where the substrate spinning at lowest spin speed. Figure 1 shows recommended resist spin coat cycle to obtain the desired uniformly thin layer and the resist spin speed curve versus resist thickness for different viscosity. The resist thickness uniformity was influenced by the volume of the resist dispensed and properties of the resist such as viscosity, percent solids, and solvent composition. Further, practical aspects of the spin operation, such as exhaust, temperature and humidity control, and spinner cleanliness often have significant effects on the resist film. The resist thickness varies as one over the square root of the spin speed and is roughly proportional to the liquid resist viscosity (Mack, 2008).

There are several issues during spin coating process such as comets shaped, air or nitrogen bubbles, uncoated area and pinholes. The common issue is comets shaped in the thin film due to particles from an insufficient substrate cleaning or an expired resist. Otherwise, air bubbles in the resist that often caused by transportation, refilling or dispensing of the resist, while nitrogen bubbles due to the gradual decomposition of the photo active compound in the liquid resist. The nitrogen gases that dissolved in the resist after resist bottle opened and stored for a certain time can overcome with delay before dispersing. While, the uncoated resist areas on the substrate occurred when too small resist volume. The thin film was drying by pre-baked or softbake on hot plate after spin coating to remove excess solvent for stabilizing during lithographic processing. An unbaked photoresist film will lose solvent by evaporation, thus changing the properties of the film with time at room temperature. Removing solvent were reduced film thickness, change post-exposure bake and development properties, improve adhesion and the film becomes less tacky and thus less susceptible to particulate

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contamination. After prebake process, only three to eight percent of residual solvent leave in the film (MicroChemicals GmbH, 2012 &2013).

When PMMA is exposed to e-beam, scission can occur both on the main chain and the pendent $COOCH_3$ groups to leaving low molecular weight fragments which are soluble in a developer such as methyl isobutyl ketone (MIBK): isopropyl alcohol (IPA) or diethylene glycol monobutyl ether. Chain scission is the irreversible breakings of covalent bond within the polymer which reduces the mean molecular weight of the material and increases the solubility leading to a positive resist responding. Implementation bi-layer of high molecular weight (HMW) and low molecular weight (LMW) of PMMA is important because undercut pattern profile that developed required for metal deposition and good lift-off process as illustrated in Fig. 2 to avoid the sidewall of the resist (Mohamed, 2009). This study focused on effect of spin coat speed, the percentage of solid content and molecular weight of PMMA solution toward the resist thickness.The photoresist film thickness can be determined using filmetrics or ellipsometer that based on refractive index. Another simple way is from scratch the pre-baked resist on a substrate with tweezers and measure the depth of the scratch with atomic force microscope (AFM).

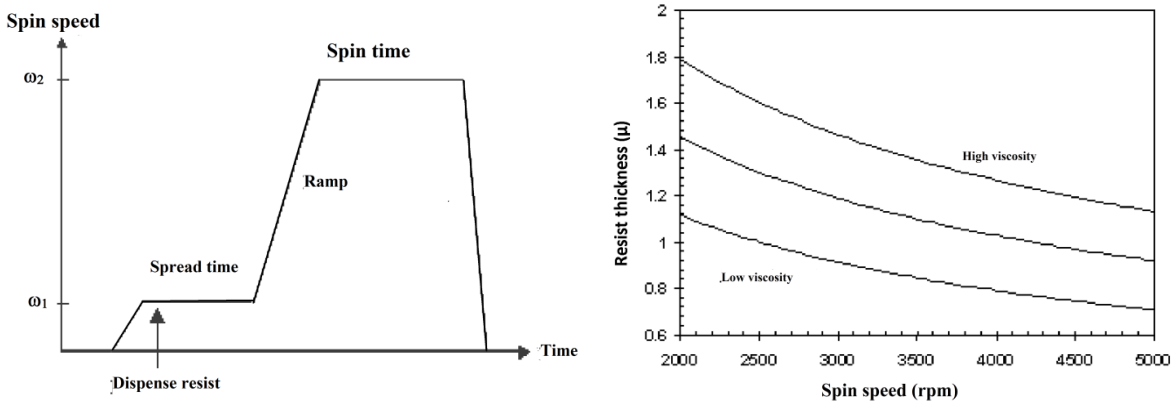

Fig. 1: Recommended resist spin coat cycle to obtain the desired uniformly thin layer and the resist spin speed curve versus resist thickness for different viscosity.

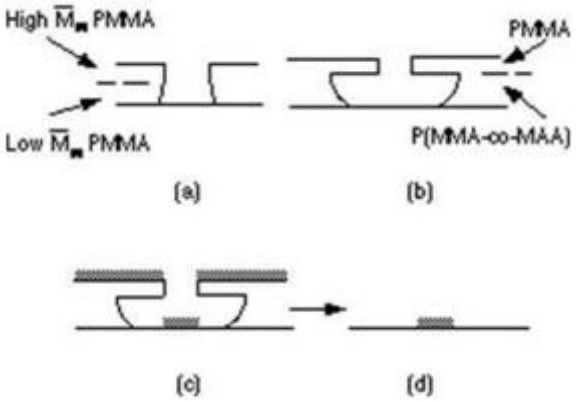

Fig. 2: The undercut pattern profile from implementation bi-layer PMMA.

Experimentation:

In this research work, a P-type silicon wafer of <100> orientation are cut (1cm x 1cm) using diamond scriber before clean using Radio Corporation of America (RCA) cleaning method to remove organic contaminations from the wafer surface, any oxide layer that may build up and ionic or heavy metal contaminations (Kern, 1993).PMMA have been utilized for electron beam lithography due to very high-resolution capability and low contrast, ease of handling, excellent film characteristics such as not sensitive to white light, and wide process latitude. Exposure of e-beam causes scission of the polymer chains. The exposed photoresist is then developed in a solvent developer. PMMA polymer with a molecular weight 120 K and 996K was dissolved with 2 percent and 4 percent by weight in an anisole and chlorobenzene, respectively as listed in Table 1. The required mass of PMMA to dilute in solvent is calculated as equation 1;

$$m_{solute} = \frac{Cm_{solvent}}{(100-C)} \quad \text{(Eq. 1)}$$

Where,

C is concentration in weight percentage (w/w)

$m_{solvent}$ is mass of the solvent (eg mass of chlorobenzene or anisole)

m_{solute} is mass of PMMA

The samples were spin coated with each PMMA at various spin speed (1000 rpm, 2000 rpm, 3000rpm, 4000 rpm, 5000 rpm) for 50 second, then prebake 30 minutes at 140 ºC to drive the solvent out of the resist and to harden resist for improved adhesion and followed by measuring the thickness using filmetric.

Table 1: PMMA dilution in Anisole and Chlorobenzene.

Resist	Molecular Weight	Solvent	Solid Content (%)
120K PMMA	120000	Chlorobenzene	2
			4
		Anisole	2
			4
995K PMMA	995000	Chlorobenzene	2
			4
		Anisole	2
			4

RESULT AND DISCUSSION

The resist thickness was measured at different spot using filmetrics, and then was confirmed by measure the depth of the scratch with atomic force microscope (AFM). The data gained from experiment conducted was plotted graphically to show correlation between solid content, type of solvent and molecular weight toward resist thickness. Fig. 3 shows the thickness of 120K PMMA (2% and 4% solid content) dilutedin (a) anisole and (b) chlorobenzeneat respectively spin speed. The lowest thickness (47.4 nm) achieve from PMMA 120K (2% solid content) in anisole at 5000 rpm. As shown in the graph below, the resist thickness are decreased when the spin speed increase and the solid content was decreased. PMMA 120K in anisole give thinner resist layer compared to PMMA 120K diluted in chlorobenzene.

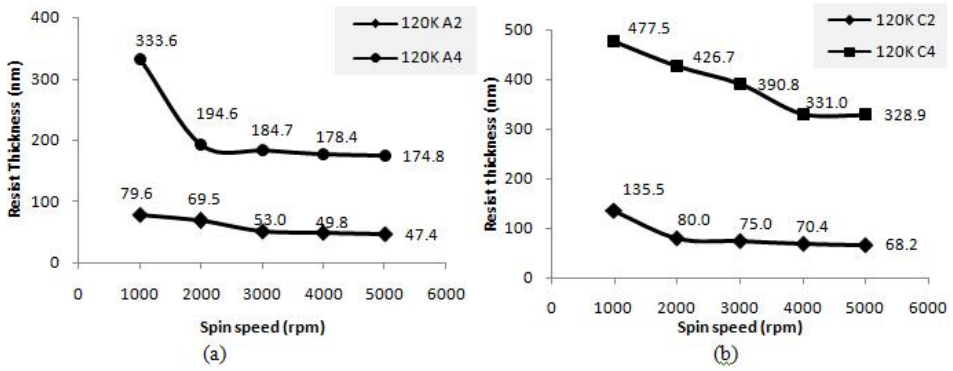

Fig. 3: Graph of resist thickness versus spin speed for PMMA 120 K in (a) Anisole and (b) Chlorobenzene.

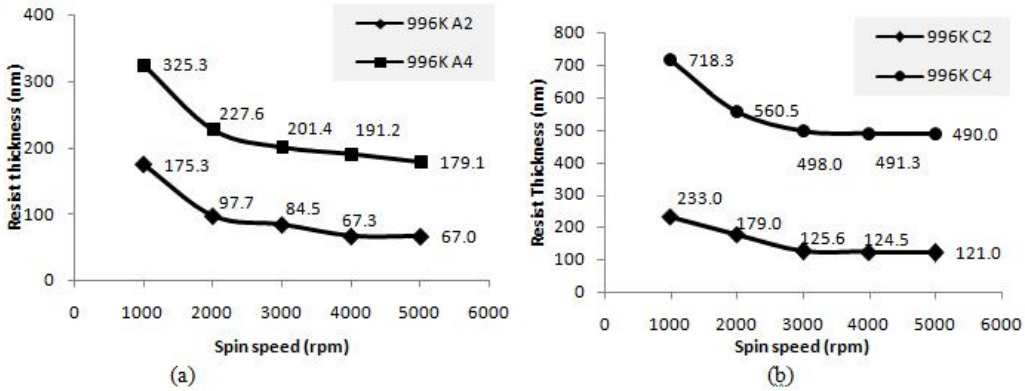

Fig. 4: Graph of resist thickness versus spin speed for PMMA 996 K in (a) Anisole and (b) Chlorobenzene.

Thethickness of PMMA 996Kdilute 2% and 4% solid content in (a) anisole and (b) chlorobenzeneat respectively spin speed illustrated in Fig.5. The resist thickness also decreased when the spin speed increase and

the solid content was decreased.The thinner resist layer (67.0 nm) achieved from PMMA 996K (2% solid content) in anisole at 5000 rpm, while the PMMA 965K (4% solid content) in chlorobenzene form thick layer of resist (718.3 nm). The thickness of resist from PMMA 996K diluted in chlorobenzene was twice compared to the resist layer from PMMA 996K in anisole.

The solids content, spin speed and type of solvent contribute to resist layer formation thickness. The thickness of resist layer using PMMA lower solids content and viscosity is thinner compared to PMMA with high solids content and viscosity (S. Niza*et. al.,* 2005). Molecular weight of PMMA doesn't give significant different toward the resist thickness, as can seen from Fig 3 (b) and Fig 4 (a) where resist thickness PMMA 996K in anisole thinner compared to PMMA 120K in chlorobenzene. However, selection of PMMA molecular weightis important especially in multilayer processes. The lower molecular weight of PMMA easily soluble in a suitable developer after exposure compared to high molecular weight PMMA. The dissolution rate increases when molecular weight decreases (Xiao, 2001). The trend of the result obtained from experimental work similarly with reference provide by Micro Chem Corporation (2001), where the resist thickness become uniform at spin speed 3000 rpm and above.

Conclusion:

The thin film thickness of the photoresist layer was dependent on the coated spin speed, molecular weight, type of solvent as well as solid content. The higher spin speed easilyspread the resist on the wafer and produced thinner layer of resist compared to lower spin speed. For PMMA 120K, the lowest thickness of resist (47.4 nm) achieved from 2% solid content in anisole, while highest resist thickness is 477.5 nm from 4% solid content in chlorobenzene. For PMMA 996K, the lowest thickness of resist is 67.0 nm achieved from 2% solid content in anisole, while highest resist thickness is 718.3 nm from 4% solid content in chlorobenzene. Molecular weight of PMMA doesn't give significant different on resist thickness formation.However, for bi-layer application in EBL, the selection of PMMA molecular weight is important to get better resist profiles with sharp edges and sidewall.

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