Structural Evolution of Nano-Porous Ultra-Low-k Dielectrics under Broadband UV Curing

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Introduction

PECVD-based nano-porous dielectrics (k ≤ 2.5) are used for BEOL integration for the 45-nm node and beyond [1]. The synthesis of these ultra-low-k (ULK) materials is divided into two steps—PECVD followed by UV curing. In the PECVD, a nanocomposite comprised of an organosilicate-glass (OSG) as the matrix and a thermally-labile organic (TLO) as the filler is formed. The nano-porosity is subsequently created via UV curing, which facilitates TLO removal and cross-linking, or strengthening, of the OSG matrix. This paper investigates the evolution of TLO content, k value, porosity, and the degree of cross-linking during broadband UV curing. The study of structural evolution helps determine how the curing process can be optimized.

Experiments and Results

A series of as-deposited ULK films on Si substrates were processed in a broadband-UV chamber for different curing times. All films had as-deposited thicknesses of 600 nm except for those used for refractive-index (RI) measurements and SIMS. Figure 1 shows the FTIR spectra of (A) as-deposited and (B) UV-cured ULK films. The spectra can be divided into three components: C–H stretching (3000-2800 cm^{-1}, labeled Peak 1 in figure), Si–CH_3 deformation (1275-1255 cm^{-1}, Peak 2), and Si–O–Si stretching (1250-980 cm^{-1}, Peak 3). The Si–O–Si band can be subdivided into two categories: cage Si–O–Si (centered at 1135 cm^{-1}, Peak 3a) and network Si–O–Si (centered at 1040 cm^{-1}, Peak 3b) [2]. There are two major differences between the spectra. First, the C–H intensity diminishes significantly due to UV curing, which indicates substantial removal of organic content—the TLO. Second, the relative intensity of Si–O–Si cage to network decreases, which is a result of cross-linking leading to a more networked, stronger structure.

Plot A in Figure 2 shows the C–H intensity as a function of UV curing time. The intensity is expressed as a percentage of peak area remaining relative to that of an uncured sample. The quick initial drop is due to TLO removal and is confirmed by RI measurements, which show rapid initial RI decrease that signifies quick porosity generation for films of various as-deposited thicknesses (Figure 3). For every thickness, RI reaches a plateau by 60 s, indicating that most TLO has already been removed. This behavior is thickness-independent. The time of 60 s is also when the drop in C–H intensity transitions from being fast to slow. Plot B in Figure 2 represents curing under higher UV intensity and shows that TLO removal accelerates as UV intensity strengthens. Figure 4 shows that porosity is indeed quickly generated within 60 s, corroborating that TLO removal is rapid, and agrees with Figure 5, which shows a steep drop in k value in the same timeframe. This behavior also applies to TLO-based nano-porous dielectric with k of 2.2 after broadband UV curing (Plot C in Figure 2). As for composition homogeneity, dynamic SIMS depth profiles in Figure 6 show homogeneity across the entire thickness for a 1-μm ULK sample after broadband UV cure.

Figure 7 shows the extent of cross-linking as a function of UV curing time. This extent is defined as the Si–O–Si network area as a fraction of the entire Si–O–Si area in the FTIR spectrum. These areas were determined by peak fitting. The figure shows that the backbone is increasingly networked as curing progresses. One should note that degree of cross-linking advances linearly and is slow compared to TLO removal. Figure 8 relates Young's modulus (E) to the degree of cross-linking.

Conclusions

While the degree of cross-linking increases linearly throughout curing, TLO removal occurs rapidly in the beginning and is near complete after 60 s. In other words, cross-linking and TLO removal happen simultaneously in the early stage, and cross-linking takes over as the only process when TLO removal is complete. This behavior is true for ULK (k ≤ 2.5) and also films for the next generation (k = 2.2), showing that the same phenomenon is expected for films for the 32-nm node under broadband UV curing.

References

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[2] A. Grill and D. Neumayer, J. Appl. Phys. 94, 6697 (2003).

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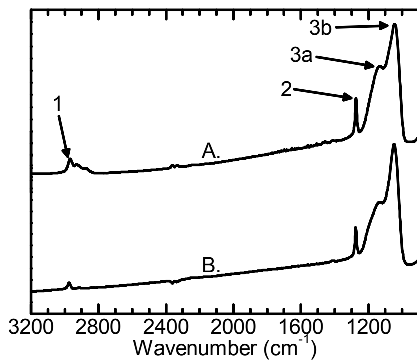

Figure 1. FTIR spectra of (A) as-deposited and (B) UV-cured ULK films.

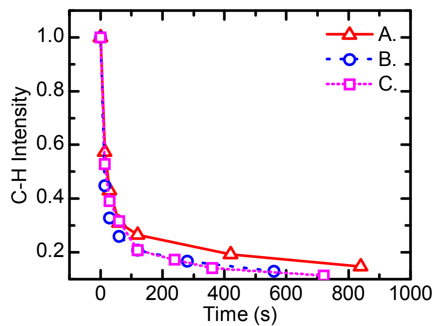

Figure 2. FTIR C–H intensity vs. UV curing time. Plots A and B represent ULK films cured under normal and increased UV intensity, respectively. Plot C represents films with increased TLO content cured under increased UV intensity.

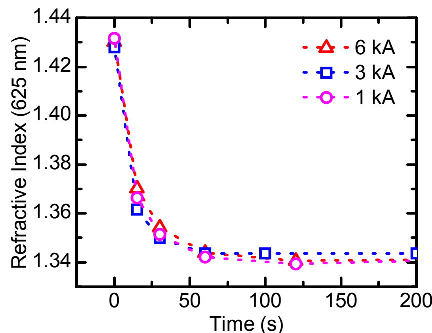

Figure 3. RI vs. UV curing time for ULK films cured under normal UV intensity for different as-deposited thicknesses.

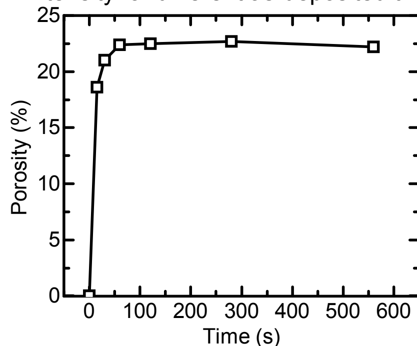

Figure 4. Porosity vs. UV curing time for ULK films cured under increased intensity.

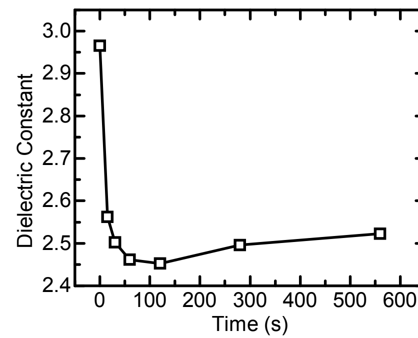

Figure 5. Dielectric constant vs. UV curing time for ULK films cured under increased intensity.

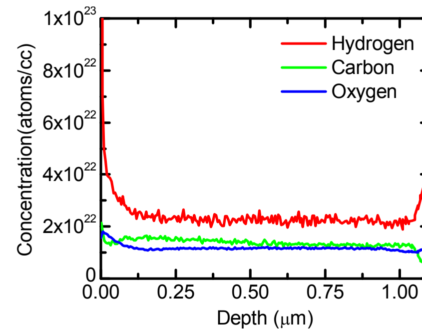

Figure 6. Dynamic SIMS depth profiles of H, C, and O atoms across a UV-cured 1-μm film.

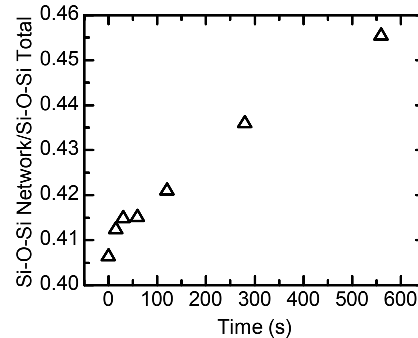

Figure 7. Degree of cross-linking vs. UV curing time for ULK films cured under increased UV intensity.

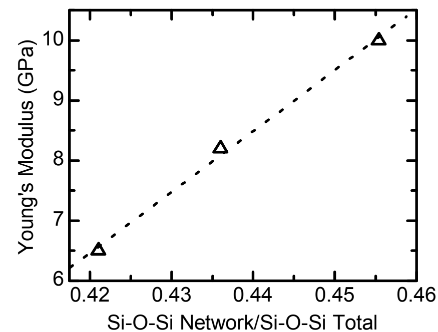

Figure 8. Young's modulus vs. degree of cross-linking.