Porosity engineering for ultra-low k spin-on dielectric materials

Hanna Luusua [a,*], Heli Kekkonen[a], Jyri Paulasaari[a] , Amanda Ihalainen[a], Thomas Gädda[a], Juha Rantala[a]

[a] *PiBond Oy, Kutojantie 2B, Espoo, 02630, Finland*

Ultra-low dielectric constant (ULK) materials are attractive option for the next generation intermetallic and interlayer dielectric materials due to their significant contribution for resistive-capacitive (RC) delay decrease. A common strategy for ULK material development is to reduce the dielectric constant (κ) of the material by introducing air to the structure with porosity. Typically, ULK materials include thermally labile components "porogens" which can be removed during the material curing [1]. Challenges associated with the increasing porosity include compromised mechanical properties and higher risk for plasma-induced damage, which can be detrimental for the dielectric performance during the process integration. Often, dielectric strength is compromised as well. However, not all porosity is the same: size, connectivity and structure of the pores have huge impact on the material performance.To achieve ULK SOD material with acceptable hardness and dielectric strength, careful porosity engineering is required to form a material with controlled pore structure consisting of small, isolated and well-organized pores. For uniform pore distribution, porogens bound to the polymer matrix are preferred. We have introduced a polymer-bound porogen to an organosiloxane polymer composition and carefully characterized the material properties. In addition, we investigated if polymerization process conditions could affect the material performance. Materials were cured with combined thermal and UV curing for effective porogen removal [2].

Material characterization revealed significant differences between the different polymerization processes, even though polymers consist of the same amount of organosiloxane polymer matrix and polymer-bound porogen. "Process A" refers to our typical polymerization process and "Process B" to a new-found, optimized polymerization process. "Reference" material is used to benchmark ULK material performance compared to porogen-free SOD. Refractive index (RI) comparison shows decreased RI for both porogen containing samples, as expected when air is introduced to the material (Figure 1). Film shrinkage between soft bake and cure increases similarly (Figure 2). Dielectric properties are excellent for both Process A and B materials: low $\kappa < 2.4$ is achieved (Figure 3). In addition, breakdown voltage of both ULK materials are comparable or even increased compared to Reference, which is not typical for highly porous materials (Figure 4). Modulus and hardness of the materials were analyzed with nanoindentation. Process A material had clearly lower hardness compared to the reference (Figure 5). However, Process B material had higher hardness than process A, providing mechanical properties close to the porogen-free Reference material. Porosity analysis with variable angle spectroscopic ellipsometer (VASE) revealed major differences between the materials as well: Process B had lowest relative porosity below 2%, whereas Process A and even the Reference had relative porosity 9 and 6%, respectively (Figure 6). Therefore, Process B material possesses a rare combination of ultra-low dielectric constant, high dielectric strength and decent mechanical properties. Low RI suggests that pores have been formed into the material, but VASE method did not detect significant amount of porosity. Our hypothesis is that Process B can form isolated pores to the material, whereas process A has more connected pores. Isolated pores may not be detected with VASE, as it is based on solvent penetration to the pores, and penetration is easier for an open, connected pore network. To confirm the hypothesis, more advanced porosity analysis is required, e.g. positron annihilation lifetime spectroscopy (PALS).

To summarize, the polymerization process was found to have a dramatic effect to the performance of ULK SOD by improving mechanical properties while maintaining excellent dielectric performance. Therefore, it is a promising alternative to be the next generation interlayer or intermetal dielectric material.

References

1. D.J. Michalak *et al.*, Porosity scaling strategies for low-k films, Journal of Materials Research, **30**, 22 (2015)
2. Zenasni, Aziz *et al.* The role of ultraviolet radiation during ultralow k films curing: Strengthening mechanisms and sacrificial porogen removal, Journal of Applied Physics, **102**, 9 (2007).

[*] *corresponding author e-mail: hanna.luusua@pibond.com*

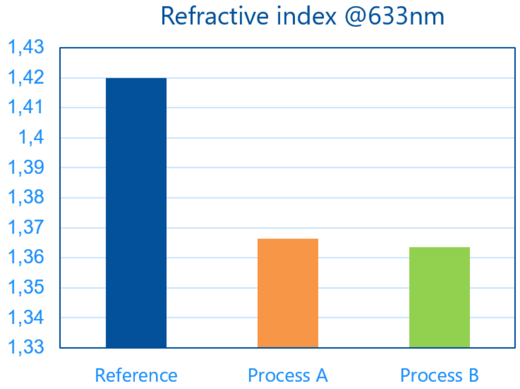

Figure 1. Refractive index comparison.

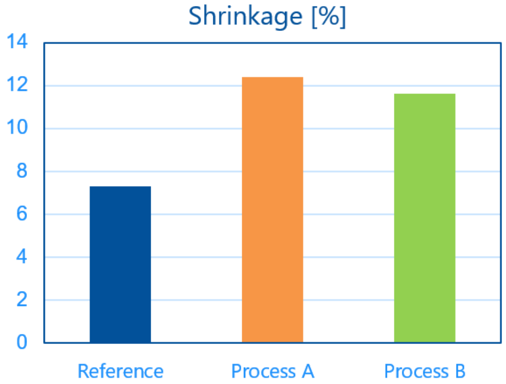

Figure 2. Shrinkage between soft bake and cure.

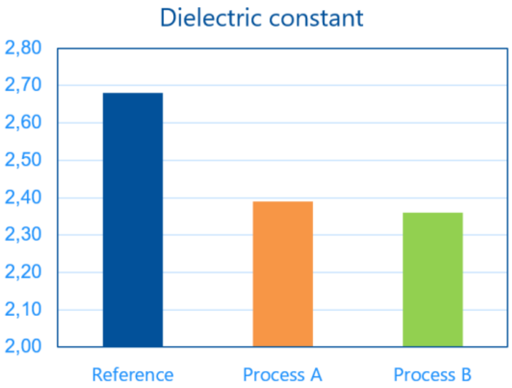

Figure 3. Dielectric constant reduction demonstration.

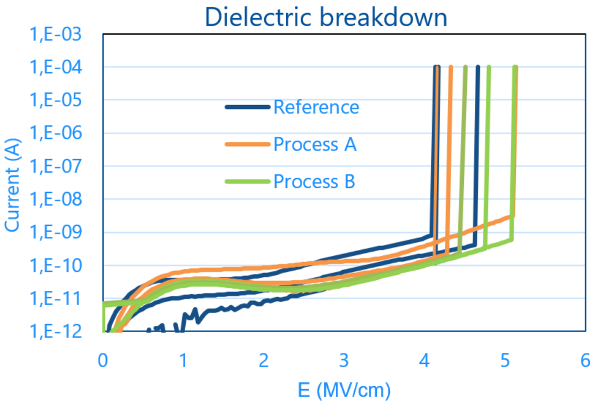

Figure 4. Current vs electrical breakdown voltage.

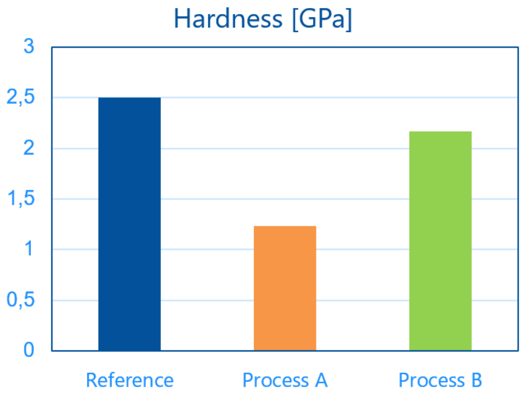

Figure 5. Hardness comparison.

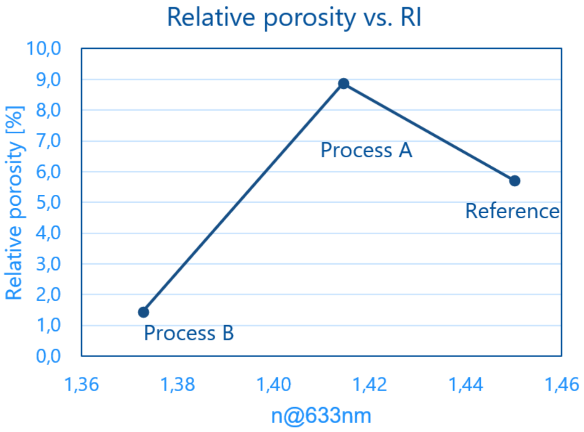

Figure 6. Relative porosity vs refractive index.