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Effects of bake temperature and surface modifications on hardmask materials for trilayer applications

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ABSTRACT

A comparison of bake temperature effects on two hardmask materials was performed. The first hardmask was a silicon-based material, BSI.M06092K, and the second was a titanium-based material, BSI.S07051. The materials have inherently different chemistries that performed differently as bake temperature was varied. BSI.M06092K undergoes condensation of silanols on the wafer during baking and BSI.S07051 undergoes removal of the ligand followed by condensation during baking. In general, the performance of BSI.M06092K showed little or no dependency on bake temperature. BSI.S07051 showed an increase in contact angle with water, slower etch rates, and square profiles as bake temperature increased.

Keywords: hardmask, trilayer, Si-BARC, titanium, multilayer

1. INTRODUCTION

As the feature sizes of integrated circuits decrease to smaller than 65 nm, thinner photoresists are being used. The thinning of the photoresist is required to prevent line collapse due to high aspect ratios. However, a thinner photoresist layer does not have the etch budget needed for pattern transfer into the substrate. To meet the requirements for pattern transfer, trilayer schemes are being used. With these schemes, the photoresist is used to pattern a hardmask material, which is in turn used to pattern a thick carbon layer.

With the introduction of a trilayer scheme, new demands are placed on the materials[1]. The optics of the materials must be matched to obtain good reflectivity control, and the etch selectivity must be optimized to ensure pattern transfer into the substrate. In addition to these requirements, the hardmask must be

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compatible with both the carbon layer and the photoresist. With most hardmask materials, compatibility with the photoresist has been a difficult goal to attain, and oftentimes, footing or scumming of the photoresist has been observed[2,3,4]. The scumming arises from detrimental interactions between the hardmask and the photoresist, and these interactions are not well understood.

To better understand these hardmask-photoresist interactions, a bake temperature study was undertaken for two hardmask materials. The materials were chosen due to their inherently different chemistries of silicon or titanium. The chemistry of these materials causes them to undergo different changes during baking. The silicon-based material was hydrolyzed to the silanol prior to use. During the gelation of this material on the hot plate, it undergoes a change from hydrophilic to hydrophobic (Figure 1). In contrast, the titanate contains an organic ligand and changes from hydrophobic to hydrophilic during baking (Figure 2). With these changes, differences in bulk composition as well as differences in surfaces chemistry are expected.

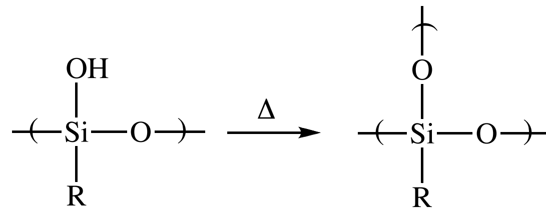


Figure 1. Condensation of silicon-based material.

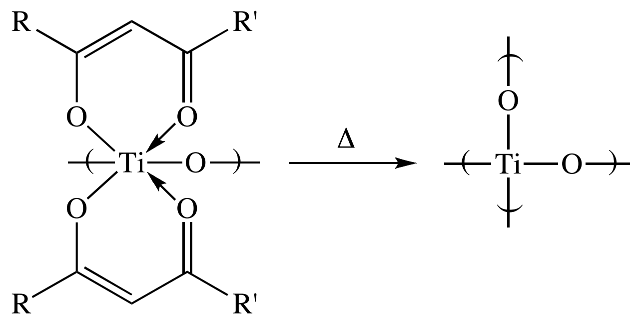


Figure 2. Condensation of titanium-based material.

The effects of bake temperature on a silicon-based material, BSI.M06092K, and on a titanate-based material, BSI.S07051, were studied. The bulk composition was studied by infrared (IR) spectra analysis, and the surface chemistry was studied by contact angle analysis. The effects of bake temperature on optics, lithography, and etch rate were also studied.

2. EXPERIMENTAL

2.1 Materials

BSI.M06092K was prepared by condensation of vinyltriethoxysilane with phenytriethoxysilane. BSI.S07051 was a blend of the silicon-based material and a commercially available titanium bis(1,3-dicarbonyl). Both materials were spin-cast from solution onto a wafer at 1500 rpm for 60 seconds and baked at temperatures ranging from 140º to 240ºC.

2.2 Quartz Crystal Microbalance [QCM] Testing

After the bottom anti-reflective coating (BARC) was spin-coated onto the wafer, it was placed onto a metal plate with thermocouple and a funnel-shaped enclosure placed over the wafer (Figure 3). Air was drawn over the wafer and passed through a chamber with a quartz crystal microbalance (QCM). The amount of sublimate was then monitored versus time.

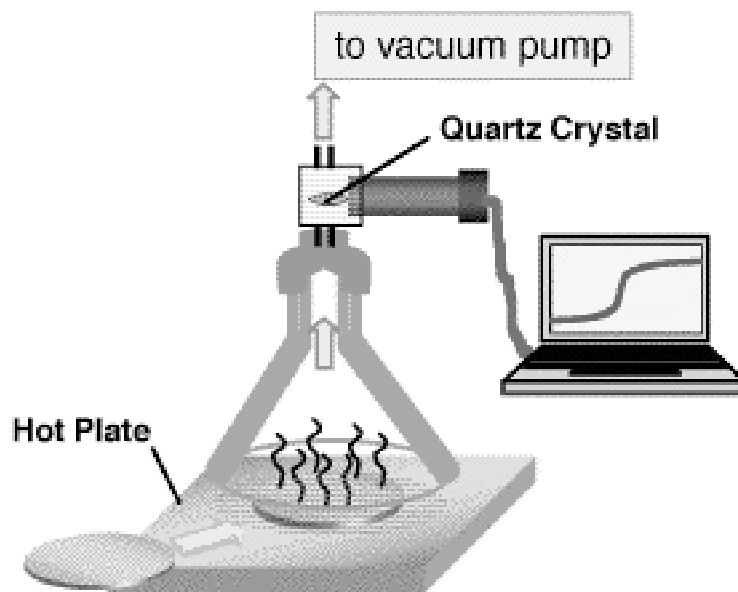


Figure 3. QCM apparatus.

2.3 Testing

Contact angle measurements were obtained with a VCA Optima system from AST Products, Inc. Optical constants, *n* and *k*, were measured with a J.A. Woollam variable-angle spectroscopic ellipsometer

(VASE®). Etching of the materials was performed with an Oxford Plasmalab®80Plus. Profiles were obtained from cross sections of the wafers after exposure with an Amphibian™ XIS immersion microstepper from Amphibian Systems.

3. RESULTS AND DISCUSSION

3.1 Thickness and Optics

Samples of BSI.M06092K and BSI.S07051 were spin-cast onto a silicon wafer at 1500 rpm for 60 seconds and baked at temperatures ranging from 140º to 240ºC. The thicknesses of the films were then measured with an ellipsometer (Figure 4). For BSI.M06092K, no significant change in thickness was observed over this temperature range. These results indicated that little or no organics were being volatilized from the film during baking. In the case of BSI.S07051, the thickness changed from 1010 to 800 Å as the temperature changed from 140º to 240ºC. The thickness decreased significantly for this sample, suggesting a large amount of the ligand was removed at high bake temperatures.

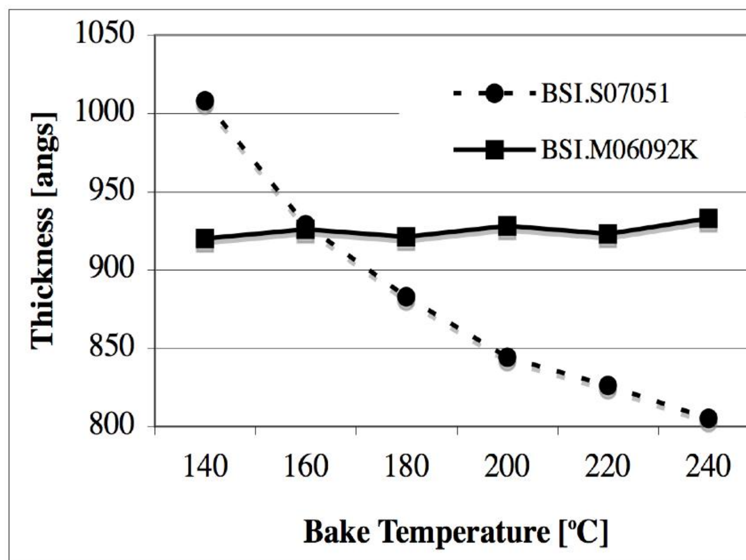


Figure 4. Thickness versus temperature for BSIS.06092K and BSI.S07051.

The optics, *n* and *k*, were measured for each sample over the same bake temperature ranges. BSI.M06092K and BSI.S07051 showed *n* and *k* values of n=1.81, k=0.21 and n=1.76, k=0.28, respectively. These values were independent of bake temperature. Because BSI.M06092K does not change in thickness with temperature, no change in optics was expected. In contrast, as BSI.S07051

becomes denser with increasing bake temperature, an increase in the k value would be expected. However, this was not observed and may suggest that the absorbency changes as volatiles were removed from the film.

3.2 QCM testing

To better understand the volatiles coming from BSI.S07051 during baking, a QCM test was performed (Figure 5). After spin-casting the film, the wafer was placed under a funnel and air was drawn through the funnel and onto the quartz crystal. After stabilization of the QCM for 60 seconds, the film was baked at 205ºC. This procedure was also used for BSI.M06092K and ARC®29A-8, a commercially available BARC from Brewer Science, Inc. Both BSI.M06092K and ARC®29A-8 showed normal QCM plots with an initial increase in sublimate with leveling after about 30 seconds. However, BSI.S07051 showed an initial rise followed by a decrease in sublimate. This may be due to the volatilization of the ligand onto the quartz crystal followed by evaporation from the crystal. Because the ligand is an organic species with a boiling point below 200ºC, condensation followed by evaporation onto the crystal would explain the behavior observed in the QCM plot.

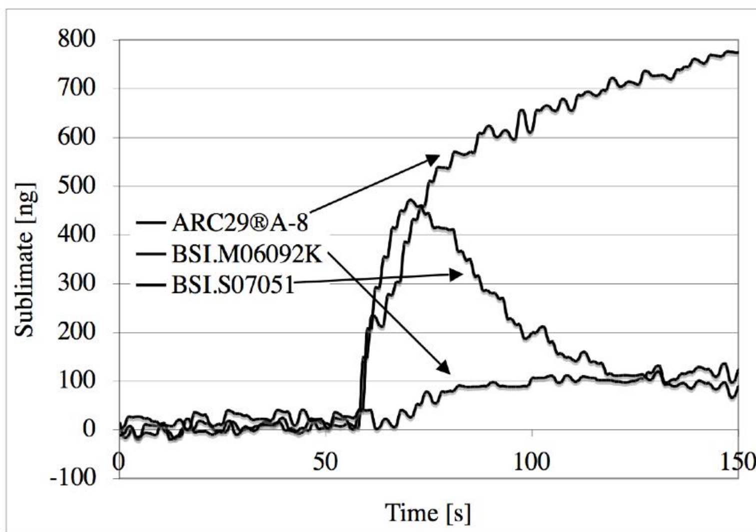


Figure 5. QCM testing of ARC®29A-8, BSI.M06092K, and BSI.S07051.

3.3 IR Spectra

To confirm that the organic ligands were the volatiles coming from BSI.S07051, a series of IR spectra were taken. IR spectra were recorded at bake temperatures of 140º, 160º, 180º, 200º, 220º, and 240ºC using silicon wafers polished on both sides for both BSI.M06092K and BSI.S07051 (Figure 6). The IR

spectra of BSI.M06092K did not show significant change from 140º to 240ºC. The IR spectra of BSI.S07051 showed decreases in the peaks at 1625, 1550, and 1280 cm^{-1}. These peaks are from the carbonyls and the carbon-carbon double bond in the ligand. The IR spectra change showed loss of ligand as the temperature increased, and this was consistent with the decrease in thickness and the QCM results observed for this material.

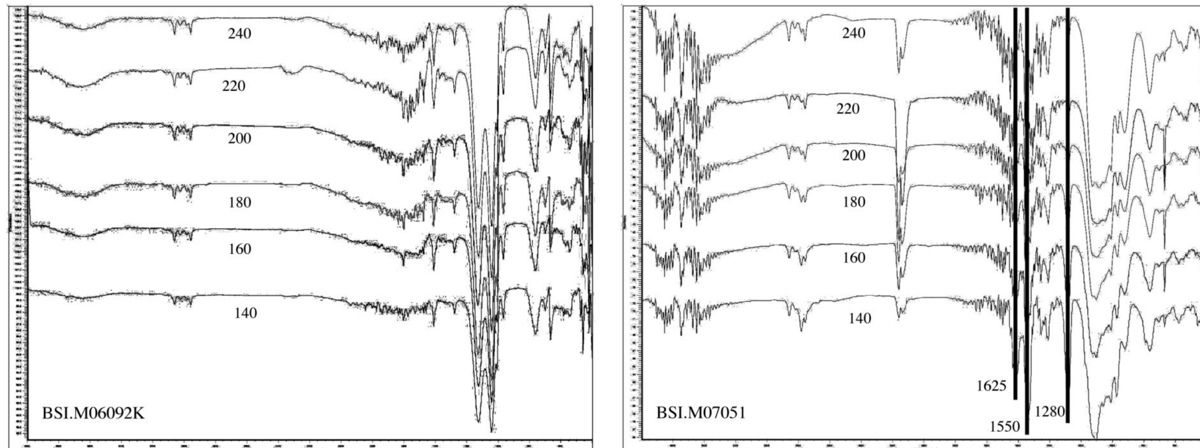


Figure 6. IR spectra of BSI.M06092K and BSI.S07051 at bake temperatures of 140º, 160º, 180º, 200º, 220º, and 240ºC.

3.4 Etch Testing

Etch testing of BSI.M06092K and BSI.S07051 was performed with CF_4 gas for times of 40, 60, and 100 seconds at bake temperatures of 140º, 190º, and 240ºC. The thicknesses of the films were recorded before and after etching. The differences in film thicknesses were then plotted and the etch rates determined from the slope of the line (Figure 7). An etch rate of 8.08 Å/s was observed for BSI.M06092K regardless of bake temperature, suggesting that the material does not change sufficiently to affect its etch rate. Etch rates of 5.73, 4.73, and 4.40 Å/s were observed for BSI.S07051 at bake temperatures of 140º, 190º, and 240ºC, respectively. The decrease in etch rate with increasing temperature was unexpected. Theoretically, as more organic material is removed during baking, the percentage of titanium in the film increases and therefore the etch rate is expected to increase. The opposite was observed and could be due to increased spacing within the sol-gel material, making it more susceptible to etching at lower temperatures.

3.5 Lithography

A trilayer scheme was used for photolithography with BSI.M06089A (250-nm thickness) used as the carbon material and AM2073J (130-nm thickness) from JSR as the photoresist. The hardmasks,

BSI.M06092K and BSI.S07051, were used at 82- and 85-nm thicknesses, respectively, and baked at temperatures of 160º, 180º, 200º, 220º, or 240º. Profiles were obtained at 64 nm, 1:1 L/S (Figures 8 and 9). As observed for the previous properties of BSI.M06092K, lithographic performance was not affected by bake temperature. Straight profiles with a slight foot were observed regardless of bake temperature. For BSI.S07051, the profiles showed a foot at lower temperatures of 160º and 180ºC, square profiles at bake temperatures of 200º and 220ºC, and a slight undercut at a bake temperature of 240ºC. The change from footing to slight undercut showed the effect of ligand removal on lithographic performance. As ligand was baked from the film, it increased in density and decreased the interactions between the photoresist and the hardmask. This decrease in interaction led to excellent profiles with AM2073J.

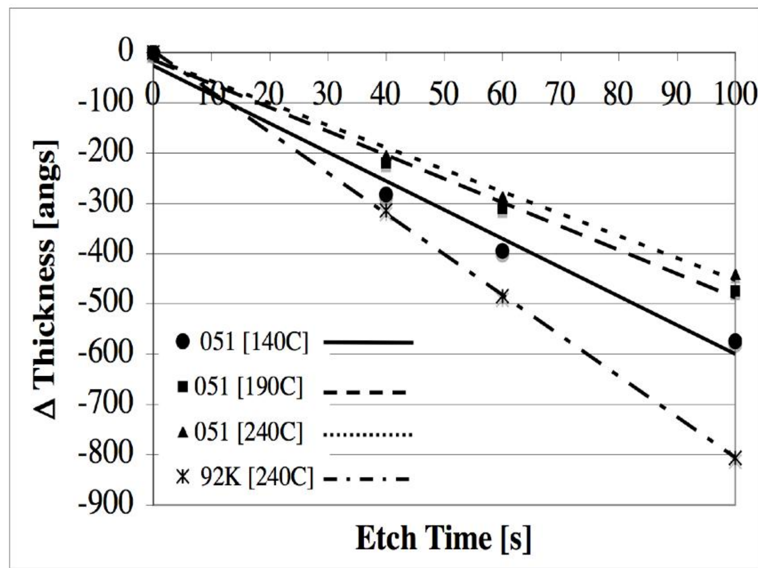
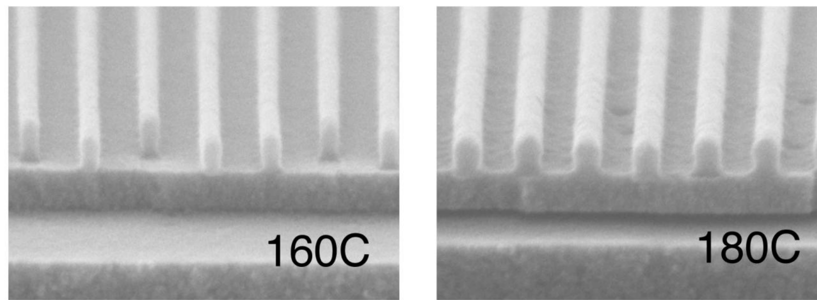


Figure 7. Etch versus time of BSI.M06092K and BSI.S07051 in CF_4.

4. CONCLUSION

Significant differences were observed when comparing the performance of silicon-based and titanium-based hardmasks. The silicon-based hardmask, BSI.M06092K, showed little or no dependency on bake temperature. Contact angle with water, etch rate, and lithographic performance remained the same. In contrast, the titanium based hardmask, BSI.S07051, showed a dependency on bake temperature. Contact angle with water increased with baked temperature, indicating the material was becoming more hydrophobic. Etch rate decreased with bake temperature, and lithographic performance showed a change in profiles from footing to square with increasing bake temperature. These changes were due to a loss in ligand and an increase in film density as bake temperature increased.



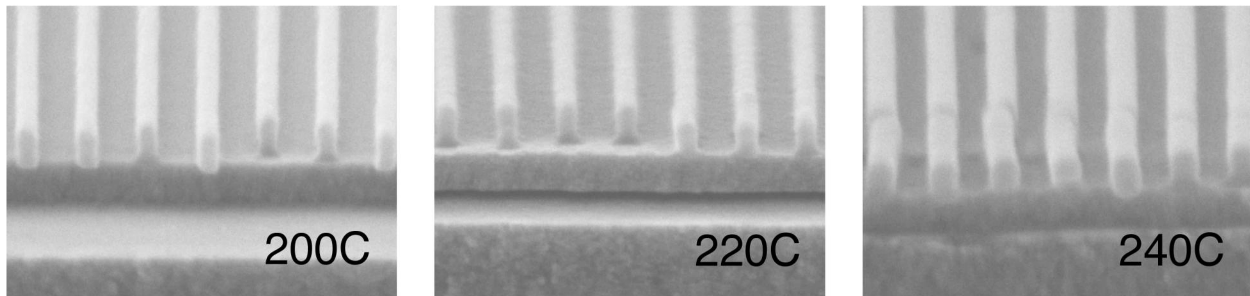
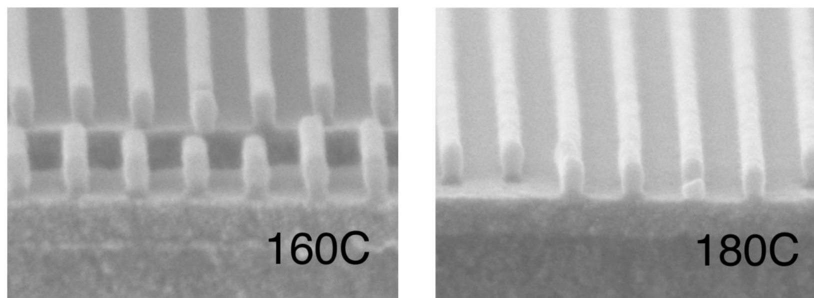


Figure 8. Profiles with BSI.M06092K [64 nm 1:1 L/S] with BSI.M06089A as the carbon layer and AM2073J from JSR as the photoresist.



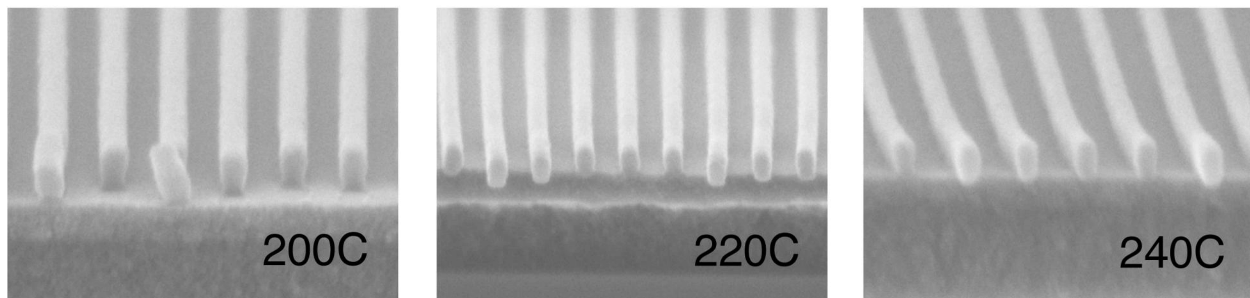


Figure 9. Profiles with BSI.S07051 [64 nm 1:1 L/S] with BSI.M06089A as the carbon layer and AM2073J from JSR as the photoresist.

5. REFERENCES

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