High performance dielectric film using SiO₂-coated short carbon nanotubes in BaTiO₃-polymer composite


Three-phase composite films consisting of BaTiO₃/singlewalled carbon nanotube (SWCNT)/polymer were fabricated. The SWCNTs were shortened and coated with SiO₂ to minimise the conducting paths of the SWCNTs in the film. The film showed a dielectric constant and dielectric loss of 92 and 0.031, respectively, at a frequency of 1 kHz. The SiO₂-coated short SWCNTs can play important roles in enhancing the capacitance by space charge polarisation at the interface between the SWCNTs and SiO₂, and reducing the dielectric loss.

Introduction: Recently, the demand for flexible devices has necessitated a flexible dielectric film for two phases, i.e. ferroelectric powder and polymer. The dielectric constant (εr) of this two-phase film is generally lower than that of a dielectric film consisting of a ferroelectric powder, e.g. barium titanate (BaTiO₃, εr: 3000–4000 depending on its crystallinity) only, because the dielectric constant of the polymer is quite low. If carbon nanotubes (CNTs) are used in the two-phase dielectric film, resulting in a three-phase film, the dielectric constant could be improved by the space charge polarisation. It might be caused by trapped charge carriers formed at the interface between the CNTs and ferroelectric powder (or polymer), because of isolating and covering SWCNTs by insulating BaTiO₃ powder and thin polymer [1]. On the other hand, reported three-phase dielectric films exhibit relatively high dielectric loss (~0.6 at 100 Hz) and are relatively thick (~1 mm), which might have a low breakdown voltage [1] and be a disadvantage for very small devices [2].

In this Letter, we propose a new method to increase the dielectric constant, while maintaining or reducing the dielectric loss. Three-phase dielectric films having a few micrometre thickness were fabricated using a mixture of BaTiO₃ powder, SiO₂-coated short single walled CNTs (SWCNTs), and cyanoresin-based polymer. All the SWCNTs (CNI Co., 601B) were shortened to reduce unintentional electric short circuits using the cryo-crushing method. A SiO₂ layer was coated on the SWCNTs from a spin-on-glass (SOG) solution. Therefore, this new dielectric film can improve the dielectric constant by space charge polarisation with low dielectric loss.

Structure and fabrication: The SiO₂-coated SWCNTs were prepared as follows. The SWCNTs were dispersed in a 0.1 M NaOH solution by ultrasonication for 30 min. The modified SWCNTs were dispersed in isopropyl alcohol with the addition of 7 ml of a SOG solution (Nanohiy, 512B). Two types of films, BaTiO₃-polymer films with no SWCNTs (reference film) and BaTiO₃-polymer films with non-coated SWCNTs (NS film), were also fabricated to compare the dielectric performance of the BaTiO₃-polymer film with SiO₂-coated SWCNTs (SS film).

Three sets of the SS films were prepared by varying the SWCNT concentration, i.e. 0.03, 0.07, and 0.1 wt%. The SiO₂-coated SWCNTs were mixed with a cyanoresin-based polymer, i.e. a copolymer of cyanoethyl pullulan and cyanoethyl polyvinyl alcohol (Shin-Etsu Chemical, CR-M). BaTiO₃ powder (Samsung Fine Chemicals, SBT03) at 60 wt% was mixed with the prepared SWCNT-polymer binder. All the films were deposited on ITO-coated glass substrates using the spin-coating method. Finally, an electrode (~200 nm) was deposited by sputtering aluminum and patterned by a shadow mask. The reference and NS films (SWCNT concentration of 0.03, 0.07, and 0.1 wt%) were prepared using the same procedures as for the SS film. The measurement condition of the films for the dielectric properties were 0.1 V and 1 kHz. After measuring the dielectric constant and loss, the thickness and morphology of the films were examined by SEM and TEM. Characterisations of the films were also examined by energy dispersive X-ray (EDX) and Raman spectra.

Results and discussion: The thickness of all dielectric films was approximately 2 µm (see Fig. 1a). The films had smooth surfaces, which were confirmed from the tilting view SEM image of Fig. 1a. Raman spectroscopy of the dielectric films with and without SWCNTs was performed to confirm the mixing status of the SWCNTs and BaTiO₃, as shown in Fig. 1c. The peaks at approximately 520 and 715 cm⁻¹ represent the third asymmetric A₁(TO₃) and A₂(LO₂) phonon modes propagating along the c-axis in tetragonal BaTiO₃, respectively [3]. The peaks at approximately 1320 and 1600 cm⁻¹ represent the disordered state of carbon (D) and tangential C-C stretching vibration (G), respectively [4], which appeared only in the dielectric film with SWCNTs. Energy dispersive X-ray (EDX) spectroscopy of the SiO₂-coated SWCNTs was performed to determine the amount of SiO₂ (Fig. 2a). C, O, and Si, as major elements, were detected along with a small unintentional Na peak. This Na peak was attributed to the Na residue of the NaOH solution during filtration of the SWCNT-NaOH solution. Figs. 2b and c show TEM images of the SWCNTs before and after the SiO₂ coating. The SWCNTs before the SiO₂ coating had smooth CNT walls, whereas those after the coating exhibited rough CNT walls.

The measured dielectric constants of the reference, NS, and SS films were 55, 39, and 92, respectively, at a SWCNT concentration of 0.1 wt% using an LCR-tester (see Fig. 3a). The dielectric constants of the SS films increased with increasing SWCNT concentration, whereas those of the NS films showed no noticeable change. The dielectric losses of the reference, NS and SS films were 0.04, 14.5 and 0.03, respectively, at a SWCNT concentration of 0.1 wt% (see Fig. 3b). The NS film exhibited the worst result. This might be due to the SWCNTs forming a conducting network, leading to dielectric breakdown. The experimental results imply that the SiO₂ coating on SWCNTs (i.e. SS film) could improve the dielectric performance with minimising the dielectric loss. The increase in dielectric constant of the SS film with low dielectric loss might be interpreted as follows. The SiO₂ layer induces space charge polarisation by an alternating electric field, i.e. space charge polarisation [1, 5]. In addition, the SiO₂ layer can minimise the conducting networks of the CNTs in the film. Therefore, the SiO₂-coated SWCNTs can induce space charge polarisation with less dielectric loss.
Conclusion: Three-phase dielectric films consisting of BaTiO$_3$/SWCNT/polymer were fabricated. Short SWCNTs were coated with SiO$_2$ using a SOG solution. A high dielectric constant of the SS film was achieved without sacrificing dielectric loss. A SiO$_2$ coating can enhance the dielectric performance by space charge polarisation and reduce the dielectric loss.

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References