Challenges and novel approaches for photo resist removal and post-etch residue removal for 22 nm interconnects

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Abstract

The critical challenges of removal of post metal hard mask etch photo resist removal and post low-k etch residue removal are described. An overview of some new non-plasma based approaches is presented.

Introduction

With the continuous reduction in pattern dimensions the photo resist left behind after metal hard mask (MHM) etching is much more difficult to remove as there is no or only a very small portion of the photo resist (PR) left not cross-linked [1]. As low-k dielectric materials also contain carbon based groups (e.g. methyl groups) the chemical selectivity requirements for removing photo resist without attacking the low-k material are very stringent. The introduction of porous low-k dielectric materials further increased the sensitivity to plasma damage. With MHM patterning a dry PR strip typically results in a first type of plasma damage of the top corners of the low-k material, extending underneath the edges of the MHM layer as shown in Fig. 1. This damaged region gets easily attacked in subsequent cleans and thus results in dielectric lines with a non-planar top surface. This in turn can result in severe interline capacitance and isolation problems. Therefore alternative non-plasma routes are explored to remove the PR on top of the MHM.

Resist dry

Fig.1 Schematic showing the damage induced by plasma resist strip extends underneath the metal hard mask.

Also cleaning after dielectric etch (or post-etch residue removal, PERR) is becoming a critical step to achieve high yield and reliability. In previous generations, depending on the thickness of sidewall polymers, PERR could be performed using conventional commercial cleaning media or a combination of a short plasma treatment (or plasma flash) and a diluted aqueous clean (e.g. HF-based). Polymer removal could be obtained by dielectric under-etching. In those cases CD control could be achieved by slightly over

sizing the low-k structures. At 50 nm ½ pitch and below, the cleaning process window is strongly decreased. Constraints on CD control do not allow anymore for polymer removal by under-etching. At the same time there is a need to deposit thicker polymers during etching to protect the dielectric from plasma damaging and to maintain profile control. Dielectric damaging will likely also push plasma flash processes out of production lines.

Therefore novel approaches of plasma-less PR and residue removal that address these concerns are reviewed here. Most of the results shown here are obtained on CVD OSG SiOCH porous low-k dielectric (k = 2.5, 25 % porosity, 1.7 nm pore size). The photo resist under study is poly(meth)-acrylate-based resin for 193-nm DUV lithography, with lactone and adamantane as side-chain groups.

Photo Resist removal

Good results for PR removal from MHM have been obtained by a two step process consisting of a UV-pretreatment followed by an immersion in solvent with dissolved O_3, as shown in Fig. 2 [2]. This process resulted in removal of the entire plasma modified PR as well as the organic BARC layer. The UV treatment was performed under vacuum by 222nm excimer lamp at 25 mW/cm2, without intentional heating. O_3 was obtained by an O_2 flow to an O_3 generator at 2 standard-l/min total flow resulting in a 20 w-ppm O_3 concentration at the outlet. This O_3 and O_2 mixture was bubbled through a diffuser in the bottom of the solvent container. It was also demonstrated that all three aspects are necessary: the UV pre-treatment the O_3 and the solvent, by selectively eliminating each one individually [2-4].
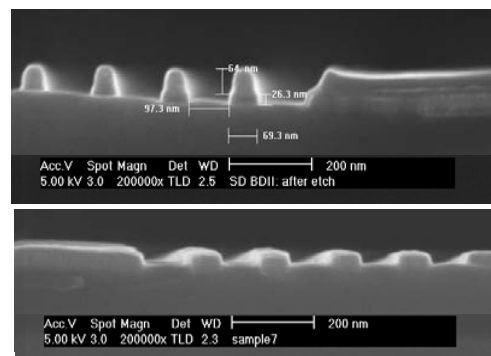

Fig.2 top: after patterning of TiN MHM. Bottom: after 2 min UV treatment and subsequent 5 min immersion in propylene carbonate solvent with dissolved O_3 at 60C [2].

First measurements using mercury probe show that the increase in k-value due to the O₃-solvent process and UV treatment individually applied, to partially etched blanket low-k material is less than 0.1.

The process is believed to work as follows. The UV treatment results in an increased concentration of C=C bounds in the PR crust [5,6], as was interpreted from FTIR analysis [3]. These C=C are oxidized by O_3 through ozonolysis, resulting in breaking of the polymer chain [1]. For C=C present in the main chain of the cross-linked PR crust this will result in effective breakdown of the network, ultimately making it soluble in the propylene carbonate. The combined use of solvent and O_3, however, may raise issues with respect to stability of the solvent, mixture lifetime and even safety. Therefore the search was continued to other approaches.

One promising alternative consists of a sequence of a UV irradiation, then an exposure to an O_3+ H_2O (vapour) at 90C [7,8] and finally a rinse in an organic solvent [4]. The O_3 process was performed as described in Refs [7,8]. The total flow of O_2 was 2 standard-l/min containing an O_3 weight concentration of 200 ppm. This process resulted also in the removal of the entire plasma modified PR as well as the organic BARC layer. The exposure time to the O_3 + H_2O vapour has to be limited to approximately 1 min to keep the k-value increase at 0.1. Longer exposure time resulted in k-value increase. This is attributed to the presence of reactive radicals in aqueous O_3 systems. These radicals are expected to be less selective for the PR with respect to the low-k material.

In other studies also the additional application of mechanical agitation to solvent based mixtures was found to enhance the Photo Resist removal [3,9,10]. This could be sonic agitation or the use of high velocity liquid aerosol spray.

Post etch residue removal

Ones the low-k is etched the next challenge is to selectively remove the post etch polymers. In the past often dilute HF containing mixtures have been tried. In general d-HF does not fully dissolve the polymers because of their organic content. Therefore solutions based on solvents are considered.

Since chemical selectivity requirements are very stringent it is believed that successful post etch residue removal procedures will not be purely chemical but need to be assisted by other physical removal mechanisms. Most likely candidates are mechanical "micro-forces" induced by e.g. high frequency acoustic agitation or the use of high velocity liquid aerosol spray. Some solvents show a tendency for particles such as post-etch residues to redeposit [11,12]. The use of megasonic agitation can also be beneficial to prevent such deposition. Fig.3 shows the beneficial effect of megasonic agitation applied to a solvent based mixture for overall PER removal.

Of course the use of mechanical forces needs to be well tuned as too strong forces can lead to structural damage. Chemical-mechanical cleaning processes should not only feature appropriate chemical selectivity but also mechanical selectivity.
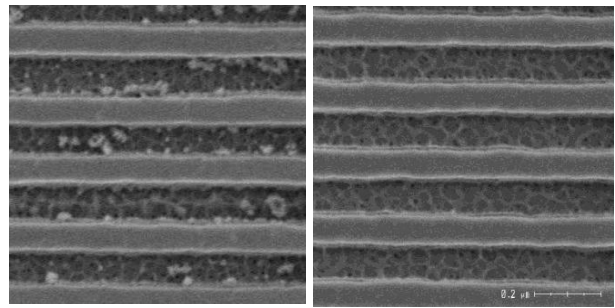

Fig.3 Left: solvent based mixture applied in absence of mechanical agitation, showing residues remaining in the trenches
Right: identical solvent treatment but with application of megasonic agitation removed all big residues from the trenches.

In order to optimize the mechanical component a better understanding of the mechanical strength of the structures needs to be developed and an assessment of the forces needed to remove particles needs to be done. Measurements and understanding of mechanical strength will result in the establishment of mechanical specifications for chemical-mechanical cleaning process. This is quite a paradigm shift in cleaning processes. A measurement method based on lateral force AFM has recently been applied successfully to silicon gate stack lines (Fig. 4) [14] The obtained values could be modeled to extract failure stress values [15]. Isolated lines of porous low-k material with a width of 90 nm and a height of 150nm were used for lateral force AFM measurements. The lines where found to fail at a lateral force of 4.5 +/- 0.5 mN [16]. From SEM inspection (Fig. 5) it could be observed that the failure occurred inside the low-k line itself, and not at the bottom interface.
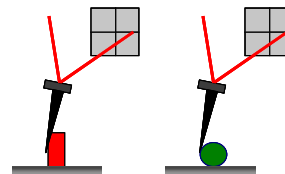

Fig.4 Schematic of lateral force AFM for measuring lateral strength of low-k lines and removal force for particles [14].
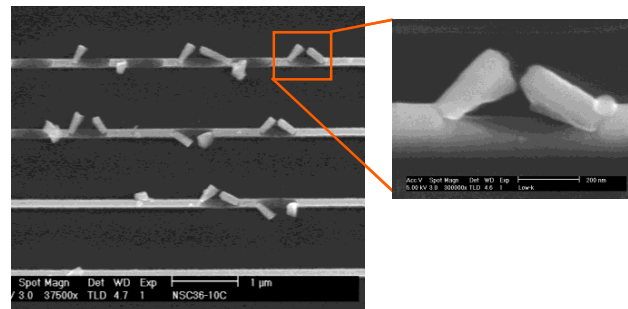

Fig.5 SEM of collapse induced by lateral force AFM measurements on 90 nm lines of 150 nm thick CVD OSG SiOCH porous low-k dielectric (k = 2.5, 25 % porosity, 1.7 nm pore size) [16].

Stress analysis was done neglecting built-in stress reported particularly in the case when the MHM is still

present [17,18]. The analysis shows that failure corresponds to stress values in the low-k line on the order of 50 to 70 MPa. It is remarkable to see that the interface did not fail, though for this particular geometry, the interface stress levels were estimated to be also on the order of 50 MPa. Using the same model the failure force of a 30 nm wide and 100nm high low-k line is estimated to be on the order of 1 uN.

Using the same lateral force AFM technique the removal force for Poly Styrene Latex (PSL) spheres with a diameter of 125 nm was measured as shown in Fig. 6. It was found to be on the order of 20 nN. Since this force is almost 2 orders of magnitude lower than that estimated for damaging a 30 nm low-k line, a window for mechanical cleaning indeed exists.
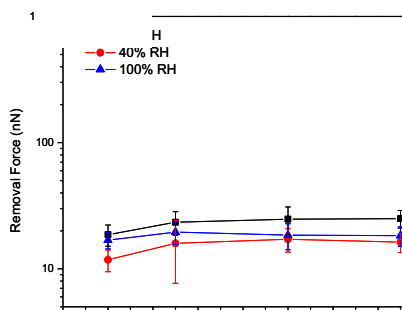

Fig.6 Lateral removal force required to remove Poly Styrene Latex (PSL) spheres with a diameter of 125 nm, as was measured by lateral force AFM [16].

Recently a rather unconventional liquid approach that involves reductive chemistry using radical anions has been proposed [19,20]. Radical naphthalene anions are formed by the reaction of metallic sodium and naphthalene in a compatible solvent. In order to assess the performance fluorocarbon films deposited from a detuned etching plasma are introduced as a model system [20]. The anion treatment results in a defluorination of the polymer resulting in a polymer, containing double bounds, as shown in eq. (1). Also swelling by the solvent is believed to contribute to the removal. The double bounds are subsequently attacked by O_3. The method was demonstrated to successfully remove the challenge polymers both for the model system as well as from patterned wafers. Preliminary test using Hg-probe showed that this approach is compatible with 2.7 MSQ based CVD layer.

(1)
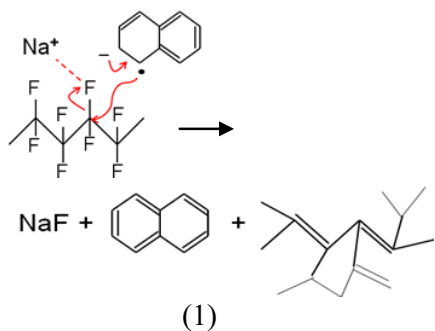
Also alternative techniques making use of scC O_2 could be considered for aggressively scaled features because of superior wetting and absence of surface tension. An intriguing alternative approach has been proposed referred to as gas expanded liquids (GXL) with properties intermediate between SCFs and liquid baths [20]. GXLs are formed when a gas is introduced into a liquid at elevated pressure [21,22]. Upon gas incorporation, the liquid volume expands and the density, viscosity, and surface tension decrease, while maintaining more liquid-like properties (e.g., improved solvent strength) relative to those of SCFs. These GXL properties allow tuning of liquid properties by inclusion of high pressure gases. TMAH and CO_2 based mixtures have been successfully used. PER were succefully removed from MSQ films while maintaining the k-value.

Conclusion

UV pretreatments followed by O_3 and solvent treatments have resulted in full removal of post MHM etch PR. Megasonic agitation of solvent based removal has a benefical effect if tuned properly to avoid structural damage. Radical anion based followed by O_3 and gas expanded liquid processes show promising PER removal.

References

[1] M. Claes *et al.* ECS Transactions, **11** (2), 177 (2007).
[2] Q.T. Le *et al.*, MRS spring 2009, to be published in the proceedings.
[3] Q.T. Le *et al.*, Proceedings of UCPSS2008, Solid State Phenom. **145-146,** 323, (2009).
[4] Q.T. Le *et al.*, Sematech Surface Preparation and Cleaning Conference (2009).
[5] D. M. Ruck, J. Schulz, and N. Deusch, Nucl. Instr. Methods Phys. Res. **B 131**, 149 (1997).
[6] J. O. Choi, J. A. Moore *et al.* J. Vac. Sci. Technol. **B 6**, 2286 (1988).
[7] S. De Gendt *et al.* Proceedings IEEE VLSI Symposium 1998, 168.
[8] S. De Gendt *et al.* Proceedings of UCPSS1998, Solid State Phenom. **65-66 ,** 165 (1999),.
[9] P. W. Mertens, G. Vereecke and R. Vos, Semiconductor Fabtech, **31**, 86 (2006).
[10] M. Claes *et al.* Proceedings of UCPSS2006, Solid State Phenomena Vol. **134**, 325 (2008).
[11] F. Barbagini *et al.*, Proceedings of UCPSS2006, Solid State Phenom. **134**, 165 (2008).
[12] F. Barbagini, PhD dissertation KULeuven 2009.
[13] P.W. Mertens, proceedings Acoustics'08 Paris: Euronoise – ECUA, 29 June – 4 July 2008, 555.
[14] T.G. Kim, *et al.* ECS Transactions, 11 (2) (2007), 123.
[15] K. Wostyn *et al.*, Proceedings of UCPSS2008, Solid State Phenom. **145-146**, 55 (2009).
[16] T.G. Kim, *et al.,* ECS fall 2009 to be published in transactions.
[17] F. Iacopi *et al.*, Applied Physics **82**, 1380-1382 (2003).
[18] M. Darnon *et al.*, Appl. Phys. Lett. **91**, p 194103 (2007).
[19] C.L. Timmons and D.W. Hess, J. Electrochem. Soc, **155**, H771 (2008).
[20] I. Song *et al.*, Proceedings of UCPSS2008, Solid State Phenom. **145-146**, 303 (2009).
[21]. C. A. Eckert, D. Bush, J. S. Brown, and C. L. Liotta, Ind. Eng. Chem. Res., 39, 4615 (2000).
[22]. M. T. Spuller and D. W. Hess, U.S. Pat. No. 6,786,977 (2004).