

# Impact of reducing resist stripping processes at elevated temperature on ULK and HM materials

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## Abstract

Ultra low- $k$  materials for interconnects in chip manufacturing require new or adapted procedures for integration into copper damascene metallization, including patterning processes. This work deals with the impact  $H_2$  containing stripping processes at elevated temperatures on porous ultra low- $k$  materials and low- $k$  hard mask/capping materials. Porous MSQ and  $SiO_2$  and a low- $k$  hard mask have been prepared by spin on deposition (SOD) and for comparison dense  $SiOCH$  by PECVD deposition. Resist stripping was done with a downstream microwave discharge in an advanced strip passivation chamber (ASP) of Applied Materials using mixtures of  $H_2/N_2$  and  $H_2/He$ . Shrinkage (change of thickness) and electrical properties ( $k$ -value and field break down) were investigated. FTIR spectra were used to support the investigation. Ashing parameters, like time of plasma treatment, temperature and gas composition, have been characterized. It was found that the advantage of nitrogen admixture is the high rate of ashing, but shrinkage and impact on  $k$ -values will be higher than with He admixture. Helium admixture reduces shrinkage and  $k$ -values will be only slightly impacted, but stripping time has to be increased for resist removal.

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## 1. Introduction

The International Technology Roadmap for Semiconductors (ITRS) demands ultra low- $k$  materials of next generation for the 45 nm node, which

must be porous and therefore, require new or adapted procedures for integration into copper damascene metallization. New techniques have to be developed in order to compensate for the lower mechanical strength and to protect the larger inner surface in relation to bulk. Critical processes, like etching of low- $k$  materials and the various available processes for resist removal [1] in conventional integration must be adapted or exchanged. Earlier studies have shown [2,3], that porous Si based materials

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are sensitive against plasma treatment with oxygen. An interface delamination in the stack between porous material and cap layer and an increased  $k$ -value were detected. In order to avoid or at least to minimize such impacts during resist stripping, different approaches were published. One of the most promising approaches is a hydrogen based plasma process at elevated temperatures. For example, Han [4] describes the advantage of  $H_2$  activated resist removal. Different admixtures, e.g. nitrogen, helium or argon are known. It is assumed that microwave excited  $H_2^*$  molecules assist in sublimation and in cracking remaining resist. Other novel approaches in order to remove resists are super critical fluids and all wet strip [5].

We have investigated the impact of admixtures of nitrogen and helium to hydrogen microwave plasma. Shrinkage (change of thickness) and electrical properties were studied. FTIR spectra were used to understand the occurring changes in dielectric materials.

## 2. Experimental

Porous MSQ (p-MSQ) with  $k$  value of  $\sim 2.2$  was chosen as ultra low- $k$  (ULK) material. As potential cap layer, a spin-on hard mask (SOHM; slightly porous SSQ;  $k \sim 3.2$ ) has been introduced to fulfil the demand for hardmask (HM) and CMP stop, especially for a post-CMP burnout approach. For comparison also  $SiO_2$  aerogel ( $k \sim 2.1$ ) and PECVD  $SiOCH$  ( $k \sim 2.9$ ), were taken into consideration. To minimize the impact of stripping on the properties of the dielectric layers investigations with non-patterned films were done. Deposition of all porous dielectrics ( $SiO_2$  aerogel, p-MSQ, and SOHM) was carried out with a spin on process. The porous MSQ was processed after removal of porogen. This processing leads to a porosity of 31% and 18% for the porous MSQ ULK dielectric and porous spin on hard mask single layers, respectively.

Wafers of high ( $24.6\text{--}32.9\ \Omega\text{ cm}$ ) and low ( $4\text{ m}\Omega\text{ cm}$ ) resistivity have been used for FTIR and mercury probe measurement, respectively.

The plasma assisted stripping process was studied by means of an Advanced Strip Passivation Chamber (ASP) of APPLIED MATERIALS™.

Downstream microwave plasma of hydrogen with admixture of nitrogen or helium at a pressure of 1 Torr was used. The temperature was typically  $300\ ^\circ\text{C}$  and the magnetron was adjusted to 1000 W. The shrinkage was ellipsometrically measured by change of thickness. The electrical properties, i.e.  $k$ -value, leakage current and field break down (FBD) were measured by Hg-probe. The FTIR spectra were recorded with a Bruker spectrometer. The spectra were collected for films with a thickness of 100 nm (hardmasks) and 500 nm (low  $k$  and ULK materials). The sample was tilted about  $20^\circ$  against the incident beam. Spectra normalization was used and the impact of the Si wafer was corrected.

## 3. Results and discussion

### 3.1. Stripping with mixtures of $H_2/N_2$ and $H_2/He$

Fig. 1 shows typical SEM images for a 200 s treatment at  $300\ ^\circ\text{C}$  in the ASP chamber. The resist was completely ashed by  $H_2/N_2$  mixture (on the left), whereas by  $H_2/He$  mixture (on the right) the resist was only partly removed. The admixture of nitrogen impacts the rate of stripping positively, only small residues remain, which have to be removed by a following wet clean step. The admixture of helium reduces the rate of stripping and thus leads to increased stripping times.

As seen, gas mixture and time of process are important parameters of stripping. In order to evaluate the impact of stripping on hardmask and ultra low- $k$  materials, the plasma treatment was investigated with respect to time of treatment, temperature and gas mixture.

### 3.2. Shrinkage vs. treatment time for $H_2/N_2$ and $H_2/He$ mixtures

The admixture of nitrogen not only ashes the resist but also causes a substantial shrinkage of porous hardmask and low- $k$  material (Fig. 2). The material with the larger porosity was stronger attacked causing larger shrinkage. The mixture of  $H_2/He$  affects the hardmask SOHM hardly and p-MSQ material only after a long time of plasma treatment.

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