Laser anneal of oxycarbosilane low-k film

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***Abstract*—Submilisecond laser anneal has been experimentally investigated for porogen removal and its ability to improve the mechanical strength in oxycarbosilane ultra low-k films compromised due to the introduction of porosity. We report the occurrence of extensive bond rearrangements inferred from Fourier-transform infra-red (FTIR) spectroscopy, elastic recoil detection (ERD) and spectroscopic ellipsometry (SE) in the energy range of 1.4-8 eV. The laser anneal affects most notably the organic content of the organosilicate matrix leading to depletion and reorganization. Nevertheless, the tested conditions reveal a processing window which allows for 13% improvement of Young's modulus as compared to the reference film, annealed in a conventional furnace at 400°C for 2 h, while not impacting the relative dielectric constant of 2.25.**

Keywords— Oxycarbosilane, laser anneal, low-k

I. INTRODUCTION

Reliable ultra-low-k materials are needed in order to reduce the resistance-capacitance signal delay in future generation ultra-large scale integrated interconnects. [1,2] In order to reduce the dielectric constant below 2.5 porosity needs to be introduced in the organosilicate films. However, due to the detrimental effect of this approach on the mechanical reliability treatments for improved stability are under investigation. The most popular approach for enhancement of the Young's modulus has been the application of ultra-violet (UV) irradiation with wavelength longer than 200 nm. The UV cure (UV irradiation at temperature ≈ 400°C) is used for both template removal and promoting crosslinking in the porous film. Alternatively, short pulse laser anneal has been investigated for improving the mechanical properties of low-k films. Volksen and co-authors [3] investigated the laser anneal of dense and porous organosilicate films and noted the ability of this approach to improve the Young's modulus with a limited negative impact on the dielectric constant. On the other hand, Raymunt et al. [4] reported theoretical and experimental investigation of the effect of laser anneal on the bonding structure of an organosilicate low-k film. Nevertheless, these studies did not consider laser anneal for porogen removal or investigate its effect on oxycarbosilane films which contain backbone carbon as bridging alkylene (Si-$(CH_2)_x$-Si) groups. The latter have been shown [5,6] to be more promising than the conventional carbon-doped oxides where carbon is present solely as a –CH_3 group.

II. EXPERIMENTAL

The investigated film was prepared by using a sol-gel method where a stabilized sol is spin-deposited onto a Si wafer. The coating sol was prepared by mixing a matrix and a template solutions. The former was obtained by stirring 1.1 ml 1,2-bis(triethoxysilyl)ethane (BTESE), 0.56 ml 0.02 molar hydrochloric acid and 0.64 ml methyltriethoxysilane (MTES) in 2 ml ethanol at 60°C for 1 hour. The BTESE is the source of the bridging ethylene groups (Si-CH_2-CH_2-Si) while the MTES is the source of methyl groups making the film hydrophobic. In parallel, the template solution was prepared by dissolving 0.3763 g polyoxyethylene (18) tridecyl ether in 16 ml 1-methoxy-2-propanol after stirring for ca. 45 min at room temperature (RT). Next, the template solution was added to the cooled down to RT matrix solution and further stirred for 15 min at RT. Finally, the solution was transferred to a 50 ml polyethylene bottle and aged for 24 hours at RT. The formulation was spin-coated on a 300 millimeter diameter Si wafer at 1500 rpm for 1 min. Following the deposition, the wafer was soft baked at 150°C for 2 min in ambient atmosphere in order to promote polycondensation and solvent evaporation. The resulting thickness was ca. 216 nm.

The soft-baked wafer was treated in an Ultratech LSA201 system equipped with a CO_2 infrared laser with an output peak around 943 cm^{-1} out of the resonance frequency of the organosilicate matrix. The absorption of the CO_2 radiation is facilitated by the free carriers in the n-type Si substrate. Eight power densities with a dwell time of 800 µs were used to generate eight test patterns with width of 30 mm on the wafer. The wafer was additionally heated by a hot plate to 150°C. Temperatures between 900 and 1145°C were observed by a pyrometer calibrated to the melting temperature of undoped Si. The treatments were performed in inert N_2 atmosphere.

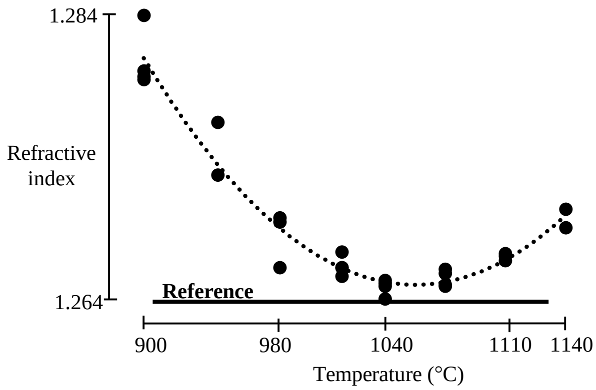

Fig. 2. The differences in refractive index above 980°C were found to be statistically not significant

III. Results and Discussion

The evolution of the refractive index (RI) with the measured temperature is shown in Fig. 1. The lowest RI is observed at ≈1040°C while at lower and higher temperatures slightly higher RIs are measured but these differences in the temperature range above 980°C are found to be statistically not significant. Additionally, toluene ellipsometric porosimetry (EP) measurements reveal that there is no difference in the open porosity, calculated to be 38 %, for the annealing conditions above 940°C. The only condition which leads to incomplete template removal is the annealing at 900°C in which case 3% lower open porosity is calculated. The calculated pore size distribution (PSD) further supports this interpretation by indicating narrower PSD for the film cured at 900°C which is explained by the remaining template on the pore walls effectively making the pores smaller. No differences in PSD are observed for the films cured at temperature higher than 900°C. The EP data additionally indicates lack of pore collapse or significant densification which might have been expected [4] given the high temperatures achieved. Furthermore, it is important to limit the shrinkage of the film since it contributes to the compressive stress during integration. The shrinkage observed for the reference films, furnace annealed at 400°C in N_2 ambient for 2 h, is ca. 11 % while for laser annealed films we observe steady increase with laser power of the shrinkage up to 19.4 % for the highest laser power utilized in this study. Temperatures up to 1040°C allow to achieve shrinkage comparable to the one observed in the reference film.

Nevertheless, the FTIR spectra (Fig. 2) reveal removal of the organics from the film even for the lowest laser power applied. This is further observed by ERD spectra where C content decreases from ca. 22% to 15% when the measured temperature exceeds 1000°C. Furthermore, FTIR analysis indicates faster reduction of the bridging ethylene groups as compared to the methyl groups and virtually complete depletion at the highest laser power. ERD and FTIR further agree on the Si-O bond formation which is seen in FTIR as a blue shift as well as intensity increase of the Si-O-Si region and as increase in the relative content of Si and O in ERD. Nevertheless, while FTIR indicates further removal of organics with higher temperature the C-content inferred from ERD stays constant. The latter might point to bond redistribution which was discussed in a previous study [3]. One manifestation of the bond rearrangements seems to be the formation of $Si\text{-}CH_2\text{-}Si$ structures evident by a weak peak at 1360 cm^{-1}. The latter can be explained by the cleavage of the C-C bonds in $\equiv Si\text{-}CH_2\text{-}CH_2\text{-}Si\equiv$ groups in combination with the presence of ≡Si• radical due to $\equiv Si\text{-}CH_3$ bond dissociation. Another modification of the films evident by peaks at 885 and 2245 cm^{-1} is the appearance of ≡Si-H bonds. These compositional changes evident from FTIR reveal the numerous passivation processes occurring with ≡Si• radicals formed due to the breaking of the ≡Si-C bonds. Additionally, the C-extraction leads to surface hydrophilization for the highest temperatures achieved. The surface water contact angle (WCA) was measured to be around 90° for temperatures below 1100°C when statistically significant decrease occurs leading to a WCA of 80° after applying the highest laser power.

The modifications of the films were further monitored using spectroscopic ellipsometry in the energy range from 1.4

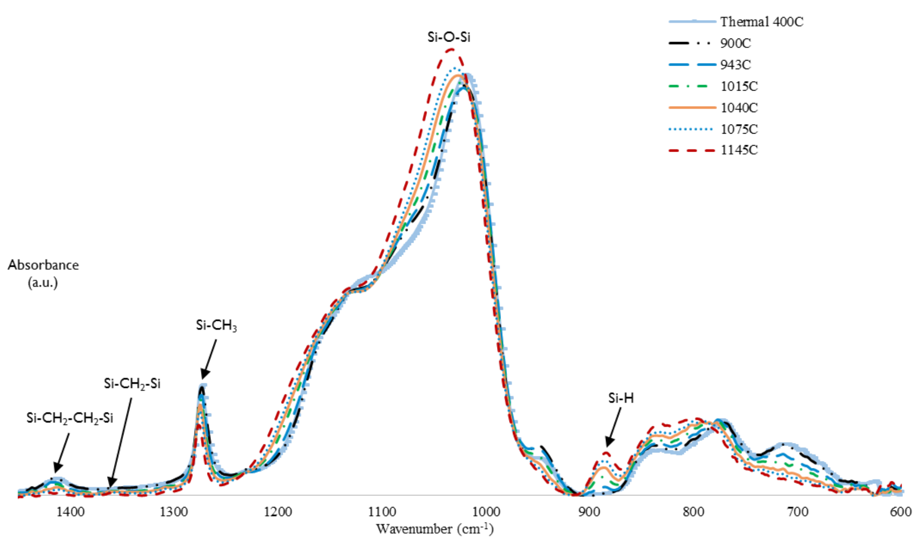

Fig. 1. FTIR spectra indicate C-depletion and formation of Si-O-Si and Si-H bonds

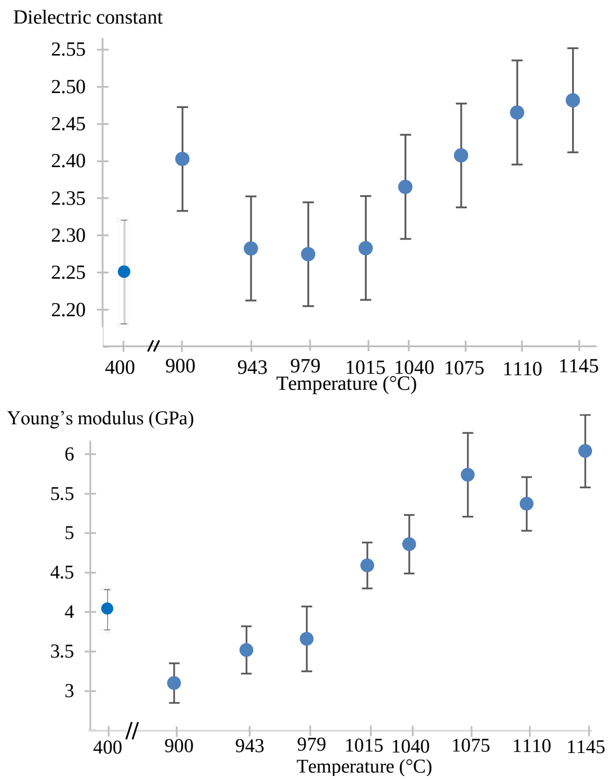

Figure 33. Dielectric constant (a) and Young's modulus (b) increase with anneal temperature

to 8 eV. Those revealed the appearance of an absorption edge at 6.7 eV for the curing conditions above 1000°C. The latter may be attributed to the formation of $O_3\equiv SiSiSi\equiv O_3$ structures [7] which additionally indicate the extensive modifications of the low-k matrix.

The Young's moduli (YM) and dielectric constants as a function of curing temperature are shown in Fig. 3 a) and b). It can be seen that both increase with higher laser power which is consistent with the inferred bond rearrangements. The higher dielectric constant observed for the film cured at 900°C further supports the hypothesis for incomplete template removal. In spite of the relatively damaging effect of laser anneal to the chemical structure of the low-k film we find a window of processing conditions around 1000°C which result in virtually the same dielectric constant as for the reference film annealed at 400°C and an improvement of the elastic modulus. For instance, curing at 1015°C leads to about 13% improvement of YM leading to 4.59 GPa as compared to the reference film with YM=4.07 GPa without increase in the dielectric constant of 2.25.

IV. Summary

Laser anneal was investigated for porogen removal and its ability to improve the mechanical strength in oxycarbosilane ultra low-k films. Extensive bond rearrangements mostly related to the replacement or reorganization of the organic content of the organosilicate matrix are reported. However, a processing window exists which allows for 13% improved Young's modulus as compared to the reference films annealed in a furnace at 400°C with no impact on the dielectric constant calculated to be 2.25.

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