JOURNAL OF MATERIALS SCIENCE 27 (1992) 3297–3300

Polyimide-silica microcomposite films

E. BREVAL, M. L. MULVIHILL, J. P. DOUGHERTY, R. E. NEWNHAM
Center for Dielectric Studies, Materials Research Laboratory, Pennsylvania State University, University Park, PA 16802, USA

Planarizing films of fine-grained silica embedded in polyimide have been prepared by a spin-coating technique and their structure has been investigated by optical and electron microscopy. The films were found to be diphasic. A silica content near 9 vol % yields a well mixed silica/polyimide composite which is homogeneous down to nanometre scale and has good planarization characteristics. Films with contents of 3 and 6 vol % silica have rough surfaces and exhibit two forms of segregation. In the 3% case, elongated inclusions of such silica/polyimide material appear at ~ 100-μm islands in a pure polyimide matrix. In the 6% case, the pure polyimide appears as ~ 100-μm elongated lakes surrounded by silica/polyimide material.

1. Introduction

Conventional ceramic substrates are unsuitable for fine-line metallization because of surface roughness. In this study, silica/polymer composites were spun-on to coat conventional 96% Al_2O_3 substrates to planarize the surface. The polymer, a fluorinated polyimide [1], was chosen for its low dielectric constant, low dielectric loss and excellent planarization characteristics (M. L. Mulvihill and co-workers, personal communication). A nanoscale silica particle-filled polyimide composite [2] was chosen, as silica has a low thermal expansion which can lower the thermal expansion stresses between the composite substrate and the surface-mounted components.

The silica/polymer composite films exhibited different distributions of silica-rich polyimide and pure polymer for different compositions. The purpose of this paper is to examine these composition-related patterns from the milimetre scale down to the nanometre scale, in order to obtain an understanding of a mechanism of formation, and to tailor new silica/polyimide composites with useful properties.

2. Experimental procedure

Different amounts (corresponding to 0, 3, 6 and 9 vol % silica in the final product) of fumed silica (R 974 from Degussa Co. Teterboro, New Jersey) were dispersed in the organic solvent Thermid T-3 (National Starch and Chemical Corporation, Bridgewater, New Jersey) thinner consisting mainly of 1-methyl 2-pyrrolidinone with small amounts of cyclopentanone and 1-methoxy 2-propanole. Monomer polyimide, EL-5512 (National Starch) which is based on a fluorinated oligomer, was added and mixed with a magnetic stirrer at room temperature for 12 h. A spin coating was performed on a plate spinning for 40 s at 2000 r.p.m. The film was then gel-like and heat curing was carried out using a ramp of 5 °C min^{-1}, with holds at 150 °C for 60 min, 230 °C for 90 min, and 300 °C for 120 min, followed by cooling at 5 °C min^{-1}. The surface films were deposited on alumina substrates and Ton glass plates the film could easily be peeled off the glass plates after steaming over a boiling water bath to give a free standing film.

Scanning electron microscopy (SEM) together with energy-dispersive spectroscopy (EDS) was carried out on fracture surfaces of the films deposited on the alumina substrate. It revealed that the higher regions consisted of a submicrometre size grainy substance giving a large Si signal, and that the lower regions appeared more homogeneous with no Si signal.

Transmission electron microscopy (TEM) was carried out on specimens prepared in three ways. One was a dispersion of fine material in isopropanole, a drop of which was transferred to a carbon coated TEM grid. Specimens of this type were prepared from aerosil and from crushed fragments of the free films. The second type of specimens was a cross-section of the free film embedded in a polymer yielding a 60-nm-thick specimen, and the third was prepared by ion-beam thinning. All TEM specimens were coated very lightly with carbon before examination. A Philips EM 420 transmission electron microscope with an acceleration voltage of 120 kV was used for the TEM study.

3. Results

The free films were studied on the milimetre and micrometre scales using an optical microscope (OM) with polarized transmitted light (POL) in order to study the distribution and crystallinity on the micrometre scale. A differential interference contrast (DIF) reflected-light microscope was used to detect differences in height on the film surface. In this way a three-dimensional image of the composites was obtained.

The optical microscope studies showed that the specimens with 0 and 9% silica appeared homogeneous. DIF microscopy showed that the specimen containing 3% silica possessed elongated higher regions

0022-2461 © *1992 Chapman & Hall*

(islands) of 20–100 µm in width, distributed evenly over the surface about 100 µm apart. The specimen containing 6% silica possessed lower regions (lakes) of approximately the same shape, size and distribution. Optical microscopy using transmitted light (see Fig. 1) successfully imaged the islands in the specimen containing 3% silica and the regions between the lakes in the specimen containing 6% silica. These regions refracted and reflected the light more efficiently than the polyimide regions in the films. Sketches of types of microstructures are shown in Fig. 2. No birefringence indicative of non-cubic crystalline phases was observed in any of the specimens.

The TEM bright-field image of the silica fume (Fig. 3) showed that the particles appear to be almost spherical. Even though the specification indicates 16 nm size there is, in fact, a size distribution ranging from ~ 1 to ~ 50 nm. The 100% polyimide film was difficult to crush and only the edges were electron transparent for study in the TEM. These regions were completely homogeneous and amorphous, giving very diffuse reflections of ~ 2.1 and 1.2 A.

During ion-beam thinning, it was observed that the polyimide film partially melted. Therefore an ion-beam-thinned specimen of the film without silica could not be obtained. Melting occurred to a lesser

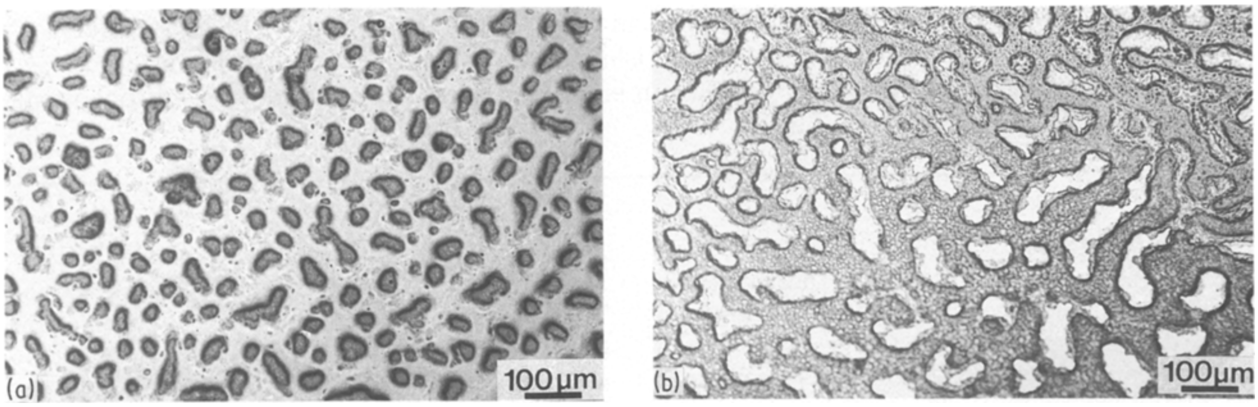

Figure 1 Transmitted light microscopy of films with (a) 3% silica showing islands of strongly refracting/reflecting silica rich material (appear dark) in weakly refracting/reflecting polyimide (appear light); (b) 6% silica showing polyimide inclusions (lakes) in the silica-rich material.

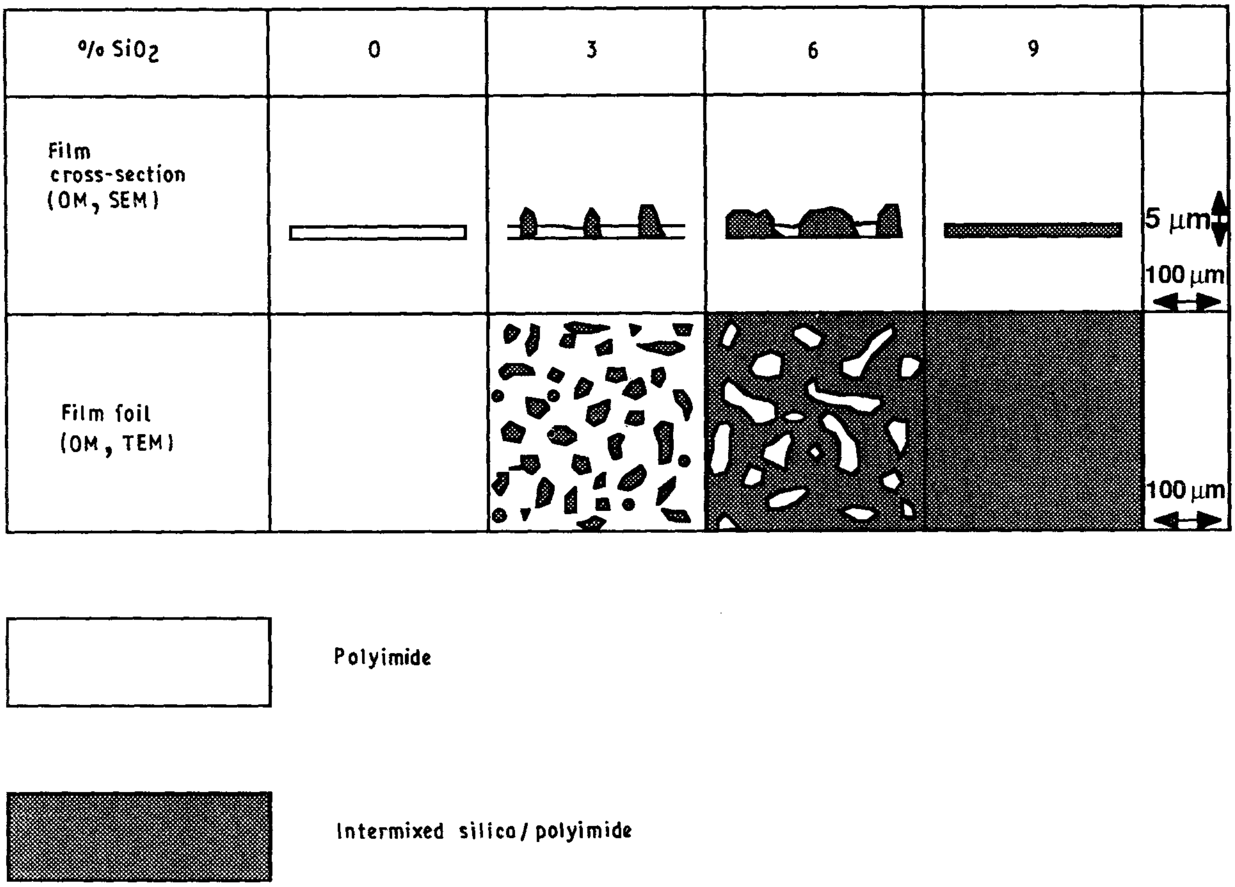

Figure 2 Structure of the four films investigated in this study. Cross sections were studied on fractured film pieces by optical microscopy and SEM; foil features were studied viewing films perpendicular to foil by optical microscopy and TEM.

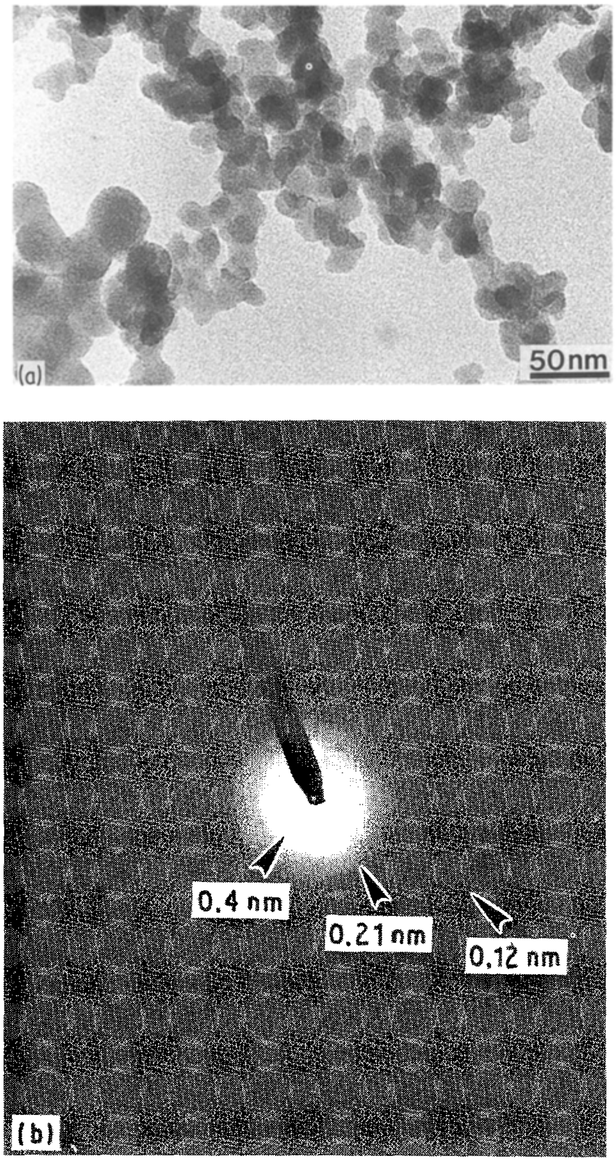

Figure 3 (a) Aerosil (fumed silica) used for the sol–gel process. TEM, bright-field image. (b) Selected area electron-diffraction pattern shows diffuse rings at ~ 4, 2.1 and 1.2 A.

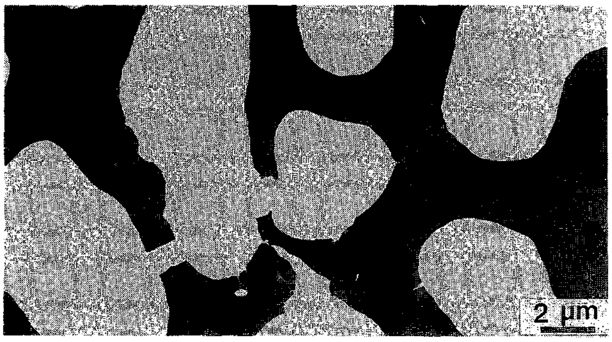

Figure 4 Low-magnification TEM bright-field image of ion-beam-thinned film with 6% silica, showing the disappearance of polyimide during ion-beam thinning.

degree in specimens containing silica, which made it possible to prepare reasonably good ion-beam-thinned specimens of the films with 3 and 6% silica, which contained silica-rich regions and pure polyimide regions. Low-magnification images obtained from these specimens (Fig. 4) show how the polyimide disappeared during ion-beam thinning, leaving the silica-rich regions. The silica-rich regions in the specimens containing 3, 6 and 9% silica all have the same appearance in the cross-sectioned specimens. They give diffuse electron diffraction reflections at ~ 2.1 and 1.2 A, which is typical for many amorphous materials. However, there is also a diffuse reflection near 4 A corresponding to the strong quartz peaks at 4.26 and 3.343 A. The TEM bright-field image in Fig. 5 shows the position of the original silica spheres uniformly distributed in the polyimide material.

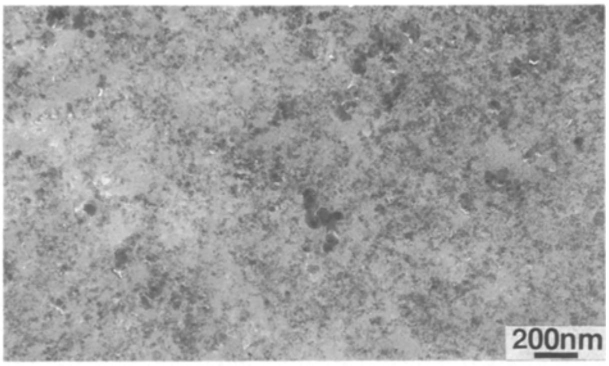

Figure 5 TEM bright-field image of cross-sectioned film with 9% silica. This appearance of silica spheres (arrowed) in the polyimide is typical for the silica-rich material in all specimens.

4. Discussion

Structural investigations showed that specimens containing 0 and 9% silica were homogeneous on the mm and µm level. The optical studies showed that, in specimens containing 3 and 6% silica, the regions of silica-rich material in polyimide material refract the light better because it is much thicker than the polyimide, even though the refractive index of crystalline SiO_2 is only 1.54 compared with 1.82 for polyimide [1].

Another explanation of the higher contrast of the silica-rich regions is the reflection of light from clusters of silica spheres. The SEM studies confirmed the identification and distribution of the silica-rich and pure polyimide regions.

The TEM studies of the silica-rich regions showed uniformly distributed nanometre-size silica spheres from the aerosil in the polyimide matrix, demonstrating the successful fabrication of a silica-filled polyimide composite using the spinning technique.

The results indicate that a silica content near 9% yields a well mixed silica/polyimide composite which is homogeneous down to the nanometre scale. Materials with contents of 3 and 6% silica exhibit two forms of segregation. In the 3% case, inclusions of such silica/polyimide material appear as islands in a pure polyimide matrix. In the 6% case, the pure polyimide appears as lakes surrounded by silica/polyimide material.

This phenomenon can be explained in different ways. One approach is the lack of coupling agents to enhance the interfacial bonding [2]. As no destabilizer has been added to the fumed silica it has a tendency to aggregate. Presumably, the uniform distribution in such aggregates exists in a material containing around 9% silica, which makes it homogeneous on the milimetre and micrometre scale and well dispersed on the nanometre scale. A possible explanation is the gel-phase separation shown in the TEM by Low and McPherson [3] explained with two theoretical concepts. One is attributed to the unfavourable free energy of mixing two phases, sometimes referred to as spinodal decomposition. In our case, the unmixing involves a silica-rich phase and the polyimide phase. In a three-dimensional system the two phases of the decomposed spinodal are both interconnected [4], but in our case this is only true for the polyimide phase in the 3% silica specimen and for the silica phase in the 6% silica specimen. However, as our film is only a few micrometres thick, the observed segregation may still be attributed to spinodal decomposition. The other concept described by Low and McPherson [3] is the inherent polymerization and condensation of a polymer species for certain compositions in a gel, giving rise to the formation of polymer-rich (polyimide) and solvent-rich (silica-rich) phases.

From a practical point of view, the results show that a silica/polyimide composite containing 9% silica is an excellent candidate for planarizing substrates for fine-line metallization. The possibilities exist of combining the compressive strength (~ 1 MPa), the relatively high hardness (~ 4 GPa), and high elastic modulus (~ 73 GPa) of silica glass [5] with the polyimide's low elastic modulus (~ 3 GPa) and high tenacity (~ 6% elongation) [1].

5. Conclusions

Films consisting of a silica/polyimide microcomposite have been prepared of mixtures of polyimide and nanometre-size silica spheres using a spin-coating technique. A silica content near 9% yields a silica/polyimide composite which is mixed intimately with the silica particles and which has a plane surface. Films with contents of 3 and 6% silica yield rough surfaces and exhibit two forms of segregation. In the 3% case, elongated inclusions of such silica/polyimide material appear as ~ 100-μm islands in a pure polyimide matrix. In the 6% case, the pure polyimide appears as elongated ~ 100-μm lakes surrounded by silica/polyimide material.

Acknowledgements

The authors are grateful for useful discussions with A. Das. The work was supported by the Alcoa Technological Center, Pittsburgh, PA.

References

1. R. D. ROSSI and P. D. MACHIESKY, *Solid State Technol.* **31**(2) (1990) S1–S4.
2. J. E. THEBERGE, *Polym. Plast. Technol. Engng* **16** (1981) 41.
3. I. M. LOW and R. McPHERSON, *J. Mater. Sci.* **32** (1988) 4141.
4. L. VAN VLACK, "Materials Science for Engineers" (Addison-Wesley, Reading, Massachussetts, 1971) p. 390.
5. D. C. BOYD and D. A. THOMPSON, in "Kirk-Othmer Encyclopedia of Chemical Technology" Vol. 11, 3rd edn, (Wiley, New York 1980) p. 826.

Received 4 April
and accepted 30 July 1991