

Characterization of Self Assembled Monolayers for Ultra Low-k Films

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1. Introduction

The main advantage of the Self Assembled Monolayers (SAM) is its "near zero" thickness which is just one molecular length. This is attractive for future technologies that will require nano-sized interconnects [1]. SAMs are typically attached to a substrate on one end by moieties such as a thiol (-SH) or a silane (-SiX₃) where X is typically a halogen or an alkoxy group). The molecules of SAM are composed of three parts namely terminal functional group, alkyl chain and the anchor group.

Feasibility of employing SAM as a diffusion barrier for Cu/Low-k interconnects was first reported by A. Krishnamoorthy et. al. [1] and subsequently further studies were carried out by several researchers. However, it is evident that most of the work related to SAM had been carried out predominantly for silicon-di-oxide films ($\kappa > 4$) with almost no work reported for new generation materials such as ultra low-k films which are the potential candidates for advanced Cu interconnects in the efforts to reduce RC delay. Porous SiLK semiconductor dielectric resin (p-SiLK™, a trade mark of The Dow Chemical Company) is an aromatic carbon rich organic polymer, with κ value of 2.2. This is one of such potential ultra low-k materials being explored for possible integration into Cu damascene processes [3]. As the dielectric constant is conventionally achieved by introducing nano-pores into the bulk, porosity related issues are indeed a concern in damascene process integration. Many methods have been tried to seal the pores at the surface which in turn may help to improve dielectric and metallization reliability. In this study we explored SAM as a pore sealing barrier layer when applied on ultra low-k films. We report for the first time results on characterization of SAM coating on p-SiLK and its electrical testing..

2. Experimental

p-SiLK film preparation

Ultra low-k film was fabricated by spin-coating p-SiLK material on 8-inch Si wafers and subsequent thermal curing at 400 °C. The coating uniformity was <3% and the surface roughness measured by Atomic Force Microscopy (AFM) technique showed an RMS value of 0.473 nm. *SAM coating on p-SiLK*

We have used a commercially available SAM, 3-mercaptopropyltrimethoxysilane (MP-TMS). Coating solution is prepared by mixing Ethyl alcohol (as a carrier solvent) in pre-determined proportions. The solution thus prepared was coated on p-SiLK film by immersion method at ambient temperature. During the coating process SAM molecules align themselves on the surface by forming a strong bond between the surface atom and the head group of SAM by chemisorption, forming an ordered one molecular thickness film. The thiol (SH) group tethers to the film surface by forming a strong bond with the p-SiLK.

p-SiLK film thus coated with SAM was analyzed and characterized to confirm the attachment of SAM to p-SiLK. As the thickness of SAM is negligibly small precision analytical techniques such as AFM, Auger and XPS were used. p-SiLK film with and without SAM coating was further electrically characterized by fabricating MOS dot structures with Cu.

3. Results and Discussion

Auger analysis of SAM

After SAM coating an increase of 30% in surface roughness (RMS value) was observed. This indicated the surface modification of p-SiLK film by SAM. However, SAM is basically coated by the attachment of anchor/head group to the substrate film, change in the surface roughness may not be the key parameter to confirm the attachment of SAM to p-SiLK. We further characterized the film surface by Auger analysis of p-SiLK film and later compared with that of SAM coated p-SiLK film,

From the Auger spectra it was found that an additional element such as sulphur which is part of the thiol group (SH) was present on the SAM coated p-SiLK film. However, from the film composition it is well known that p-SiLK does not contain any thiol group. Based on this analysis it can be confirmed that SAM is attached to p-SiLK. Fig. 1 and Fig. 2 below show typical Auger analysis spectra for p-SiLK film before and after SAM coating, the latter showing the presence of sulphur.

XPS analysis of SAM

p-SiLK film was subjected to XPS analysis before

and after SAM coating and spectra were compared. Fig. 3 shows a typical spectra super imposed before (spectrum 'a') and after (spectrum 'b') SAM coating. Unlike the spectrum a, additional peaks are seen in spectrum b at the binding energies of 165.5 and 230 eV, which correspond to 2p_{3/2} and 2s peaks respectively for sulphur. This confirmed the attachment of SAM to p-SiLK through the chemical bonding of the thiol group

Electrical Characterization of SAM

I-V characteristics of MOS dot structures showed improved dielectric break-down and reduced leakage for SAM coated p-SiLK film as shown in Fig. 4. SAM coated capacitors consistently show more than 3-orders-of-magnitude lower leakage currents above the electric field of 0.9 MV/cm as compared to the corresponding values from the capacitor without SAM at the interface.

It is apparent from the I-V curves that leakage current has reduced after coating SAM. This is observed even at higher electric fields upto 3.3MV/cm. We speculate that the reduction in leakage current may be due to the improved adhesion of Cu to the ultra low-k film achieved by the interface provided by SAM layer. In addition, the attachment of SAM to Cu through probable bonding at its terminal group could have prevented the movement of Cu atoms down to the p-SiLK film inhibiting Cu diffusion. Moreover, smaller molecular size of SAM (expected to be <2nm) compared to pore size of p-SiLK (~7nm) would have enabled partial sealing of the pores in p-SiLK. This may subsequently prevent the formation of charge trapping sites in the film causing reduction in leakage.

4. Conclusions

Coating process of self assembled monolayers on ultra low-k film, p-SiLK, is successfully demonstrated and characterized. The attachment of monolayer to p-SiLK is experimentally confirmed through Auger and XPS analyses.. Based on reduced leakage revealed by I-V characteristics of SAM coated p-SiLK film, further evaluation of SAM as a potential candidate material for pore sealing or diffusion barrier will be of great interest for advanced interconnects technology.

Acknowledgements

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References

- [1] A. Krishnamoorthy, K. Chandra, S. P. Murarka, and G Ramanath and J.G. Ryan, *Appl. Phys. Lett.*, **78** (2001) 2467
- [2] G. Ramanath, G. Cui, P.G. Ganesan, X. Guo, A.V. Ellis, M. Stukowski, K. Vijayamohan, P. Doppelt and M. Lane, *Appl. Phys. Lett.*, **83** (2003) 383
- [3] B. Ramana Murthy, M. Mukherjee-Roy, A. Krishnamoorthy and Don C Frye, *IEEE Trans. Semiconductor Manufacturing*, **18** (2005) 174

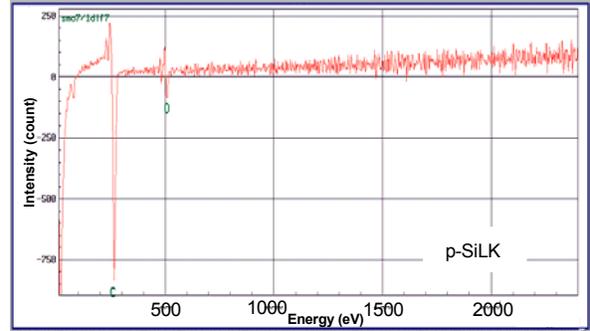


Figure 1: Auger analysis of p-SiLK before SAM coating

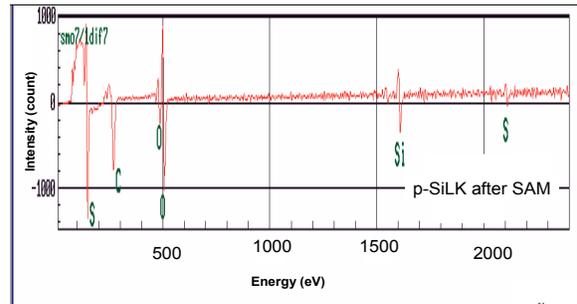


Fig. 2 Auger analysis of p-SiLK after SAM coating

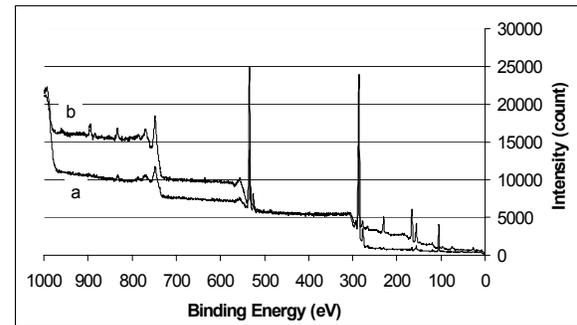


Fig. 3 XPS analysis of p-SiLK before (a) and after (b) SAM coating

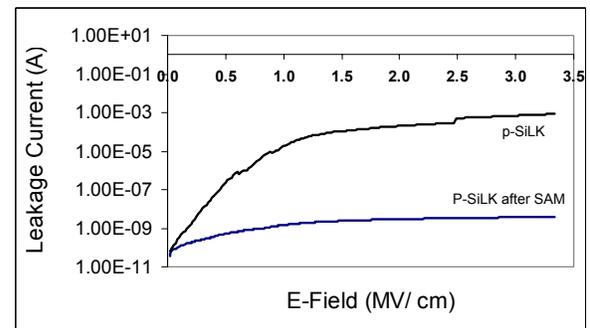


Fig. 4 I vs E-field plot of p-SiLK film before and after SAM coating.