Recent Progress in High-Performance Intrinsic Ultralow-*k* Polyimide Films

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The search for new low-*k* dielectric materials has always been dictated by industrial needs, resulting in a strong connection between fundamental research and technology. With the development of flexible ultra-large-scale integration (flexible ULSI) in the microelectronics industry, an urgent need for high-performance flexible low- and ultralow-*k* dielectric materials (low-*k*: $k \leq 2.5$; ultra-low-*k*: $k \leq 2.0$) has arisen because such dielectrics would reduce the capacitance between the metal interconnects, the resistance-capacitance delay, the line-to-line crosstalk noise, and the power dissipation. More importantly, such dielectrics could be used in roll-to-roll processing to achieve large-scale production, improve the productive efficiency, and minimize the processing costs. So far, the most important method to obtain ultralow-*k* materials is by incorporating nanosized air voids (with a *k* value of approximately 1) into low-*k* matrices. The *k* value of these porous materials can be less than 1.5. However, the method itself is complicated, difficult to control, and expensive. Moreover, the pore structure, size and distribution will greatly affect the homogeneity of the materials, which makes this technique difficult to be used in large-area production. The porosity tends to dramatically reduce the mechanical strength and gas tightness of the materials, thereby making them too fragile for practical use. Thus the acquisition of high-performance intrinsic ultralow-k materials remains one of the most important bottlenecks restricting the leapfrog development of the whole microelectronics industry. .

Here we introduce the recent advance in the research of high-performance intrinsic ultralow-*k* polyimide films in our laboratory [1-8], by considering the polarizability and the free-volume theory from the molecular level (**Figure 1-4**). The intrinsic ultralow-*k* property was obtained by the molecular design and the control of the steric and aggregation structure of the polymers, which led to the formation of uniform distributed free-volume holes with sizes at the Ångström scale, measured by positron annihilation lifetime spectroscopy (PALS). Such a strategy is beneficial for lowering the *k* value and simultaneously maintaining the overall properties of polyimide, such as excellent mechanical properties, thermal properties, and good processing properties.

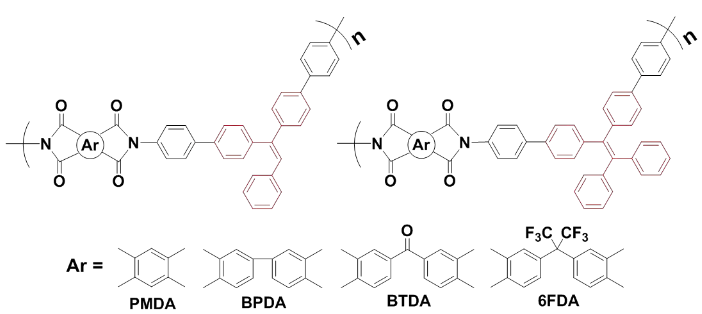

Figure 1 Intrinsic low-*k* polyimide films containing triphenylethylene and tetraphenylethylene moieties.

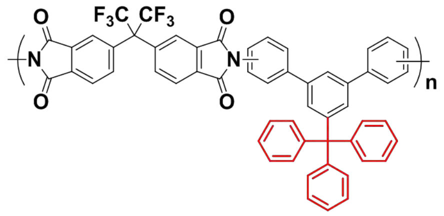

Figure 2 Intrinsic low-*k* polyimide films containing triphenylmethane moieties.

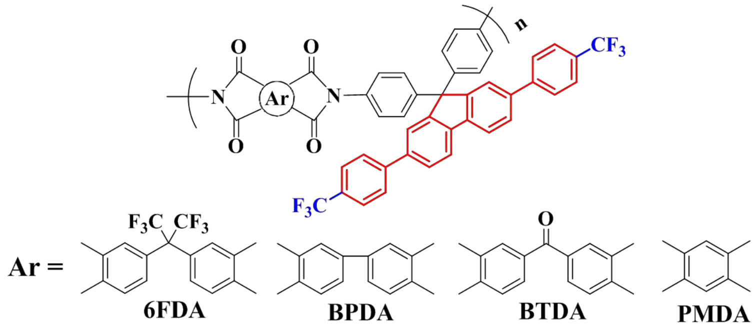

Figure 3 Intrinsic ultralow-*k* polyimide films containing fluorene moieties.

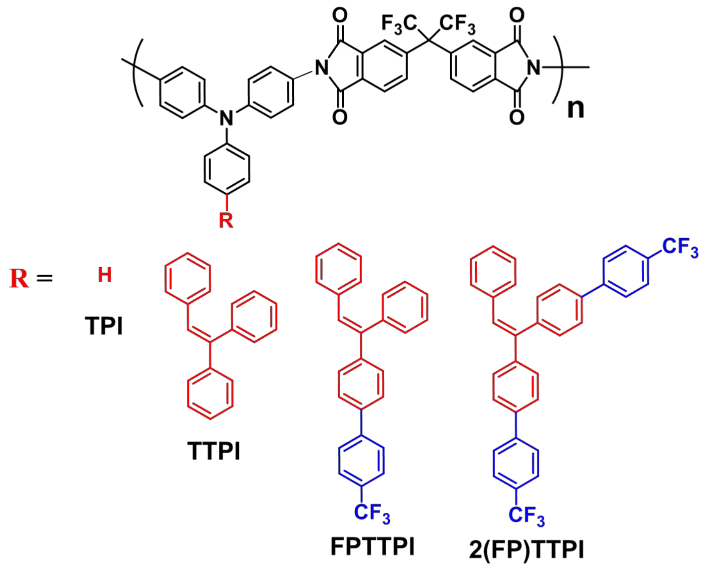

Figure 4 Intrinsic ultralow-*k* polyimide films containing triphenylethylene and triphenylamine moieties.

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