

this, we should be able to identify novel approaches to manipulate the micro/nanostructure and the macroscopic properties of these materials.

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Layered Silicates/Fluorinated Polyimide Nanocomposites for Advanced Dielectric Materials Applications

By Liang-You Jiang, Chyi-Ming Leu, and Kung-Hwa Wei*

Layered silicates/polyimide nanocomposites have attracted a great deal of research interest recently owing to substantial improvements over their pristine state in thermal, mechanical, and gas barrier properties by incorporating only few (by weight percent) layered silicates, dispersed on the nanometer scale.^[1–10] However, no study has been reported on the electrical properties of these nanocomposites. In this communication, we report that layered silicates/polyimide nanocomposites are suitable as advanced dielectric materials for

microelectronics applications since these nanocomposites display much lower water absorption, substantially lower leakage-current density, and a lower dielectric constant and thermal expansion coefficient than that of pristine polyimide.

Typically, polyimide is used for interlayer dielectrics^[11–14] in printed circuit boards and multichip modules for microelectronic applications. During operation, the absorption of water in the dielectric material of the device can lead to an increase in dielectric permittivity and an enhancement in the mobility of ionic impurities. This would reduce the electrical resistivity^[15–17] of the dielectrics and cause a degradation in the reliability of the device. The moisture barrier properties of dielectrics are therefore critical to the durability of the device. Another important requirement of the interlayer dielectrics is that their thermal expansion coefficients have to be close to that of the neighboring metal or ceramic layers, for instance. Large differences in the thermal expansion coefficients between the dielectric and the neighboring conducting layers can cause undesired stress, which in turn results in a failure in the interfacial adhesion of the device.^[18] In this paper, the mechanical, thermal expansion, moisture barrier, and electrical resistivity properties of layered silicates/polyimide nanocomposites are investigated for assessing these nanocomposites as advanced dielectric materials for microelectronic applications.

Fluorinated polyimide (6FDA-ODA) was synthesized by 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA) and 4,4'-oxydianiline (ODA) in the present study. Synthetic mica (DMA-350) supplied by Topy Industries, Japan, containing layered silicates with a chemical composition of NaMg_{2.5}Si₄O₁₀F₂ was used in this study. The chemical structure of the mica is presented in Figure 1a. In order to make layered silicates miscible with organic polymers, the layered silicates must become partially organophilic through an ion-exchange step, where the sodium ion in the layer gallery was replaced with an organic molecule containing an ammonium ion. This small organic molecule is termed the swelling agent. The swelling agent used in this study is 4-(4-1,1-di[4-(4-aminophenoxy)phenoxy]phenyl)phenylmethane.

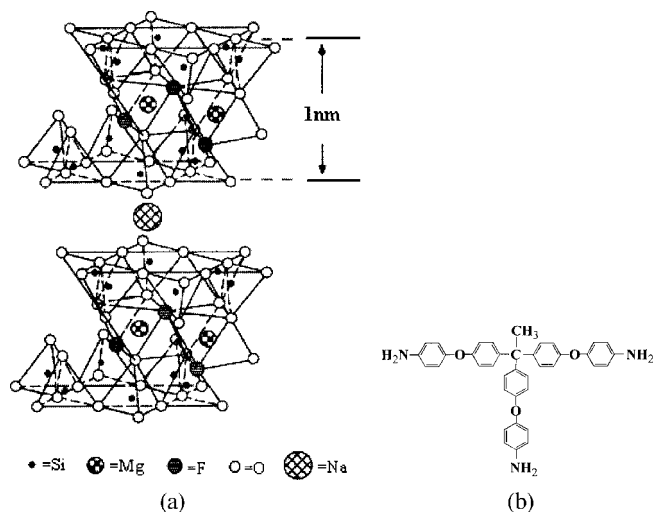


Fig. 1. The chemical structure of synthetic mica (a) and synthesized swelling agent (b).

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nyl]ethylphenoxy)aniline (3NH_2), which is synthesized in our laboratory,^[8] and its chemical structure is shown in Figure 1b. The swelling agent was protonated by hydrochloric acid prior to intercalation. The detailed procedure for preparing organic-modified mica and the synthesis of 6FDA-ODA and 3NH_2 -silicates/6FDA-ODA have been described elsewhere.^[6–8] The X-ray diffraction curves of 3NH_2 -silicates and 3NH_2 -silicates/6FDA-ODA films are shown in Figure 2. No X-ray diffraction peaks at $2\theta = 2\text{--}10^\circ$ appear in the 3NH_2 -silicates/6FDA-ODA films of various compositions, indicating that either the d -spacings of the intercalated 3NH_2 -silicate layers are larger than 4 nm or they are exfoliated in 6FDA-ODA.

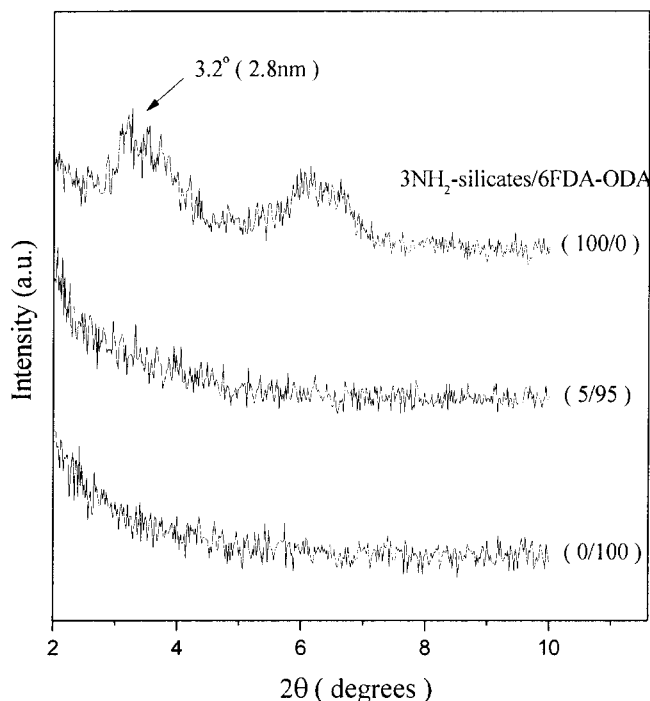


Fig. 2. The X-ray diffraction curves of 3NH_2 -silicates/6FDA-ODA films at different compositions.

The evolution of water absorption in the 3NH_2 -silicates/6FDA-ODA nanocomposite films under the ambient condition of 90% relative humidity (RH) and 40°C are shown in Figure 3. In Figure 3, for the pristine 6FDA-ODA film, the amount of absorbed water is 0.27% and 0.43% after remaining under ambient conditions for 10 and 20 h, respectively, and levels off at 0.55% after 40 h. In the case of 6FDA-ODA films containing 3 wt.-% 3NH_2 -silicates, the amount of absorbed water was 0.11% after 10 h, which was 59% lower than that of the pristine 6FDA-ODA. For 3 wt.-% 3NH_2 -silicates in 6FDA-ODA, the saturated amount of absorbed water is 0.23%, which is 58% lower than that of the pristine 6FDA-ODA. The saturation in water absorption of 3NH_2 -silicates/6FDA-ODA nanocomposite films indicated that a ther-

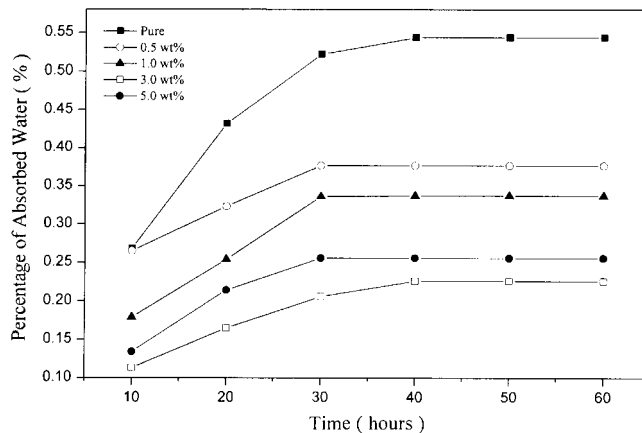


Fig. 3. The evolution of water absorption of 3NH_2 -silicates/6FDA-ODA nanocomposites at different compositions.

modynamic equilibrium has been reached after 40 h. The phenomenon that the water absorption of 6FDA-ODA reduced dramatically in the presence of silicates therefore is not a result of a diffusion-controlled behavior but rather has to do with the property of the polyimide in the intercalary of the layered silicates. Although some water molecules can bind to the dioctahedral cavities on the basal surface through physical adsorption, the layered silicates are impermeable to water molecules because of its high density ($2.8\text{--}3.1\text{ g/cm}^3$).^[12,19] The amount of silicates actually present in 6FDA-ODA film is rather small (at most 2.5 vol.-%) and can not account for the more than 50% reduction in water absorption. The only plausible explanation is that the 6FDA-ODA in the intercalary of the layered silicates absorbed very little water, which could be manifested by the model in Figure 4. Figure 4a shows the water-absorption by neat polyimide, and in Figure 4b, the aspect ratio of layered silicates is about 1000 to 1. Consequently, water molecules have to go a long way around the edges of the silicates to enter into the intercalary. However, the silicates are already partially hydrophobic after modification by swelling agents, and therefore it is rather difficult for water molecules to diffuse into the polyimide between silicates. Consequently, polyimide intercalated in layered silicates absorbed almost no water. The amount of water absorbed in equilibrium in the nanocomposites does not decrease monotonically with the increasing amount of silicates and attains a

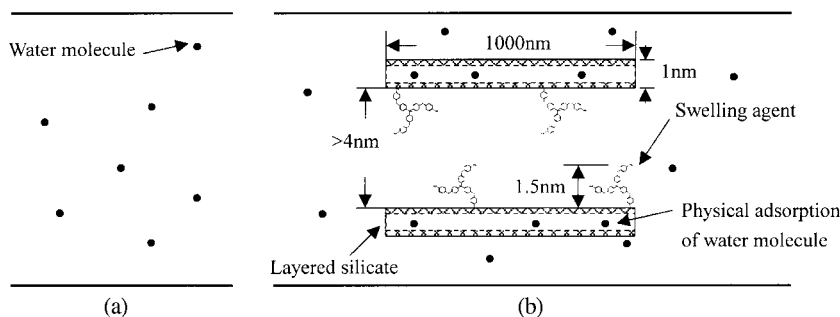


Fig. 4. The schematics of the water-absorption retardation of the layered silicates in silicates/polyimide nanocomposites: a) the neat 6FDA-ODA film, and b) the 3NH_2 -silicates/6FDA-ODA nanocomposite film.

minimum value at 3 wt.-% silicate content. This behavior can be explained by the fact that the amount of water molecules bound to the basal surfaces increases as the amount of silicates increases. Additionally, the dispersion of silicates in 6FDA-ODA became more aggregated, which reduces the amount of 6FDA-ODA intercalated in layered silicates, when the silicate content increases.

The evolution of the leakage-current density of 3NH₂-silicates/6FDA-ODA nanocomposites at 40 °C and under 90 % RH are given in Table 1. Table 1 shows that the leakage-current densities of 3NH₂-silicates/6FDA-ODA nanocomposites

Table 1. The evolution of the leakage-current density and the dielectric constant of 3NH₂-silicates/6FDA-ODA nanocomposites at different compositions at 40 °C and 90 % RH.

Contents of 3NH ₂ -silicates [wt.-%]	Leakage-current density [pA mm ⁻²] (at 3.3 V μm ⁻¹)			Dielectric constant (at 1 MHz)		
	0 h [a]	10 h	20 h	0 h [a]	10 h	20 h
0	3.5 ± 0.1	22.0 ± 2.4	102.1 ± 11.6	2.68 ± 0.03	3.15 ± 0.04	3.53 ± 0.07
0.5	3.7 ± 0.1	18.9 ± 1.4	45.8 ± 1.7	2.69 ± 0.05	3.12 ± 0.04	3.33 ± 0.08
1.0	3.8 ± 0.1	10.5 ± 0.5	30.4 ± 1.7	2.74 ± 0.06	3.05 ± 0.03	3.18 ± 0.06
3.0	4.1 ± 0.1	8.8 ± 0.5	22.9 ± 0.8	2.83 ± 0.07	3.06 ± 0.04	3.20 ± 0.02
5.0	4.9 ± 0.1	16.6 ± 0.4	42.6 ± 2.2	3.07 ± 0.05	3.25 ± 0.05	3.65 ± 0.07

[a] 0 h indicates just after coming out of the vacuum oven.

just after coming out of the vacuum oven (0 h) increase slightly with the amount of layered silicates due to some residual intercalary ions such as Na⁺ and H⁺.^[19–22] However, the leakage-current density increased dramatically with exposure time, particularly for the pristine fluorinated polyimide. It is well known that the electrical resistivity of polyimide decreases with an increasing amount of absorbed water.^[15–17] The leakage-current density of the pristine 6FDA-ODA increased dramatically with exposure time under ambient conditions. However, the increase in the leakage-current density of 3NH₂-silicates/6FDA-ODA nanocomposites with exposure time is sharply retarded. For example, the leakage-current density of 6FDA-ODA after being treated under ambient conditions for 20 h is about 29 times that of pristine 6FDA-ODA, but for 6FDA-ODA containing 3 wt.-% 3NH₂-silicates, there is only a 5.6-fold increase. Table 1 also shows the dielectric constants of 3NH₂-silicates/6FDA-ODA just after coming out of the vacuum oven with an increased amount of 3NH₂-silicates in polyimide. This is due to the fact that the dielectric constant of the bulk silicate layer is higher than that of the polyimide layer (4.5 vs. 2.8). Specifically, the dielectric constants of pure 6FDA-ODA and 3 wt.-% 3NH₂-silicates in 6FDA-ODA are 3.53 and 3.20, respectively, after exposure to ambient conditions for 20 h. This is attributed to the same kind of retardation effect on water molecules, exerted by the layered silicates, which affects the dielectric constants of the nanocomposites.

The coefficients of thermal expansion (CTEs) of 6FDA-ODA nanocomposite films at different temperatures are shown in Figure 5. The CTE of 6FDA-ODA containing 1 wt.-% 3NH₂-silicates decreases sharply compared to that of

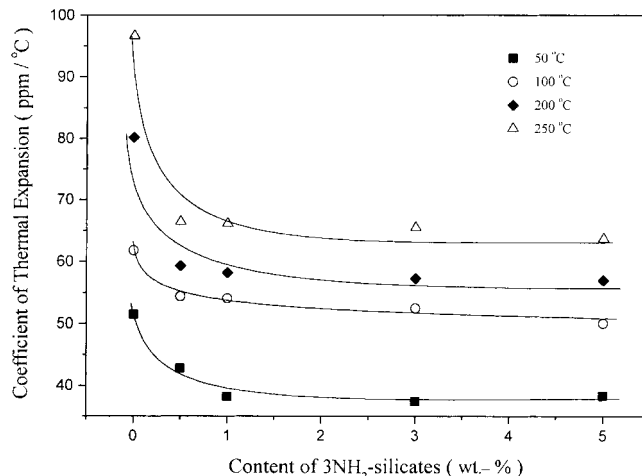


Fig. 5. The coefficients of thermal expansion of 3NH₂-silicates/6FDA-ODA films of different compositions at different temperatures.

pure 6FDA-ODA, but levels off at more than 3 wt.-% content of 3NH₂-silicates. The reduction in CTE for these nanocomposites becomes more pronounced with temperature. For example, the CTE of 6FDA-ODA containing 1 wt.-% 3NH₂-silicates decreases by 27 % at 200 °C and 32 % at 250 °C, respectively, compared to that of pure 6FDA-ODA at the same temperatures. The tensile mechanical properties of these nanocomposites are given in Table 2. The Young's modulus of the 6FDA-ODA nanocomposite increased dramatically with the amount of 3NH₂-silicates. In the case of 1 wt.-% 3NH₂-silicates, the Young's modulus was 50 % higher than that of the

Table 2. The tensile mechanical properties of 3NH₂-silicates/6FDA-ODA nanocomposites at different compositions.

Contents of 3NH ₂ -silicates [wt.-%]	Modulus [GPa]	Max. stress [MPa]	Elongation [%]
0	2.0	102.8	20.8
0.5	2.4	110.4	18.8
1.0	3.0	111.0	16.1
3.0	3.3	113.9	13.7
5.0	3.8	114.2	11.1

pure 6FDA-ODA (3.0 vs. 2.0 GPa). This behavior is attributed to the reinforcement of 6FDA-ODA by much stiffer silicates. The maximum stress of the 6FDA-ODA nanocomposite increased slightly compared to that of pristine 6FDA-ODA.

In conclusion, the nanostructured silicates/fluorinated polyimide nanocomposite, containing only a few silicates (by weight percent), displays excellent water-absorption retardation behavior, which therefore results in a lower leakage-current density and lower dielectric constants under higher humidity conditions than those of the pristine fluorinated polyimide. Additionally, the thermal expansion of these nanocomposites is substantially lower than that of the fluorinated polyimide at elevated temperatures, and the tensile modulus of the nanocomposites is improved. Hence, these nanocomposites are quite suitable for being used as advanced dielectric materials in microelectronic applications.

Experimental

The electrical property measurements on the nanocomposites were carried out in an aluminum (Al)/(3NH₂-silicates/6FDA-ODA)/indium-tin-oxide (ITO) glass-sandwich device. The top Al electrode, with a thickness of 3000 Å, was deposited by thermal evaporation in a vacuum at 4×10^{-6} Pa on 3NH₂-silicates/6FDA-ODA nanocomposite films, which were spun and imidized on a clean ITO glass with a sheet resistance of 25 Ω cm⁻². Then, these films were dried at 160 °C under vacuum for 4 days. The leakage-current density and the dielectric constant of the samples were determined with a HP4156B precision semiconductor parameter analyzer and a HP4194A impedance/gain-phase analyzer, respectively, at 25 °C under 40 % RH. For the samples for X-ray diffraction, the thermal, mechanical, and water absorption measurements were prepared by applying 3NH₂-silicates/PAA on glass slides by a doctor blade screen printing method, followed by the same imidization condition as in the preceding paragraph. The water absorption study was performed at 40 °C under 90 % RH. An X-ray diffraction study of the samples was carried out with an MAC Science MXP18 X-ray diffractometer (30 kV, 20 mA) with a copper target, at a scanning rate of 4° min⁻¹. The measurement of CTEs of the samples was performed using a DuPont 2940 TMA (film probe) at a heating rate of 10 °C/min in nitrogen atmosphere. The tensile properties of these films were measured according to the specifications of ASTM D882-88, at a crosshead speed of 2 mm/min with a MTS Sintech 1/D S-92 tester.

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Novel, Bioclastic Route to Self-Assembled, 3D, Chemically Tailored Meso/Nanostructures: Shape-Preserving Reactive Conversion of Biosilica (Diatom) Microshells**

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Appreciable worldwide effort is underway to develop new microscale (10³ nm) devices with mesoscale to nanoscale (10²–10¹ nm) features for a variety of applications in: i) medicine (e.g., drug delivery capsules, in-vitro sensors, membranes for chemical purification), ii) telecommunications (e.g., optical sensors, actuators, lenses), iii) transportation (e.g., catalytic components, sensors, valves for aircraft and automobiles), and iv) manufacturing (e.g., self-assembled devices, on-line sensors, microrobots).^[1–7] Despite the technological and economic promise of such devices, current commercial micro/mesofabrication methods have largely been based upon two-dimensional (2D), layer-by-layer techniques developed for the microelectronics industry (e.g., silicon micromachining by photolithography/chemical etching).^[1–7] Such 2D processing is not well suited to the low-cost mass production of three-dimensional (3D) microdevices with complex (non-planar) geometries and meso/nanoscale features.^[2] Furthermore, the biological, chemical, mechanical, thermal, and electrical properties of silicon-based compositions are not appropriate for all device applications. New fabrication methods capable of yielding large numbers of complex-shaped, 3D meso/nanodevices with non-silicon-based compositions are needed to allow for a wider range of device applications.

Elegant examples exist in nature of intricate, 3D microstructures with reproducible mesoscale to nanoscale features.^[8] Particularly striking biological examples of self-assembled rigid structures (so-called “bioclastic” structures that possess forms attained “through the action of living organisms”^[9]) can be found in aquatic organisms known as diatoms. Diatoms are single-celled microalgae that form rigid cell walls (frustules) composed of amorphous silica.^[8,10–12] The total

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