Nanoporous Low-? Polyimide Films Prepared from Poly(acrylic acid)- and Poly(ethylene glycol)-*grafted*-Poly(amic acid) Copolymers

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The demand for faster signal speed and higher packing densities in integrated circuits has motivated the development of low capacitance dielectrics.[1] The use of interlayer materials with very low dielectric parameters can greatly reduce the RC time delays, cross-talks, and power dissipation in the new generation of microelectronic devices. In addition to exhibiting low dielectric constants, the next generation of interlayer dielectrics for advanced semiconductor device applications must also satisfy a variety of requirements, such as good thermal stability, low moisture absorption, good adhesion to silicon and metal substrates, and chemical inertness. Polyimides (PIs) have been widely used as dielectric and packaging materials in the microelectronics industry because of their good mechanical, thermal and dielectric properties.[2,3] However, with the dielectric constants (?) of about 3.1-3.5, the conventional PIs are insufficient in meeting the requirement of ? < 2.5 for the next decade.[4] One method to reduce the dielectric constant of PIs is to incorporate pedant perfluoroalkyl groups. The modified PIs have dielectric constants in the order of 2.6-3.0.[5] This approach, however, is limited by high cost and synthetic difficulties. In recent years, nanoporous materials have become an important class of dielectric materials. The incorporation of air , which has a dielectric constant of about 1, can greatly reduce the dielectric constant of the resulting nanoporous structure/material.[6,7]

In the present work, a new method for preparing PI nanoporous films with pore size in the nanometer range is demonstrated. Initially, molecular modification of the ozone-pretreated poly(amic acid) (PAA) via thermally-induced graft copolymerization with either acrylic acid (AAc) or poly(ethylene glycol) (PEG) monomethacrylate in *N*-methyl-2-pyrrolidone (NMP) solution was carried out. The resulting PAA copolymers with grafted AAc and PEG side chains (the PAAc-g-PAA and PEG-g-PAA copolymers, respectively) were characterized by Fourier transform infrared (FTIR) spectroscopy, elemental analysis, X-ray photoelectron spectroscopy (XPS), thermogravimetric (TG) analysis and differential scanning calorimetry (DSC). The nanoporous PIs were prepared from the graft copolymers with the main phase comprising of PI and the minor phase consisting of the thermally labile graft chains (AAc or PEG polymer). Films of the copolymers were cast on glass plates and then heated initially to remove the solvent and to initiate the imidization process. The copolymer films were subjected to a second thermal treatment at a higher temperature, at which the labile graft chains were selectively decomposed, leaving behind pores with size in the nanometer range in the PI matrix. The nanoporous PI films were characterized by density measurements, scanning electron microscopy (SEM), transmission electron microscopy (TEM), mechanical property measurements and dielectric constant measurements. The densities of the nanoporous films were 3-15% lower than the pristine polyimide films. SEM and TEM results showed that the pore size was in the range of 30-100 nm. Finally, the nanoporous PI films with good mechanical properties have dielectric constants in the order of 2.1.

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