Effects of carbon/hardmask interactions on hardmask performance

Charles J. Neef, Brian Smith, Chris James, Zhimin Zhu, and Michael Weigand

Brewer Science, Inc., 2401 Brewer Dr., Rolla, MO 65401, USA, 573-364-0300

ABSTRACT

Interactions between the silicon hardmask and the photoresist have received considerable attention for utilization of these materials in a trilayer scheme. In contrast, the interactions between the carbon layer and the silicon hardmask have received little or no consideration. In this paper, we present the effects of these interactions on the performance of the silicon hardmask. Poor interactions were observed to result in a more hydrophilic surface and poor lithographic performance of the silicon hardmask. However, beneficial interactions between the carbon layer and the silicon hardmask resulted in a silicon film that was denser with a hydrophobic surface. The resulting denser film had a slower CF_4 etch rate and produced square, clean profiles.

Key Words: Trilayer, Hardmask, Carbon Layer, Interactions

1.0 INTRODUCTION

As the feature sizes of integrated circuits continue to decrease, thinner photoresists are being used to prevent line collapse due to high aspect ratios. Unfortunately, a thinner photoresist layer does not have the etch budget needed for pattern transfer into the substrate. To circumvent this problem, trilayer schemes have been introduced.[1,2,3] With these schemes, the photoresist is used to pattern an inorganic hardmask material, which is in turn used to pattern a thick carbon layer. The thick carbon layer is then used to pattern the substrate. The use of a trilayer scheme places new demands on materials and greatly complicates the effects of interactions between the layers of materials. 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 compatible with both the carbon layer and the photoresist.

Advances in Resist Materials and Processing Technology XXVI, edited by Clifford L. Henderson,
Proc. of SPIE Vol. 7273, 727311 · © 2009 SPIE · CCC code: 0277-786X/09/$18 · doi: 10.1117/12.814257

While much focus has been placed on the interactions between the hardmask and the photoresist to obtain good lithography[4,5,6,7], little attention has been placed on the interaction between the carbon layer and the silicon hardmask. The effect of interactions between the carbon layer and hardmask on etch rate and lithography is not well understood. To better understand these carbon-hardmask interactions, various carbon materials were used in conjunction with a silicon-containing hardmask material. The carbon materials were chosen due to their inherently different chemistry and range from slightly acidic to slightly basic. The effects of these carbon materials on the surface of the hardmask were studied by contact angle with water. Changes in contact angle were observed with bake temperature of the carbon material and as catalyst amounts were varied. Changes in etch rates observed with different carbon layers suggested beneficial interactions, which increased the density of the hardmask film. Also, effects on lithography will be discussed.

2.0 EXPERIMENTAL

2.1 Materials

BSI.M06092L hardmask was prepared by condensation of vinyltriethoxysilane with phenytriethoxysilane. The material was spin-cast from solution onto a silicon wafer or carbon material at 1500 rpm for 60 seconds and baked at a temperature of 205ºC. WGF300 and SOC110D materials are commercially available from Brewer Science, Inc. Neutral carbon materials were prepared from epoxy resins with the appropriate amount of catalyst for curing.

2.2 Testing

Contact angle measurements were obtained with a VCA Optima system from AST Products, Inc. Etching of the materials was performed with an Oxford Plasmalab®80Plus using conditions of 100 mT pressure, 100W power and 50 sccm CF4 flow. Profiles using ARX3001JN-12 resist from JSR were obtained from cross sections of the wafers after exposure with an Amphibian™ XIS immersion microstepper from Amphibian Systems.

3.0 RESULTS AND DISCUSSION

3.1 Silicon Hardmask with Commercially Available Materials

Initial testing to understand the effects of interactions between the silicon hardmask, BSI.M06092L, and the spin-on carbon layer was performed with commercially available carbon materials, WGF300 and SOC110D materials. BSI.M06092L was spin cast onto a bare silicon wafer, WGF300 material, or SOC110D material followed by contact angle measurements of water with the BSI.M06092L (Figure 1). The contact angles of water on BSI.M06092L were 93.7º, 81.6º, and 90.6º for a silicon wafer, WGF300 material, and SOC110D material, respectively. The contact angles for both carbon materials were less than the contact angle for the silicon wafer. The decrease in contact angle showed that the silicon hardmask was more hydrophilic and may indicate an increase in silanol moieties at the surface. These results indicated that the interactions between the carbon layer and the silicon hardmask can lead to a significant change in the surface chemistry of the silicon hardmask.

To determine the effects of the silicon hardmask surface on profiles, lithography was performed with the trilayer stack using ARX3001JN-12 (from JSR) as the photoresist (Figure 2). Profiles with WGF300 as the carbon layer showed severe scumming, and profiles using SOC110D showed a slight footing. Combining the lithography and contact angle results suggests that a more hydrophilic hardmask surface leads to excessive intermixing or poor development of the photoresist. From these results, the development of a carbon layer with beneficial interaction between it and the silicon hardmask was warranted.

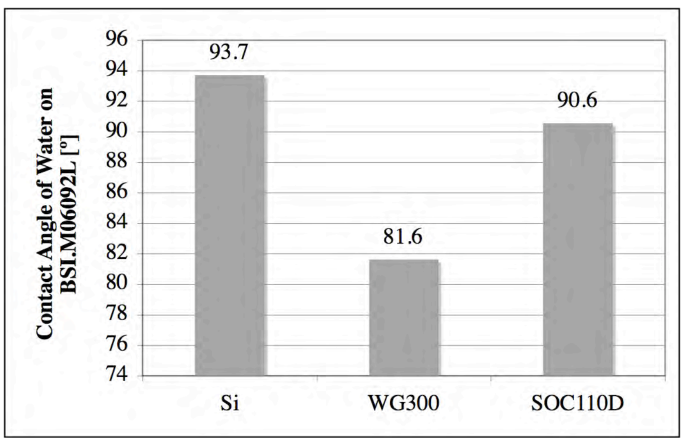
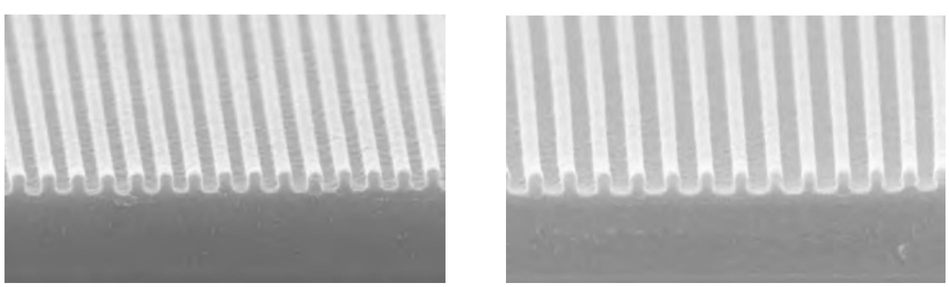


Figure 1. Contact angle of water on BSI.M06092L cast on a silicon wafer, WGF300 material, or SOC110D material.



WGF300 SOC110D

Figure 2. Lithography [64 nm 1:1 L/S] with BSI.M06092L cast on WGF300 or SOC110D using ARX3001JN-12.

3.2 Silicon Hardmask with Neutral Materials

The development of carbon materials with beneficial interaction with the silicon hardmask focused on epoxy resins with an appropriate amount of catalyst [1-5%] to thermally set the film. These films were spin cast onto a silicon wafer and baked at temperatures ranging from 160°-200°C. BSI.M06092L was spin cast on these carbon materials followed by measurement of the contact angle of water on the silicon hardmask (Figure 3). The contact angles of water ranged from 88° to 98° and increased as bake temperature or catalyst amount of the carbon material increased, indicating a more hydrophobic film surface. Compared to the commercially available carbon materials, the contact angles using the new materials were higher, which suggests fewer silanol moieties at the surface.

Film thicknesses of the silicon hardmask cast on the neutral carbon materials are shown in Figure 4. A slight decrease in film thickness was observed as bake temperature of the carbon layer increased. However, a large decrease in thickness of the silicon hardmask was observed as the catalyst amount in the carbon material increased. These results suggest diffusion of the catalyst from the carbon layer to the silicon hardmask and that this diffusion aids in densification of the silicon hardmask. A denser film is consistent with the contact angle measurements. As more of the silanol moieties condense, fewer are on the surface, which results in a more hydrophobic film surface. Although density was not measured directly, similar hardmask studies have been performed with XRR analysis and this is a future direction of research

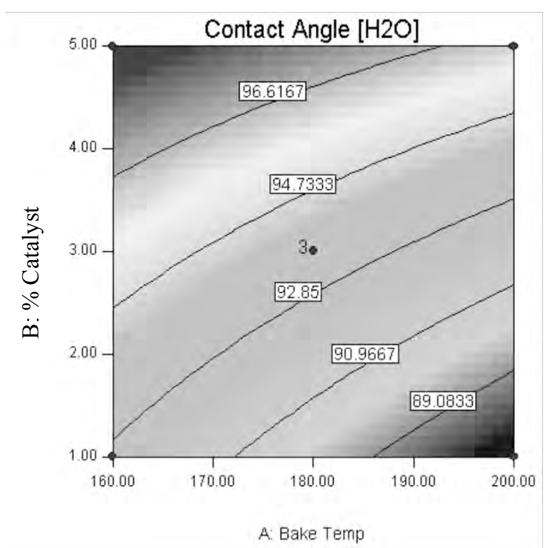


Figure 3. Contact angle of water on BSI.M06092L cast on neutral carbon materials as catalyst amount and bake temperature of the carbon layer vary.

Next, CF_4 etching and lithography were performed on the improved trilayer stack. Following spin casting of the silicon hardmask onto the carbon materials, the thickness of the hardmask was measured and then the hardmask was etched for 30 s with CF_4. The final thickness of the silicon hardmask was then measured and the CF_4 etch rate calculated. These results are shown in Figure 5. As was observed for the film thickness, bake temperature of the carbon layer had little effect on the etch rate. However, as catalyst amount in the carbon layer increased, a significant reduction in etch rate of the silicon hardmask from about 41 to 32 Å/s was observed. As expected, a denser film would have a slower etch rate, and these results suggest that catalyst migration from the carbon layer to the silicon hardmask has altered the hardmask surface as well as the bulk properties.

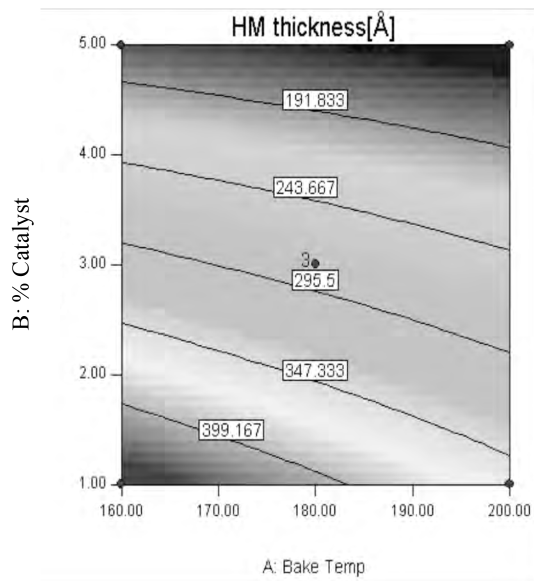


Figure 4. Film thickness of BSI.M06092L cast on neutral carbon materials as catalyst amount and bake temperature vary.

Lithography with this trilayer stack was performed at Brewer Science, Inc., with an Amphibian™ XIS immersion microstepper using ARX3001JN-12 from JSR as the photoresist. A 0.75 numerical aperture (NA) prism was used to produce 64 nm line/space patterns with 193nm exposure. Profiles were 64 nm 1:1 L/S. Lithographic results as bake temperature and catalyst amount of the carbon layer were varied are shown in Figure 6. Using 1% catalyst in the carbon layer resulted in profiles with slight footing and scumming at bake temperatures of 160^{o} or $200^{o}C$. At a catalyst loading of 3% and carbon layer bake temperature of $180^{o}C$ for the carbon layer, square profiles with no or little footing were obtained. At a catalyst loading of 5%, profiles with the carbon layer baked at 160°C showed a slight footing, while a bake temperature of 200°C resulted in square profiles with no footing at the base. These results suggest that interactions between the carbon layer and the hardmask play an important role in the resist profile. Beneficial interactions at higher bake temperatures and catalyst loadings lead to a denser hardmask, which in turn results in fewer interactions between the hardmask and the photoresist. Fewer interactions between the hardmask and the photoresist decrease the likelihood of acid migration from the photoresist into the hardmask or migration of material that neutralizes acid from the hardmask to the photoresist.

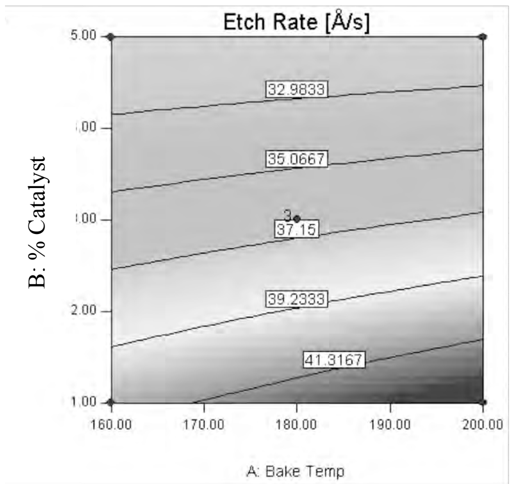


Figure 5. CF_4 etch rate of BSI.M06092L cast on neutral carbon materials as catalyst amount and bake temperature vary.

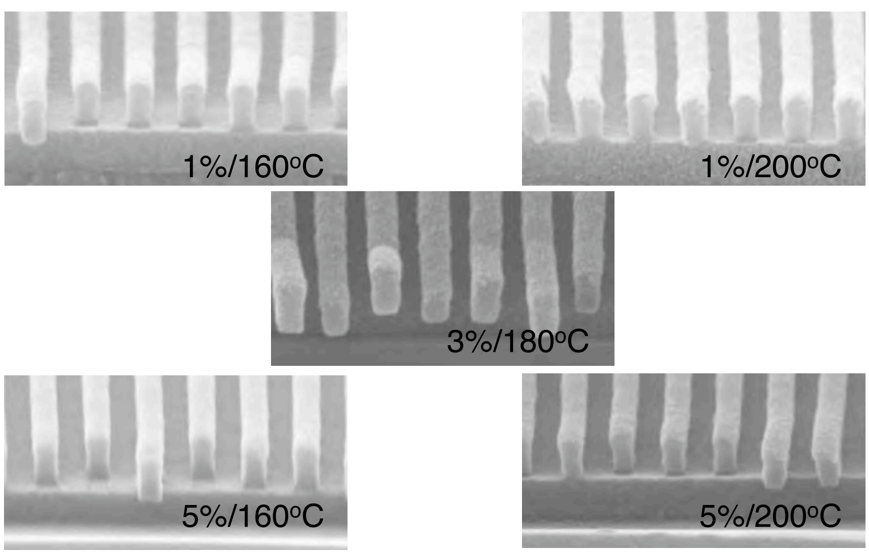


Figure 6. Lithography [64 nm 1:1 L/S] of BSI.M06092L cast on neutral carbon materials as catalyst amount and bake temperature vary using ARX3001JN-12.

4.0 CONCLUSIONS

Interactions between the carbon layer and the silicon hardmask have been shown to be important to the performance of the hardmask. Poor interactions lead to a silicon hardmask with a hydrophilic surface and less film density as observed through etch rate measurements. In contrast, beneficial interactions lead to a denser and more hydrophobic silicon material and result in better lithographic performance. As these beneficial interactions increased, a denser film resulted in a slower etch rate and square profiles with no residue. . Thus, the decrease in hardmask etch rate, leading to higher resist consumption, was offset by the greatly improved resist profile that carries through the entire trilayer stack and into the substrate. Further work with these materials will focus on optimization of the catalyst amount to obtain the desired etch rates and lithographic performance for pattern transfer through the substrate.

5.0 REFERENCES

1. Neef, C.J., Finazzo, J., Nesbit, C, & Weigand, M.; Effects of Bake Temperature and Surface Modifications on Hardmask Materials for Trilayer Applications, *Proc. of SPIE*, **6923**, 692331, *2008*

2. Moghadam, F., Zhao, J., Weidman, T., Roberts, R.J., Xia, L.-Q., & Demos, A.T.; Methods and Apparatus for E-Beam Treatment Used to Fabricate Integrated Circuit Devices, United States Patent: US 2007/0275569 A1

3. Fujii, Y., Hagihara, M., Sakamoto, Y., & Yamashita, N.; Silylphenylene Polymer Composition for the Formation of Interlayers and Process for the Formation of Patterns by Using the Same, United States Patent: US 2008/0107971 A1

4. Kennedy, J., Xie, S., Katsanes, R., Flanigan, K., Mukhopadhyay, S., Wu, B., Rutter, E.W., & Slezak, M.; A High-Si Content Middle Layer for ArF Trilayer Patterning, *Proc. of SPIE*, **6923**, 69230W, *2008*

5. Kim, M.Y., Kim, S.K., Lim, S.H., Ran, K.S., & Yun, H.C.; Hardmask Composition for Processing Resist Underlayer Film, Process for Producing Semiconductor Integrated Circuit Device Using the Hardmaks Composition, and Semiconductor Integrated Circuit Device Produced by the Process, International Patent, O 2008/063016 A1

6. Wu, H., Kim, H., Kim, W., Zhuang, H., Lu, P., Neisser, M., Abdallah, D., & Zhang, R.; Silicone Coating Composition, United States Patent: US 2008/0196626 A1

7. Abdallah, D.J., Miyazaki, S., Hishida, A., Timko, A., McKensie, D., Rahman, D., Kim, W., Pylneva, L., Wu, H., Zhang, R., Lu, P.-H., Neisser, M., & Dammel. R.; Etching Spin-on Trilayer Masks, *Proc. of SPIE*, **6923**, 69230U, *2008*