ELECTRO IQ.
The Portal for Electronics Manufacturing

Porous low-*k* dielectrics using ultraviolet curing

It is essential to introduce porosity in carbon-doped oxides (CDO) to extend their applications to 45nm and beyond with k*<2.5. Ultraviolet (UV) curing offers an integration- and production-worthy solution. The complexity of introducing porosity to low-*k *films can be mitigated by using a UV curing process that affects the chemical composition, pore size, and distribution. Such a process, including a critical in situ chamber clean, is described.*

Carbon-doped oxides deposited by plasma-enhanced chemical vapor deposition (PECVD) can be extended to future generations by introducing porosity in the films. Adding porosity imparts superior mechanical properties at lower *k* values compared to simply increasing the carbon content as determined by experiments and simulations. However, the complexity of deposition increases because of the interplay between the silicon precursor and the additional chemistry used to generate porosity. Therefore, selection of the right CVD conditions becomes critical. Curing of the films to generate porosity can be conducted by providing the energy thermally (furnace) or via photons (UV). These curing processes uniquely affect the chemical composition, pore size, and distribution. Understanding the relationship between the as-deposited film, the process parameters of each curing technique, and the resulting film properties enables better system design and operation for high-volume manufacturing.

Reduction in the RC delay has been the driving force for the implementation of copper and low-*k* in chip fabrication [1]. The decrease in *k* is followed by a concomitant decrease in other film properties such as hardness, modulus, dielectric strength, and adhesion [2] that, in turn, poses many integration challenges [3]. PECVD-based CDOs have emerged as the strong contenders for $k \approx 3.0$ because of their ability to meet stringent integration requirements [2]. CDOs are being widely implemented at the 90nm node. The industry is currently looking to extend the application of CDOs to 45nm and beyond with *k*<2.5.

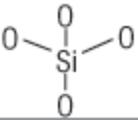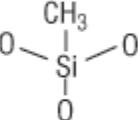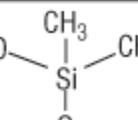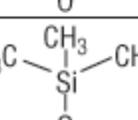| Formula	Structure		k
SiO_2	(structure)		4.2
$SiO_{1.5}CH_3$	(structure)	T	3.09
$SiO(CH_3)_2$	(structure)	D	2.71
$SiO_{0.5}(CH_3)_3$	(structure)	M	2.53

Figure 1. *Single units in CDO and associated k values. T = one methyl, D = two methyl groups, and M = three methyl groups.*

Click here to enlarge image

The logical approach to reduce k to <2.5 would be to increase the carbon content of the CDOs. There are two problems associated with this. First, increasing the carbon content dramatically lowers the mechanical properties. And second, despite increasing the carbon content, the k cannot be lowered below 2.6 [4, 5]. Further reduction in k can be achieved by introducing porosity in the films.

Role of carbon

The carbon in PECVD CDO films appears predominantly in the form of $Si-CH_3$, irrespective of the starting precursor as characterized by Fourier transform infrared (FTIR) spectroscopy [4, 6]. In order to study the role of carbon in k reduction, the CDO was broadly classified into four building-block configurations (**Fig. 1**): the SiO_2 matrix, Si with one methyl (T), Si with two methyl groups (D), and Si with three methyl groups (M). The actual films deposited also contain Si-H, $Si-CH_2-Si$, and other bonds, but based on the FTIR analysis, these bonds are considered insignificant and are ignored in the present calculations. The bond polarizability was calculated using the Clausius-Mossotti Approach per the equation below [7]:

$$\frac{k-1}{k+2} = \frac{4\pi}{3}\left(\frac{\rho}{M}\right)N_A\alpha$$

Click here to enlarge image

where ρ is the density, M is the molecular weight, N_A is Avogadro's Number, and α is the polarizability. The model assumes that the bond polarizability is additive and the ionic contribution is negligible for the Si-C and C-H bond [8-10]. However, the model accounts for the ionic and electronic contribution for Si-O bonds and fits the SiO_2 to k of 4.2. The data in Fig. 1 show that $k \approx 2.53$ with the introduction of three methyl groups to a single silicon atom. The k reduction takes place because the polarizability per unit volume decreases with the substitution of O with methyl (see **table**). The table also shows that the introduction of the $Si-CH_2$ bonds actually increases the polarizability per unit volume. Any PECVD-based CDO film comprises the four building blocks (Fig. 1) in various proportions. As the carbon content in the film increases, the D and M

fractions are likely to increase compared to the pure SiO_2 and T type units. Therefore, saturation of $k \approx 2.6$, as observed experimentally, is in good agreement with the described theory [4, 5].

Polarizability per unit volume of different bonds	
Unit	Polarizability/ unit volume
Si-O	0.123
Si-CH$_3$	0.076
Si-CH$_2$	0.132

Click here to enlarge image

Unlike the introduction of an O atom, the introduction of CH$_3$ in the SiO_2 matrix reduces the interconnect ability of the film as the CH$_3$ cannot bond to another Si atom. For example, a film containing only the D and M units can only form chains rather than a 3D network. This decrease in the "networking" is the reason the mechanical properties of the CDO films degrade with increase in the carbon content [4, 5]. Therefore, an alternative to simply increasing carbon is needed to deposit films with $k \leq 2.5$.

Porosity

The preferred approach to lowering k to <2.5 is the introduction of porosity in CDO films. Porosity is introduced by co-deposition of the Si-O-Si backbone and a labile species. The labile species is removed in a subsequent curing process to generate porosity. The nature of the porosity - i.e., volume fraction, average pore size, and pore size distribution (PSD) - is critical to the film properties and is a function of the deposition as well as the cure process.

Before discussing the process of pore generation, it is important to understand the correlation between porosity and the film properties. The introduction of porosity in CDO films offers a distinct advantage in terms of lowering the k and maintaining good mechanical properties (**Fig. 2**) as determined by the elastic modulus (the modulus in Fig. 2 is normalized to the highest experimental value obtained). The experimental data suggests that at lower k values (k<2.7) the introduction of porosity imparts superior mechanical properties compared to merely increasing the carbon content (Black Diamond I, BDI) and lowering k. The difference in elastic modulus between porous CDO (Black Diamond II, BDII) and BDI narrows at k>2.7.
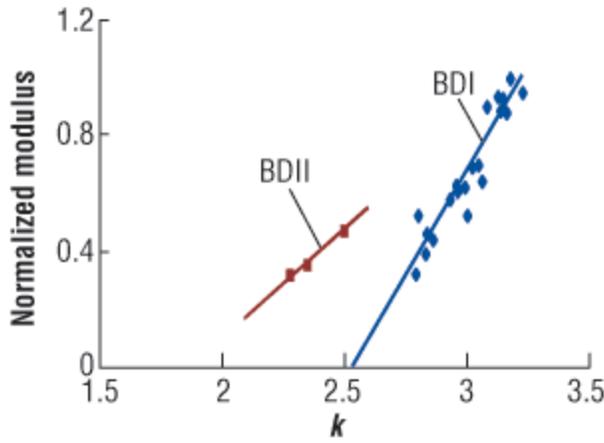
Figure 2. Modulus as a function of k for dense (Black Diamond I) and porous (Black Diamond II) CDO.
Click here to enlarge image

The tradeoff between carbon and porosity is shown in **Fig. 3** for different *k* values. The data in Fig. 3 are based on simulation using the approach dictated above (Fig. 1) with the addition of porosity in the calculations. These results indicate that carbon content and porosity are independent variables that can be controlled to modulate the film properties. Carbon in the porous films is desired, as it makes the films more hydrophobic and provides good ashing resistance [11]. A film comprising only T units and porosity would therefore be the ideal balance between *k* and mechanical properties and would meet the integration requirements.
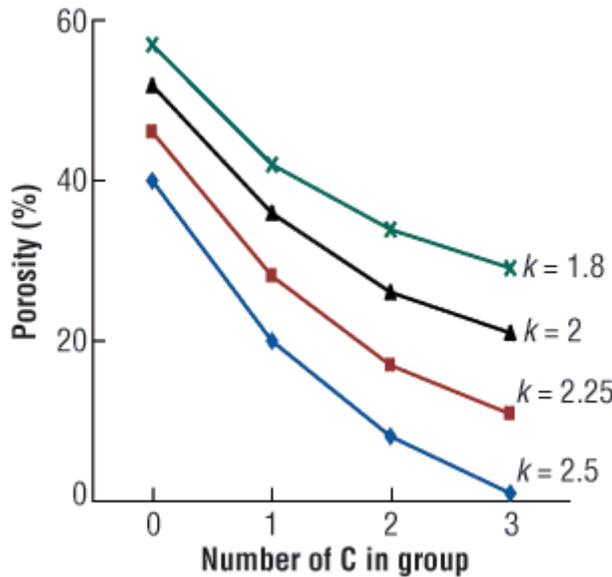

Figure 3. Role of carbon and porosity as k approaches 1.
Click here to enlarge image

It is interesting to note that the key film properties have been characterized with the carbon content and porosity with no discussion about the nature of the porosity such as PSD. However, small pore size and a PSD skewed to the lower end (rather than the larger size) are desirable for integration in the damascene process. Small pore size can prevent intrusion of etch gases and metal barrier into the films, thus obviating the need for pore sealing and dramatically simplifying the integration scheme.

Generation of porosity

In order to introduce porosity in the CDO films, the backbone and a labile species are co-deposited to form a film. This as-deposited film is then subjected to a curing process that drives the labile species out to form pores. This is true for PECVD and spin-on dielectric (SOD) approaches. In the SOD approach, the labile species undergoes phase separation to form nanoscopic domains; their subsequent removal from the film results in pore sizes that can be directly correlated to the phase-separated morphology. This approach can be used with a wide variety of materials and is discussed in detail elsewhere [12]. In the majority of cases, the labile species retains most of its original structure; therefore, the choice of chemistry and curing process becomes critical.

In contrast, the precursors for Si-O-Si backbone and for the labile species are introduced into the plasma in the PECVD approach. The plasma fragments both of the precursors into reactive species. The extent of this fragmentation can be controlled by controlling the plasma power and other process variables. Ultimately, the pore size and porosity is therefore dictated by the extent of the fragmentation and the total amount of the labile species that is eventually incorporated into the film. The k is controlled by varying the amount of the labile species that is incorporated in the as-deposited film by varying the porogen to the Si-O precursor [13]. The pore size and distribution then becomes a function of the deposition conditions (extent of precursor fragmentation) and the curing conditions.

Curing process

The key function of the curing process is the removal of the labile species that results in porosity in the films. To accelerate the removal of the labile species, the curing process typically takes place at a higher temperature than the deposition process. The additional thermal energy also results in the reconstruction of the Si-O-Si backbone that imparts additional mechanical strength to the film. It has been shown that the conversion from the cage-like structure to network-like bonding of the Si-O-Si matrix (cross-linking) results in improved mechanical properties [14]. However, the thermal budget in the back-end-of-line is restricted, and curing temperatures are limited to ≤400°C. One way to supply the additional energy required for the curing process is in the form of photons. A UV light source delivers energy in the form of photons whereby the energy delivered by each photon is inversely proportional to the wavelength of the light source.
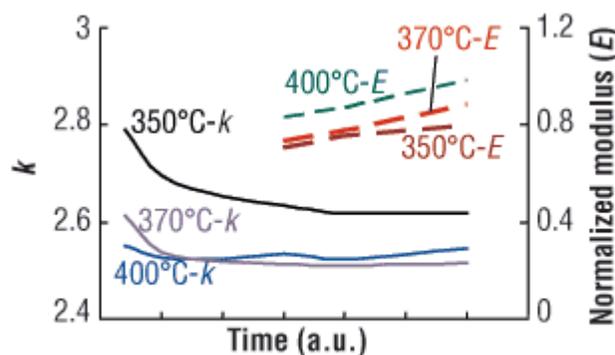

Figure 4. *Role of cure temperature in removal of the labile species and mechanical properties.*
Click here to enlarge image

The kinetics of removal of the labile species, as well as of cross-linking, can be enhanced by increasing the intensity without compromising the thermal budget. Nevertheless, the curing temperature plays a critical role in this process. For example, addition of thermal energy alone (curing up to 400°C) is inadequate for

removing the labile species, and at sufficiently low temperatures it is not possible to reduce the k below 2.5 (**Fig. 4**) [15]. This is consistent with the residual gas analyzer data presented elsewhere that show insufficient removal of labile species at lower temperature [15]. In addition, lower cure temperatures also result in lower mechanical properties (for the same k value) (Fig. 4) where the modulus is normalized to the highest value in the experimental set. This is most likely because of the slower kinetics of the cross-linking at lower temperature at a constant UV light output.
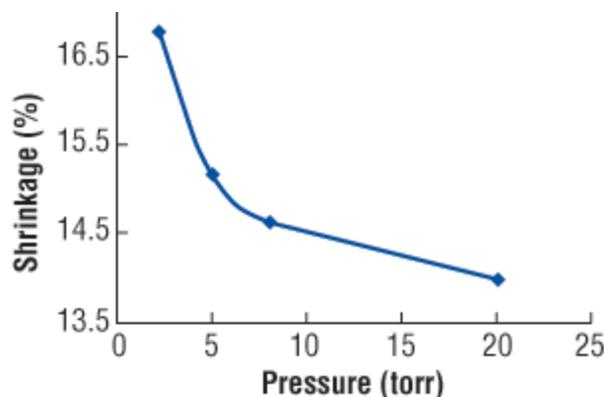

Figure 5. *Low pressure cure accelerates removal of the labile species.*
Click here to enlarge image

The cure pressure is another important process variable. The data for a CDO film at a constant cure time, temperature, and constant UV output are shown in **Fig. 5**. The removal of the labile species is measured by determining the shrinkage of the as-deposited film. The reduced shrinkage with increasing pressure suggests that lower-pressure operation accelerates the removal of the labile species.

In order to implement UV-cured CDO films in manufacturing, it is important to demonstrate repeatable performance over several thousands of wafers.

UV chamber cleaning

Because the curing of CDO films involves the removal of the organic labile species to generate porosity, these organic species deposit everywhere in the curing chamber and can block the incident UV light on the wafer over time. Therefore, in situ cleaning becomes critical for UV chambers for this application (unlike applications such as photoresist cross-linking). Because the outgassing species is predominantly organic in nature, an O-based clean is ideal for these systems so the end products, such as CO_2 and H_2, can be easily pumped away.
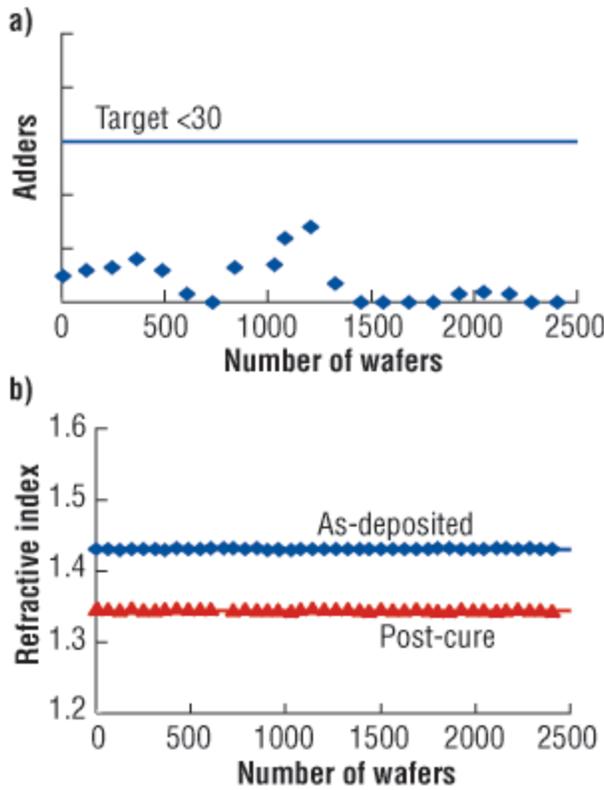
*Figure 6. UV chamber with in situ clean capability: **a**) particle performance and **b**) refractive index repeatability.*

Click here to enlarge image

The UV systems for such applications must be designed to account for in situ cleaning of the chamber. A simple approach is to keep the chamber volume as small as possible so that cleaning can be accomplished quickly and efficiently. Large-volume chambers could result in insufficient cleaning, and the performance of the chamber over time could be compromised in terms of repeatability and defects. The data in **Fig. 6a** show the particle performance in a UV chamber with clean capability over a 2500 wafer run. The film property, as characterized in terms of refractive index, is shown in **Fig. 6b**. The data were collected using ozone-based cleaning in which the ozone in the chamber dissociates into O radicals and removes the organic residue.

Conclusion

Introduction of porosity is critical to lowering k to <2.5 for CDO films. The bulk film properties such as k and elastic modulus are primarily a function of the carbon and porosity. Small pore sizes and a tight distribution are preferred to minimize integration issues. Because UV assists greater Si-O networking in the CDO films, UV-cured films result in superior mechanical properties and tighter PSD compared to a thermal-only curing. In situ cleaning of UV chambers is critical for repeatable extended performance and higher throughput of porous low-k films.

Acknowledgments

The authors would like to thank S.H. Ahn, J. Chang, N. Rajagopalan, K. Yim, Y. Zheng, K. Elsheref, D. Witty, and H. M'Saad for their support and comments. Black Diamond is a trademark of Applied Materials Inc.

References

1. B. Kastenmeier, K. Pfeifer, A. Knorr, *Semiconductor Intl.,* Vol. 27, No. 8, p. 87, 2004.
2. A. Grill, V. Patel, K.P. Rodbell, E. Huang, S. Christiansen, et al., *Proc. Mat. Res. Soc. Symp.,* Vol. 716, p. 569, 2002.
3. J.G. Ryan, *Proc. Low-*k *Dielectric Mat. Tech. Conf. SEMICON West,* p. A1, 2000.
4. K. Bochanan, *European Semiconductor,* Vol. 26, No. 1, p. 19, 2004.
5. K. Macwilliams, J. Huang, M. Schulberg, P. Van Cleemput, *Proc. IEEE Intl. Symp. on Semiconductor Manuf.,* p. 203, 2001.
6. P. Rose, E. Lopata, J. Felts, US Patent No. 6068884, 1998.
7. *Handbook of Chemistry and Physics,* ed. D.V. Lide, p. 12, 1998-1999.
8. R.J. Le Fevre, "Bond Polarizabilities and Refractions," *Adv. Org. Chem.,* Vol. 3, p. 1, 1965.
9. *Handbook of Chemistry and Physics,* ed. D.V. Lide, p. 18, 1998-1999.
10. H.J. Kim, Q. Shao, Y.-H. Kim, *Surf. Coat. Techn.,* Vol. 171, p. 39, 2003.
11. B. Xie, A.K. Muscat, *Microelectron. Eng.,* Vol. 76, p. 52, 2004.
12. J.J. Golden, C.J. Hawker, P.S. Ho, *Semiconductor Intl.*, Vol. 24, No. 5, p. 79, 2001.
13. R. Vitris, M.K. O'Neill, J.L. Vincent, A.S. Lukas, B.K. Peterson, et al., *Proc. Mat. Res. Soc. Symp.,* Vol. 766, p. 259, 2003.
14. A. Grill, D.A. Neumayer, *J. Appl. Phys.,* Vol. 94, No. 10, p. 6697, 2003.
15. L. D'Cruz, S. Ahn, Y. Zheng, J. Chang, N. Rajagopalan, et al., *MRS Spring Mtg.,* Mar. 28-April 1, 2005.

For more information, contact **SANJEEV JAIN** at *Applied Materials Inc., 3050 Bowers Ave., PO Box 58039, Santa Clara, CA 95054; e-mail sanjeev_jain@amat.com.*

VLADIMIR ZUBKOV, THOMAS NOWAK, ALEX DEMOS, JUANCARLOS ROCHA, Applied Materials Inc., Santa Clara, California

To access this Article, go to:
http://www.electroiq.com/content/eiq/en/articles/sst/print/volume-48/issue-9/features/copper-low-ik-i/porous-low-span-stylefont-style-italic-k-span-dielectrics-using-ultraviolet-curing.html