

Impact of UV wavelength and curing time on the properties of spin-coated low-k films

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ABSTRACT

Advanced spin-on k 2.3 films with ~40% porosity were enabled by liquid phase self-assembly (LPSA) mechanism on Si substrates. UV-assisted thermal template removal is investigated as a faster alternative to the conventional thermal process. The as-deposited films were exposed to narrow-band UV light of 172 nm, 222 nm, 254 nm or 185/254 nm at 400°C for different time. The optical, mechanical, chemical and electrical properties of the resulting films are discussed in this work. Photons with wavelength of about 172 nm from one side are detrimental to the electrical and chemical properties of the low-k films but from the other side notably improve the porous low-k mechanical properties. Exposure to 222 nm light as short as 3 min. is more efficient in terms of template removal when compared to 2h thermal cure, while in both cases similar mechanical and electrical properties are reported. UV-cure using 254 nm or dual band 254/185 nm photons seem to have a minor contribution to the template removal efficiency for the applied doses. Higher doses are necessary in order to better understand the effective contribution of these photon energies. Finally, the HF etching mechanism is discussed.

Introduction

Presently, low-k films based on application of self-assembling chemistries (LPSA, PMO...) are considered as the most promising for sub 10 nm technology nodes because of better process control. UV-assisted thermal removal of porogen and curing has been a standard step for PECVD films but it has not been extensively studied for oxycarbosilane LPSA and PMO materials.

The UV-cure of spin-coated MSQ [1] and nanoclustered silica [2] films has been already published. UV-cure of oxycarbosilane film has also been reported [3]. Nevertheless, the pore size distribution of these films was rather broad while the used light was not narrow-band. Recently, IBM reported [4] the use of UV-cure with a broad

spectrum lamp during an integration of oxycarbosilane films but no systematic study was presented.

Experimental

Low-k oxycarbosilane films with target k-value of 2.2 were spin-coated on a Si wafer which was subsequently cleaved into 3.5 by 3.5 cm coupons. In order to exclude the effect of atmospheric gasses on the low-k during the UV-curing the processing chamber was evacuated down to 5 mbar. Next the chamber was flushed with high purity N₂ to maintain a pressure of 20 mbar [5]. Afterwards, the temperature was increased from room temperature (RT) to 400°C by a heater element in about 2 min. Finally, the samples were UV-irradiated for variable time between 3 and 10 min. The UV irradiation was generated by Xe₂* excimer lamp (172 ± 12 nm; 1.5 mW/cm²), KrCl* excimer (222 ± 1.2 nm; 13 mW/cm²), or low pressure (LP) Hg lamps – one allowing the 185 nm line to pass through (185/254 nm, 4 mW/cm²) and the other one absorbing the higher energy photons (254 nm, 8 mW/cm²). Some samples were annealed at 400°C for 3, 5 and 10 min.

Results and Discussion

Template removal efficiency was evaluated by spectroscopic ellipsometry (SE) and Fourier-transform infra-red (FTIR) spectroscopy. A reference film thermally cured for 2 h at 400°C has a refractive index RI ≈ 1.27. A shorter anneal of up to 10 min. leads to higher RI (Fig. 1) with respect to the reference sample, pointing to the presence of

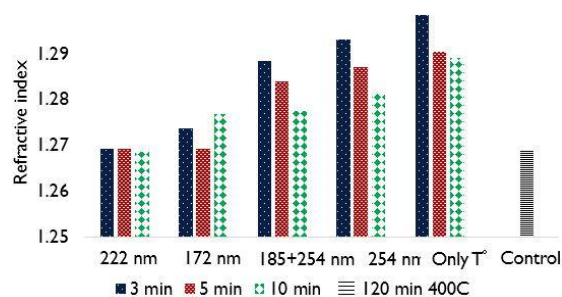


FIGURE 1. REFRACTIVE INDEX OF THE CURED LOW-K FILMS

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residual template in the film. Similarly, $RI > 1.27$ are reported for films treated with UV light emitted by the LP Hg lamps even after 10 min. treatment. Moreover, exposure shorter than 10 min. results in higher RI further supporting the hypothesis of remaining template in the film. On the other hand, the increase of RI values after 10 min. exposure to 172 nm photons is attributed to induced densification. In contrast, the doses reached by exposure to 222 nm photons lead to a $RI \approx 1.27$, comparable to the RI of the reference sample. These findings suggest an improved template removal efficiency when using 222 nm light.

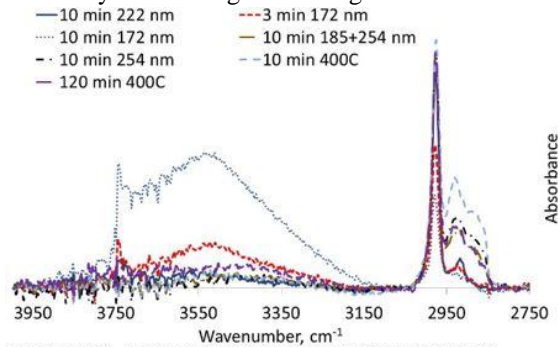


FIGURE 2A. FTIR REGION SHOWING C-H AND O-H

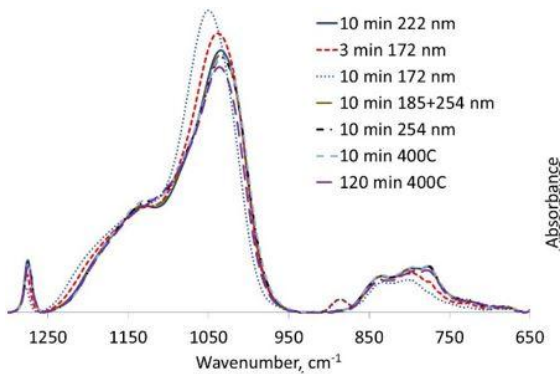


FIGURE 2B. FTIR REGION CONTAINING VIBRATIONS RELATED TO THE FILM MATRIX

The FTIR spectra allow for a better comparison of the polymers remaining in the films. The fingerprint of the hydrocarbon chain is situated between 2850 and 3000 cm^{-1} (Fig. 2A) in correspondence of the absorption caused by the C-H_x stretching vibrations. The intensity of the peak located at 2975 cm^{-1} is inferred to be mainly a result of the C-H stretching in Si-CH_3 groups, making it unsuitable for estimation of the remaining surfactant. The FTIR spectrum clearly shows the incomplete template removal for the sample thermally treated for 10 min. When additional low-energy (254 nm or 254+185 nm) irradiation is provided, a comparable template content with respect to the reference film is deduced. The apparently insignificant contribution of the 185 nm photons can be explained by their 10 fold lower intensity. As evidenced from the FTIR spectra, low-k exposure to 172 and 222 nm photons leads to the lowest amount of polymer remaining in the films. Nevertheless, the 172 nm photons cause the cleavage of the Si-CH_3 bonds, as indicated by the decrease of the intensity of both the peaks at ~ 2975

cm^{-1} and 1275 cm^{-1} . As a further confirmation of the damaging effect on the low-k, formation of Si-OH ($\sim 3750 \text{ cm}^{-1}$) and Si-H (890 cm^{-1} , 2255 cm^{-1}) bonds is observed. The formation of silanols is followed by moisture absorption (broad band above 3000 cm^{-1}). The loss of methyl groups results in a blue shift of the band attributed mainly to the antisymmetric stretching of Si-O-Si between 950 and 1250 cm^{-1} as well as in an increase in the intensity of the main peak located at 1070 cm^{-1} which indicates an enhanced cross-linking in the matrix. (Fig. 2B). The latter significant changes of the film matrix are observed only for UV light with $\lambda = 172 \text{ nm}$.

Cure Conditions @ 400°C	Label	Porosity, %	WCA, °	k,
3 min. 222 nm	3_222	38	89	2.33
10 min. 222 nm	10_222	37.9	92	2.33
3 min. 172 nm	3_172	37.3	31	2.52
10 min. 172 nm	10_172	36.6	46	3.21
10 min. 185+254 nm	10_185	36.1	95	2.34
10 min. 254 nm	10_254	35.8	93	2.36
10 min. thermal	10_T	33.6	93	2.43
120 min. thermal	reference	37.7	95	2.27

TABLE 1. SUMMARY OF POROSITY, WCA AND K VALUE AS A FUNCTION OF CURING CONDITIONS

Table 1 summarizes the measured EP, WCA and k-values. Lower open porosity is reported for the 10_T film compared to the reference sample, illustrating the need for long anneal times for enhanced template removal. The peak of the pore size distribution (PSD) for all of the treatments is situated at 2.8 nm. In spite of that, widening of the PSD and larger volume of toluene adsorbed in the micropores are observed when energy photons $\leq 5.6 \text{ eV}$ are applied. These findings can be explained by the removal of template both from the pore walls and from the micropores. On the other hand, irradiation with 172 nm photons results in a narrower PSD and an additional increase of the toluene volume adsorbed by the micropores, indicating partial collapse of the pores. When non-damaging curing conditions are applied, the observed WCAs are larger than 90°, while the damage caused by the 172 nm photons leads to surface hydrophilization resulting in a considerable k value increase.

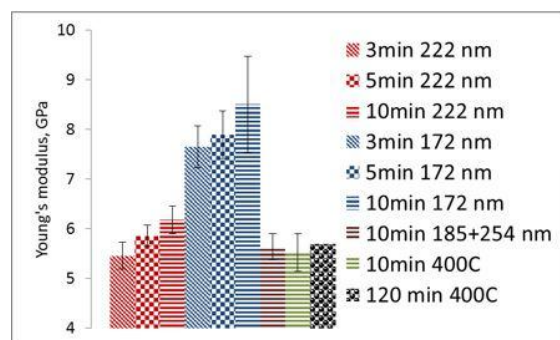


FIGURE 3. YOUNG'S MODULUS OF THE POROUS FILMS

A k value of 2.33, comparable to the k of the reference low- k is obtained upon 3 min. exposure to 222 nm light. Cure time longer than 3 min. does not seem to further affect the k -value. However, exposure time longer than 3 min. seems to be necessary in order to achieve better mechanical properties. As evident in Fig. 3, the Young's modulus (YM), obtained by nanoindentation tests with Berkovich indenter tip, increases with the UV exposure time. On the other hand, the crosslinking observed for the samples irradiated with 172 nm light leads to YM higher than 7.5 GPa.

The chemical stability in 0.5 wt% HF of thermally and UV-cured low- k s is compared. The damaged, hydrophilic films are completely etched in less than one minute. The films exposed to LP Hg lamps, the ones which only received thermal cure, as well as the reference sample, are removed in about 6-7 min. The samples irradiated with 222 nm photons show decreased chemical stability being completely etched in about 4 min. while the SE modelling performed for films dipped in HF for 3 min. using an isotropic one-layer Cauchy function becomes less adequate resulting in an increase of the associated mean square error (MSE). The observed dispersion is better modelled by a two-layers Cauchy model. For the top layer a thickness of ≈ 200 nm corresponding to a $RI=1.27$ is calculated, while a thickness lower than 5 nm associated to a $RI \approx 1$ are reported for the bottom layer. Similar values are also calculated for the HF-dipped reference low- k film. These findings suggest that the Si-low- k interface might play an important role in the explanation of the apparent difference in the chemical stability. In order to investigate if there are changes in the interfacial energy during HF dip, a tape-pull test was performed. After 5 min. HF dip of a reference sample the low- k film is easily removed by the tape, unlike the pristine film which remains on the Si substrate. Quantification of the interface energies of reference low- k samples with and without 5 min. dip in 0.5 wt% HF was performed by nanoindentation tests using wedge indenter. For the HF-treated sample a pop-in, early indication for the formation

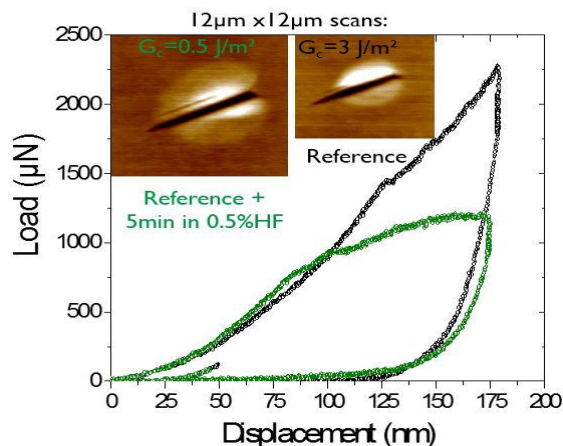


FIGURE 4. LOAD-DISPLACEMENT CURVES RESULTING FROM WEDGE INDENTATION TESTS

of interface cracks, is observed (Fig. 4) at lower load than for the reference. By using the semi-empirical solution introduced by Yeap et al.⁶ the interfacial adhesion (G_c) for pristine and HF-dipped films are calculated to be 3 and 0.5 J/m², respectively. The G_c values illustrate weakening of the interface between the Si and the low- k during HF dip which is interpreted as preferential etching of the layer close to the interface. Therefore, the faster HF etch of the film irradiated with 222 nm photons compared to the reference film might be due to difference in chemical composition of the bottom layer.

ToF-SIMS analysis was performed on a reference low- k and a film irradiated with 222 nm photons before and after HF dip. No obvious differences in the profiles of Si, C and O ions are observed for the investigated films. F⁻ accumulation close to the Si interface is observed, which further supports the conclusion that low- k etch happens preferentially at the interface with Si. Additionally, three times higher increase of F⁻ is detected after HF-dip for the film cured with 222 nm photons compared to HF-dipped reference film. The latter observation correlates, with the almost twice faster removal of the 222 nm irradiated films in 0.5wt% HF.

Conclusions

UV-cure of a spin-on oxycarbosilane LPSA low- k film is presented. The lowest k -value of 2.33 is obtained after irradiation with 222 nm photons for a time as short as 3 min. Longer time than 3 min. is needed in order to achieve improvement in the low- k mechanical properties. A YM value as high as 8.5 GPa is obtained after exposure to 172 nm photons at the expense of significant degradation of the low- k chemical and electrical properties. Preferential etching of the Si-low- k interface by HF is inferred from the decrease of the interfacial adhesion from 3 to 0.5 J/m² after HF dip. The latter mechanism in combination with possible compositional differences in the interface layers of the 222 nm irradiated films are considered in order to explain the lower HF stability observed for these films.

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