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Flexible ceramic–polymer composite films with temperature-insensitive and tunable dielectric permittivity

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Abstract. $BaTiO_3$–polymer composite layers have been produced by the spin-on technique (thickness 3–10 µm). The dielectric permittivity of the layers at room temperature can be tuned from 2.8 to approximately 33 by varying the ceramic filling from 0 to 60% by volume. The dielectric properties of the films are almost insensitive to temperature variations in the range 20–180 °C. Free-standing composite layers with ceramic content $\leq 50\%$ are flexible without noticeable change of permittivity after repeated mechanical bending.

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Composite materials are attracting much interest for technical applications and fundamental research. The blending of different sorts of materials produces composite structures which can combine different material properties, or may reveal novel properties not existing in the constituent phases. Among the simplest composites are materials of 0–3 connectivity consisting of small (0-D) inclusions dispersed in a 3-D host matrix. Flexible ceramic–polymer composite layers of 0–3 connectivity are especially intriguing because of the ease of preparation of samples with large area and complicated shape and the wide range of their applicability [1, 2]. For example, oxidic perovskite materials have been employed as a ceramic filler in various polymers and the dielectric, piezoelectric and pyroelectric properties of the composites have been investigated in relation to the filling factor and the dielectric properties of the inclusions.

In this paper we report on the fabrication and characterization of flexible ceramic–polymer composite layers (thickness 3–10 µm). $BaTiO_3$ powder particles are mixed in a dissolved fluorinated polymer and composite layers of different ceramic filling are produced using the spin-on technique. The dielectric permittivity of the composites is tuned over a wide range by varying the ceramic filling and shows only very little variation with temperature (20–180 °C). Free-standing composite layers are flexible and repeated mechanical bending does not change the permittivity for samples containing up to 50% ceramic filling.

1 Experimental

The composite films were prepared using a spin-coating technique employing a $BaTiO_3$ powder–polymer dispersion. Perfluorocyclobutene (poly 1,1,1-triphenyl ethane perfluorocyclobutyl ether, abbreviated PFCB, Dow Chemical) was used as the polymer host material. PFCB dissolved in mesitylene can be easily deposited by spin coating and forms a stable cross-linked network upon thermal treatment. $BaTiO_3$ powder (purity 99.7%, Alfa Aesar) was added to the polymer solution to achieve a volume filling factor $f = \mathrm{Vol}(BaTiO_3)/(\mathrm{Vol}(PFCB + BaTiO_3)$ ranging from 0–0.6. The $BaTiO_3$ powder particle size histogram was determined by optical scattering techniques (Coulter Beckman LS particle size analyzer, particle diameter ≥ 100 nm). The histogram shows a narrow distribution with more than 50% (99%) of all particles having diameters $d < 150$ nm ($d < 750$ nm). For high filling ($f \geq 0.3$), additional solvent was added to the dispersion to achieve sufficiently low viscosity for spin coating. Samples with $f > 0.6$ did not form continuous layers. The dispersions were stirred carefully in order to achieve a homogeneous mixture and to avoid sedimentation of particles. For film fabrication, several drops of the dispersion were deposited on $Pt/Ti/SiO_2/Si$ wafers ($1 \times 1\ \mathrm{cm}^2$) or on freshly cleaved NaCl substrates using a syringe. Samples produced by spin coating had layer thicknesses in the range 3–10 µm, depending on the amount of dispersion employed. After spinning, samples were pre-baked and cured in a N_2 atmosphere [3]. Samples produced without substrate spinning were thicker (50–100 µm). Stacks consisting of alternating PFCB and composite layers were fabricated by curing the individual layers before deposition of new layers. Free-standing samples were obtained by dissolving the NaCl substrates in deionized water after curing the composite layers. The composite films appear white with diffuse optical reflection, whereas pure PFCB films are highly transparent.

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The composite films, $BaTiO_3$ powder and ceramics were investigated by dielectric measurements (HP 4284A LCR meter), mechanical bending tests, scanning electron microscopy (SEM), microprobe analysis (EDX), surface profilometry (Dektak), X-ray diffraction (XRD) and differential thermal analysis (DTA, Bähr STA 501). Dielectric characterization was performed in the temperature range 20–180 °C and frequency range 1 kHz – 1 MHz using evaporated aluminum contact pads (diameter 3.5–6 mm). Free-standing films were characterized before and after mechanical bending (bending radius 5 mm). The density of the free-standing films was measured using a microgram balance (Mettler ME 30), optical microscopy (1000×) and SEM. The DTA was calibrated using indium metal pellets ($T_m = 156\,°C$, $\Delta H_m = 28.6\,J/g$ [4]) as a reference.

2 Results and discussion

The SEM pictures in Fig. 1 show cross-section images of free-standing PFCB–$BaTiO_3$ composite films and PFCB–PFCB/$BaTiO_3$ multilayered stacks. Samples were either cut at room temperature or broken after cooling with liquid nitrogen and images were taken at an angle of 45°. Composite layers with low ceramic filling ($f = 0.1$, Fig. 1a) reveal smooth cross sections with small protrusions and indentations. Microprobe analysis identifies the smooth areas as polymer material and the small bright protrusions as the $BaTiO_3$ inclusions (diameter $\leq 1\,\mu m$). For higher filling, the cross section becomes less smooth ($f = 0.5$, Fig. 1b). Figure 1c shows an example of a free-standing multilayer structure consisting of two composite layers ($f = 0.3$) sandwiched by three PFCB layers ($f = 0$). The PFCB layers show smoother surfaces than the composite layers. The adhesion of layers to the substrate is relatively weak and layers can peel off during sample cutting. The composite layers show an increasing modulation of the film thickness with increasing filler content (not shown in Fig. 1b). This morphology is due to the formation of hillock structures, and for layers with 20% filling and average thickness $\langle h \rangle = 5.5\,\mu m$, surface profilometry reveals a thickness modulation $\Delta h_{rms} = 1.8\,\mu m$ and a modulation period $\Lambda \sim 100\,\mu m$. The formation of hillock structures complicates accurate thickness and surface area measurements of the layers. However, the density values obtained roughly follow the expected linear dependence of density on filling factor. Mechanical polishing of the layers reduced the surface roughness by $\sim 50\%$ but also produced strong thickness variations on a macroscopic scale and damage affecting the integrity of the layers.

Figure 2 summarizes the dielectric measurements of the composite layers deposited on platinized Si substrates. The thickness of the composite layers was 3–10 μm and the measurement frequency was 1 kHz. The dielectric permittivity ε' strongly increases with increasing filling factor and reaches a maximum of $\varepsilon' \approx 33$ at $f = 0.45$. For higher filling, the permittivity levels off, possibly due to the formation of pores. Frequency sweeps reveal a decrease of permittivity by 10%–20% for different samples depending on the filling. The loss tangent is $\tan\delta < 0.06$ for all samples investigated. The dielectric properties are remarkably insensitive to temperature variations in the range 20–180 °C, considering the pronounced dielectric anomaly of bulk $BaTiO_3$ at $T_c = 120\,°C$. The composite films show an overall decrease in ε' for higher temperatures ($\Delta\varepsilon'/\varepsilon' < 10\%$) with just a weak increase ($\Delta\varepsilon'/\varepsilon' \leq 3\%$) in the temperature range 110–140 °C for higher ceramic loading ($f > 0.2$). Pure PFCB films have $\varepsilon' = 2.8$ at room temperature, with a linear decrease ($\Delta\varepsilon'/\varepsilon' \leq 1\%$) at higher temperatures due to thermal expansion [3]. The large thickness modulations of the layers

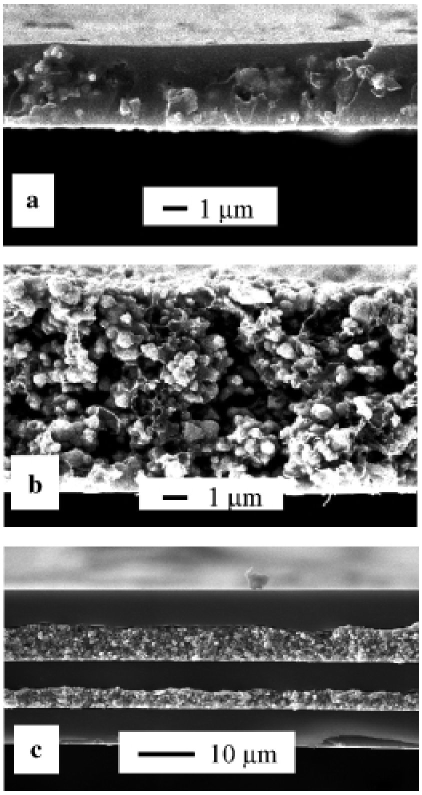

Fig. 1a–c. Cross section electron micrographs of free-standing $BaTiO_3$–PFCB composite layers (**a** and **b**), and a multilayered stack (**c**). Ceramic filling is $f = 0.1$ and $f = 0.5$ for images **a** and **b**, respectively. The stack consists of two composites layers (30% filling) that are sandwiched by three PFCB layers

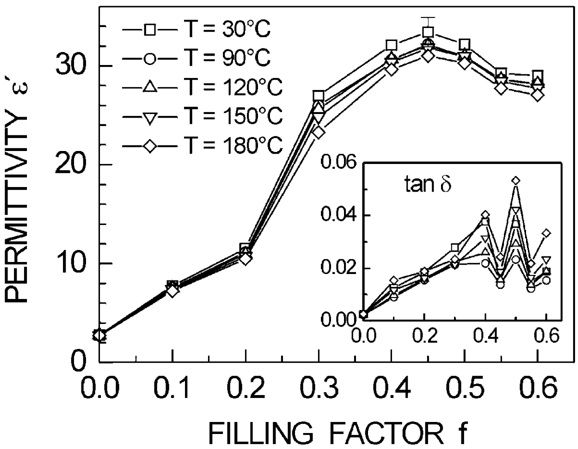

Fig. 2. The dielectric permittivity of composite layers increases with ceramic filling ($f \leq 0.45$) and reveals only a slight decrease at higher temperatures. The uncertainty of layer thickness introduces an error $\Delta\varepsilon'/\varepsilon' \leq 5\%$. The inset shows the variation of the loss tangent with ceramic filling

complicate the calculation of permittivity values from the measured capacitance data. The values given in Fig. 2 are derived using the formula for a plane-parallel capacitor with an average layer thickness $\langle h \rangle$. This simplification can be employed as long as long wavelength modulations of the layer thickness h are considered and $kh < 1 (k = 2\pi/\Lambda)$. In this case, the uncertainty of the calculated permittivity is $\Delta\varepsilon'/\varepsilon' \approx (kh)^2/6$, as derived from basic electrostatics. For the composite layers ($h < 10\,\mu\text{m}$, $\Lambda \geq 100\,\mu\text{m}$) an uncertainty $\Delta\varepsilon'/\varepsilon' \leq 5\%$ is estimated. Dielectric measurements on thicker films ($\langle h \rangle \sim 80\,\mu\text{m}$, $\Delta h_{\text{rms}} \sim 3\,\mu\text{m}$) confirm the permittivity values obtained from the thinner samples.

The relatively soft polymer matrix enables easy and nondestructive mechanical deformations of the composites. The dielectric properties of free-standing layers have been measured before and after mechanical bending of the layers (thickness of layers $\leq 10\,\mu\text{m}$). Bending was performed at room temperature and the dielectric permittivity and loss tangent were measured at 20 °C and 1 kHz. Repeated bending (up to 50×) does not change ε' for samples with filling factors $f \leq 0.5$ (Fig. 3). The $\tan\delta$ remains unchanged as well. Samples with a higher amount of ceramic particles become increasingly brittle and break after a few bending cycles.

The weak temperature dependence of the composite permittivity is due to the dielectric properties of the $BaTiO_3$ particles used as filler material. It is well known that oxygen loss modifies the dielectric properties of oxidic perovskites [5]. In addition, with powders these properties reveal a particle size dependence which is attributed to modifications of the ferroelectric domain structure [6], the formation of non-ferroelectric surface layers with low ε' [7] and the surface adsorption of hydroxyl groups [8]. For $BaTiO_3$ particle sizes below 0.2 μm, a size-driven phase transformation causes the decrease of tetragonality and critical temperature [9 and references therein]. The critical size to support the cooperative long-range ordering required for the formation of the ferroelectric state is about 50 nm [9, 10]. Dielectric, DTA and XRD investigations confirm that the $BaTiO_3$ powder does not develop the ferroelectric state. Dielectric measurements of powder pellets (relative density $\sim 55\%$) reveal $\varepsilon' \leq 45$ for all temperatures. Ceramics fabricated from such powder by sintering at 1200 °C for 12 h in air show a ferroelectric-to-paraelectric phase transition at $T_c \approx 120\,°\text{C}$ and $\Delta H \approx 110\,\text{mJ/g}$, in good agreement with literature data [11].

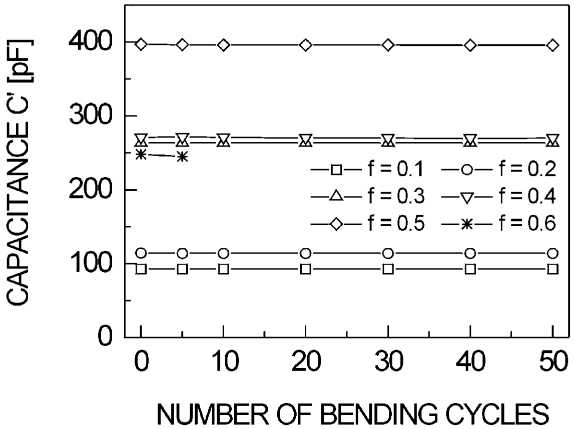

Fig. 3. Free-standing $BaTiO_3$–PFCB composite layers are flexible and mechanical bending does not affect the capacitance measured after several bending cycles. The layers had different thickness ($\leq 10\,\mu\text{m}$). Samples with ceramic filling above 50% break after a few cycles

The dielectric permittivity values of the $BaTiO_3$–PFCB composites are comparable to results achieved with other polymer matrices. Depending on the average $BaTiO_3$ particle size (≤ 500 nm up to 2 μm) permittivity values in the range 7–100 are reported for filling factors $f = 0.16 - 0.6$ and different polymer materials [6, 12–14]. Modeling of the binary ceramic–polymer composite using effective-medium-approximations [2] and logarithmic mixing [13] does not deliver satisfactory agreement with the measured permittivity values. This discrepancy may be due to size-dependent dielectric properties of the ceramic particles, the formation of pores and the non-spherical shape of the inclusions. Connectivity models could deliver more accurate estimates for ternary phase materials and higher filling factors [1]. Computer simulations revealed critical phenomena and percolation thresholds depending on size, shape and spatial orientation of the inclusions [15].

3 Conclusions

$BaTiO_3$–PFCB composite layers have been produced on different kinds of substrates. For a ceramic filling factor $f < 0.6$, free-standing and flexible layers were produced by dissolution of NaCl substrates after curing of the composite films. The use of small-grained non-ferroelectric $BaTiO_3$ powder as ceramic filler gives a material with a tunable and temperature-insensitive dielectric permittivity. The dielectric permittivity at room temperature of the composites produced varied from 2.8 ($f = 0$) to approximately 33 ($f = 0.45$).

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