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Viewpoint Paper

Hybrid low dielectric constant thin films for microelectronics

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Abstract—The fabrication of future interconnects in integrated circuits requires insulators with decreasing dielectric constants in order to maintain or improve the electrical performance of such devices. This is achieved through the introduction of air in the form of porosity. However, such porous materials suffer from two major drawbacks: lower mechanical properties and decreasing plasma resistance. In this paper we discuss the design of novel low-k materials, the structure/porosity effect on plasma damage and emerging solutions envisioned to mitigate these issues.

Keywords: Low-k; Porosity; Mechanical properties; Plasma damage

1. Introduction

Historically, the development of new, low dielectric constant materials has been driven by the semiconductor industry in order to keep improving microprocessor performance from one generation to the next [1–3]. Consequently, the approach of introducing porosity in order to decrease the dielectric constant, k, was adopted because it provided the only pathway for generational extendibility.

While this strategy was fully embraced, it was also recognized early on that the convergence of increasing porosity and decreasing feature sizes would lead to unavoidable integration issues in the ultralow-k (ULK) regime, $k \leqslant 2.7$ [4,5]. As a result, the introduction of new and lower-k dielectric materials at a given technology node has been slow. As shown in Figure 1, the only beneficial result of increasing the porosity is realized in lowering of the dielectric constant. All other properties are impacted in a negative way (see below).

From a mechanical point of view, the decrease in both density and network-connectivity strongly impacts the stiffness, fracture resistance and interfacial adhesion [6–12]. Nevertheless, combining experimental results and modeling studies, today we have a better understanding of the influence of network connectivity on mechanical properties.

Regarding ULK integration, the increase in accessible surface area of the porous network presented concerns with respect to dry and wet processes [5,13,14]. ULK materials with excellent electrical properties measured on blanket films do not automatically translate into electrically reliable structures after integration. As a result, the selection of ULK materials cannot be based solely on blanket film properties. Hence, sensitivity to integration processes such as etch plasmas, plasma-enhanced chemical vapor deposition (PECVD), hardmask deposition and chemical metal polishing (CMP) has to be evaluated [4,15].

For the materials scientist, the main challenges today are to design ULK materials with low-k dielectric constants while maintaining high mechanical properties and sufficient resistance to plasma damage. At the same time, process-engineers need to audition alternative, less damaging integration schemes, such as post-porosity plasma protection [16–18] or subtractive metal etch as exercised for aluminum metallization.

2. ULK mechanical properties

Historically, the push to lower dielectric constants was initially achieved by replacing Si–O–Si bonds with less polarizable pendant groups [3]. For example, materials with $k = 2.7$ could be readily prepared by the incorporation of carbon residues in the form of pendant methyl groups [3,19–21]. The presence of $Si–CH_3$ and $–Si(CH_3)_2$ moieties has a tremendous impact on the mechanical properties [7,10,22]. For example, the

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	POROSITY	DIELECTRIC CONSTANT	MECHANICAL PROPERTIES	INTEGRATABILITY
TREND	↗	↘	↘	↘
IMPACT	-	POSITIVE	NEGATIVE	NEGATIVE

Figure 1. Impact of porosity on ULK properties and integration processability.

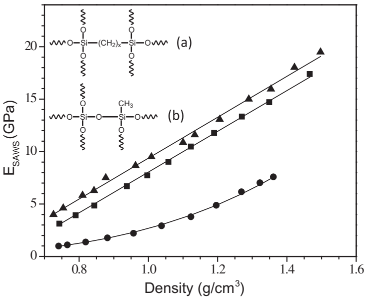

Figure 2. Young's modulus as a function of porosity. (a) Bridged organosilicates with x = 1 (▲) and x = 2 (■); (b) traditional organosilicates (●).

Young's modulus decreases by roughly one order of magnitude as compared to SiO_2 (E = 72 GPa). This clearly demonstrates the effect of network connectivity on mechanical properties. Nevertheless, mechanically reliable structures based on these dielectric materials could still be built [23,24]. As the dielectric constant was further decreased to k = 2.4, an additional penalty on the mechanical properties due to the introduction of porosity was observed. This led to a high percentage of device failures during chip packaging, suggesting that the industry was approaching a lower limit with respect to ULK mechanical requirements [25–27]. This situation is a direct consequence of the Young's modulus power law decay as a function of porosity, as shown in part in Figure 2.

The most expedient and easiest solution was the post-modification of existing ULK films using a thermal ultraviolet (UV) treatment. The impact of the thermal UV treatment is such that the Si–O–Si substructures are redistributed to form a more connected network without significantly increasing the dielectric constant [28–33]. Although thermal UV treatment could improve the mechanical properties by 20–30%, porogen residues still exist and impact the electrical properties [34]. Fortunately, a new curing scheme where the porogen is removed prior to UV treatment prevents the formation of porogen residues. As a result, better electrical and mechanical properties can be obtained [35,36]. Nevertheless, material scientists have continued to search for mechanically superior dielectric insulators by auditioning a broad range of precursors [3]. Embracing the concept of network connectivity, our group developed the strategy of incorporating carbon-bridging units into low dielectric constant spin-on materials using solution-based chemistry [37–41]. The use of carbon-bridging units leads to an increase in the Young's modulus by a factor of 3–4× as compared to other dielectric constant organosilicate materials with pendant carbon moieties at an equivalent dielectric constant. Moreover, a change in the modulus behavior as a function of porosity was observed [37,38]. As shown in Figure 2, unlike the power law decay observed for non-carbon bridged silicates, organosilicates comprising carbon-bridged units exhibit a linear decay in modulus with increasing porosity. As a consequence, lower k values at significantly higher modulus values are accessible in the case of the latter. Interestingly, the effect of network connectivity onto low-k mechanical properties was also confirmed by molecular dynamics modeling [10]. In this work, the impact of replacing of one Si–O bond with an Si–CH_3 group on both the Young's modulus and the fracture energy was investigated and a significant decrease in both above properties was demonstrated. Based on these experimental and modeling data, the semiconductor industry has redesigned PECVD-based ULK materials [42]. For future technology nodes, the majority of PECVD precursors will most likely be based on carbon-bridged silicon structures. Typically, such precursors are used in conjunction with a porogen and/or other non-carbon bridged molecules. As opposed to the bond-breaking/bond-forming mechanism of PECVD, the non-destructive nature of sol–gel chemistry approaches allows the synthesis of ULK materials not only with superior network connectivity but also with ordered porosity [43–46]. Although spin-on derived ULKs exhibit better mechanical properties at comparable dielectric constants and carbon contents, they are still only considered as back-up options. Irrespective of the mode of deposition, for $k \leqslant 2.55$, the introduction of carbon-bridging units is the only strategy that will provide sufficient back-end-of-the-line (BEOL) mechanical stability without requiring alternative engineering solutions.

Today, the ULK structure–mechanical properties relationship is well understood and has been used to guide the design of new and improved ULK materials. While this guarantees BEOL mechanical integrity, it does not address the electrical reliability and performance. The challenge for the semiconductor industry is to maintain the ULK pristine electrical properties throughout the integration process.

3. Plasma damage

While the concept of porosity has been successfully employed to generate materials with dielectric constants

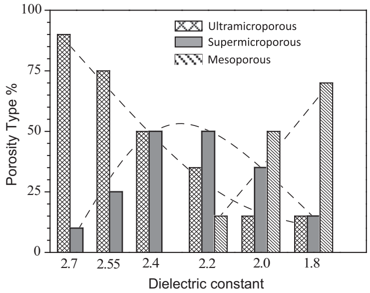

Figure 3. Pore size distribution as a function of porosity/dielectric constant. Adapted with permission from T.J. Frot et al., Adv. Funct. Mater. 22 (14) (2012) 3043.