CHARACTERIZATION OF CHEMICALLY AMPLIFIED ADVANCED NEGATIVE RESIST FOR G LINE APPLICATION.

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ABSTRACT

Chemically Amplified Advanced Negative Resist for G line application was evaluated under three different Post Exposure Bake temperatures. The photospeed increased from 22mj/cm*2 to 10mj/cm*2 as the post exposure bake temperature was increased from 120C to 140C. A contrast of approximately 2.0 was obtained for all three treatments, as opposed to the expected value of 4.0. The Optical evaluation of line and space patterns suggested the 120C post exposure bake temperature will give wider exposure process latitude than 130C or 140C temperatures. The resist exhibited high sensitivity below 30mj/cm*2 with wide exposure process latitude around 20mj/cm*2.

INTRODUCTION

Higher numerical aperture (0.48) lenses, shorter wave length exposure sources (365nm), and/or the development of novel resist process such as DESIRE permits optical lithography to reach submicron dimensions. The imaging scheme, DESIRE, has been reported to produce acceptable patterns of 0.6um lines and spaces imaged with 0.45 numerical aperture lens stepper using 436nm or G line exposure source. In the DESIRE process, only a thin top layer (2000-3000 A) of a micron thick resist is exposed. The resist is then silylated with HMDS primer. Silylated resist is dry developed under oxygen plasma to form the image [1]. These developments, coupled with readily available G and I line exposure tools in manufacturing environments, contribute to a high demand for the high resolution, speed, and contrast performance in optical resists [2].

One potential resist system which may meet all these criteria is a chemically amplified crosslinking system. Chemical amplification utilizing thermal crosslinking has been shown to result in high sensitivity, contrast and resolution [3]. Chemically Amplified Advanced Negative Resist (ANR) for deep UV and e-beam is such a system. It is mainly composed of a phenolic resin, an acid activated melamine crosslinker, and light sensitive
halogenated acid generator. The chemistry is based on photo-initiated acid generation in which acid is formed upon exposure to light. In the presence of heat (100°C), the phenolic resin undergoes crosslinking because the acid acts as a catalyst in the reaction. One of the byproducts of the crosslinking reaction is acid. Thus one unit of photon energy creates more than one chemical event. Figures 1 and 2 show the chemistry of ANR crosslinking reaction mechanism.

Figure 1: Upon exposure to heat (100°C), the phenolic resin polymers are crosslinked through melamine crosslinker.

Figure 2: Regeneration of acid from crosslinking reaction.

One shortcoming is its insensitivity to readily available I and G line exposure sources. Therefore, a photosensitizer was added to the resist so that it will work for G line exposure sources. The following mechanism was proposed for how the sensitizer works:

1) excitation of the sensitizers using appropriate light source.

\[ \text{SH} \rightarrow \text{SH}^* \]

2) electron transfer from the excited sensitizers to the Acid Generator to generate a radical cation

\[ \text{SH}^* + \text{RX} \rightarrow \text{SH}^+ + \text{RX}^- \]
3) release of halide ion from the Acid Generator radical anion and a proton from the sensitizer radical cation to generate a molecule of halogen acid.

\[ RX^- \rightarrow R' + X^- \]
\[ SH^+ \rightarrow S' + H^+ \]

where SH is the sensitizer and RX is the halogenated acid generator [2].

Chemically Amplified Advanced Negative Resist should be far superior to the conventional negative working cyclized polyisoprene based resist. Poly(p-vinyl) phenol is used as a resin because it provides requirement of low absorbance to the light and high resistance to the plasma etch. Chemically Amplified ANR uses aqueous developer unlike cyclized polyisoprene which uses organic solvents. Therefore, image swelling during development is eliminated. On the other hand, swelling of cyclized isoprene limits its resolution to 1.5um [4]. The resist under investigation is much more dependent on the post exposure baking temperature because acid generation is reaction rate dependent. Therefore, depending on the post bake temperature and time in bake, the optimum exposure requirement will vary. Chemically Amplified ANR for near UV is developed to produce high photospeed ranging 15 mj/cm² to 125mj/cm² depending on post exposure bake temperature of 130°C to 100°C, respectively. The contrast ranges from 3.4 to 6.5 depending on the exact concentration of the resist component. It has been shown to achieve resolution around 0.8um using G line source with 0.38 NA stepper [2].

The subject of this paper is to see what kind of process latitude it has and the effect of different post bake temperature on photospeed, contrast and resolution.

EXPERIMENT

The photoresist was coated at 4000 RPM for 30 seconds onto bare silicon wafers. They were softbaked for 60 seconds at 90°C. The index of refraction after the softbake was measured using Ellipsometry. Based on the computed index of refraction value, the initial coating thickness after softbake was determined using a Nanospec film thickness measurement tool. Wafers were then exposed to about 100mj/cm² of energy, and post baked at 140°C on a hot plate for 80 seconds. Ellipsometry was performed to see if the index of refraction value had changed. The mean value of index of refraction was determined, and its value was used extensively throughout subsequent film thickness measurements using Nanospec.

The experiment was carried out over 2000Å thick silicon dioxide on a silicon substrate. Softbake was kept at a constant temperature as described above. A focus - exposure matrix resolution mask was exposed with a GCA4800 Stepper and the optimum focus setting decided. Using the constant focus setting, exposure was varied across the wafer.
ranging from 0 mj/cm*2 to 180mj/cm*2 in 36 steps. The Post Exposure Bake temperatures of 120, 130 and 140C were performed with two replicates for each treatment group. The duration of Post Exposure Bake time was fixed at 80 seconds. All of the wafers were developed for 35 seconds using MF 312-CD27 developer. Figure 3 shows the process steps.

Figure 3: Near UV Advanced Negative Resist Process.

The film thickness at various exposure locations was measured using a Nanospec. The resolution was evaluated using optical microscopy and 10um line and space pairs were measured using a Nanoline Line-Width measurement tool.

RESULTS/DISCUSSION

A mean of the index of refraction of the resist after the softbake was determined to be 1.68. A mean index of refraction of the resist after post exposure bake was determined to be 1.75. The index of 1.75 was used in all Nanospec data. It was also found that about 17% of film thickness loss has occurred after post exposure bake step. Initially, wafers were developed for 1 minute, and it resulted in an unsatisfactory data. About half of 36 die exposure steps were dissolved away, and left behind dies which were well overexposed. The development time to clear an unexposed resist region was determined to be 8 seconds using interferometric techniques. It was recommended that the development time should be 5 times that of the time to clear.

Based on this parameter, the development time was carried out for 35 seconds with agitation, and it yielded acceptable results. The remaining film thickness was
measured for various exposure dose steps. The normalized thickness verses exposure dose curve shown in Figure 4 revealed that the speed of the resist increased from 22mj/cm*2 to 10mj/cm*2 as the post exposure bake temperature was increased from 120C to 140C. The contrast values were determined to be around 2.0 for all treatments. Anticipated contrast values were around 4.0. As the post exposure temperature was increased from 120 to 140C, the contrast value decreased from 1.92 to 1.66 respectively.

The resolution limit to distinguish line/space pair was evaluated as 1.2um for all treatment groups. However, the process latitude varied significantly depending on the post exposure bake temperatures. The exposure process latitude was found around 20mj/cm*2. This is the amount of variation in dose which does not change line and space dimensions significantly. The results shown in Figure 5 showed that the process latitude on resolution is greatest for 120C. The optimum processing point for resolution around 1.2um for PEB temperature of 140C is around 20mj/cm*2 with latitude range limited to less than 5mj/cm*2 as shown by Figure 7. For 130C, shown in Figure 6, the optimum resolution point shifted to 40mj/cm*2 with latitude range around 15mj/cm*2. For 120C, the mean optimum resolution point is at 50mj/cm*2 with latitude range around 20mj/cm*2. Scanning Electron Microscopy (SEM) did reveal detailed resist profile information. The slope of 2.6um line edge profile was very vertical. It showed no sign of round edge or flow.

CONCLUSION

From this preliminary experiment, reported contrast values around 4.0 were not seen. The experiment showed that the resist's contrast values were around 2.0. The resist exhibited high sensitivity. The photospeed increased from 22mj/cm*2 to 10mj/cm*2 as the post exposure temperature was increased from 120C to 140C. The process latitude curves showed that the post exposure bake temperatures affects the process latitude on resolution. As the PEB temperature was increased from 120C to 140C process latitude decreased significantly. The optimum working point of the resist shifted from the low dose point to the high dose point when the PEB was decreased from 140C to 120C. This was expected of the thermally crosslinking system.

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Figure 4: Normalized thickness vs. Exposure curve.

Figure 5: Exposure latitude for a Post Exposure Bake of 120C.
Figure 6: Exposure latitude for a Post Exposure Bake of 130°C.

Figure 7: Exposure latitude for a Post Exposure Bake of 140°C.
REFERENCES