

# Cu@SiO<sub>2</sub>-BaTiO<sub>3</sub>-EPOXY COMPOSITES WITH HIGH PERMITTIVITY FOR EMBEDDED CAPACITORS

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**Abstract:** Cu@SiO<sub>2</sub> core-shell structured particles with nano size were prepared by hydrolyzing tetraethyl orthosilicate on the fresh prepared copper particles. A series of Cu@SiO<sub>2</sub>-BaTiO<sub>3</sub>-epoxy composite films, with BaTiO<sub>3</sub>-epoxy as the matrix and Cu@SiO<sub>2</sub> as the fillers, were fabricated on the copper substrate with bar coating method. A maximum dielectric constant of 880 and a relatively low dielectric loss (less than 0.30) were obtained in the composite film. The dielectric behavior were investigated on the basis of Maxwell-Wagner-Sillars interfacial polarization and percolation theory. The effect of the SiO<sub>2</sub> layer on the Cu surface was analyzed.

## 1. Background

In electronic industry, it urgently desires materials with high dielectric constant and low dielectric loss for embedded capacitor applications to follow the transition of electronic devices toward miniaturization and multifunction. Polymer-based composites with flexibility and tailored dielectric properties are currently very popular topics in the field of electronic materials [1~3]. The dielectric constant of polymers is usually very low which results in low charge density. To improve the dielectric constant, various fillers, including ceramic powders (such as BaTiO<sub>3</sub> [4], CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>[5] and (Ba<sub>0.8</sub>Sr<sub>0.2</sub>)(Ti<sub>0.9</sub>Zr<sub>0.1</sub>)O<sub>3</sub> [6]) and/or conductive particles (such as Ag[7], Al[8], Ni[9] and Carbon[10]) were introduced to the polymer matrix. For the ceramic-polymer composite, it is hard to acquire a dielectric constant higher than 100 even with high ceramic loading (50vol%). In contrast, when conductive particles are employed as fillers, a dramatic increase (from a few tens to more than 4000) in dielectric constant can be obtained near the percolation threshold ( $f_c = 0.15\sim 0.20$ ) [10]. However, since a conduction

path forms at the threshold point, the increase in the dielectric constant will veritably accompanied with a substantial increase in dielectric loss (>1).

In order to reduce the tunnel current between conductive particles so as to suppress the dielectric loss, Nan et al [11] encapsulated the Ag nano particles with an insulating poly(vinylpyrrolidone) layer to form a core-shell structure. The polymer composites filled with the core-shell Ag nano particles exhibited stable dielectric property over a wide range of frequency and temperature. Xu et al [8] reported that a gradual increase in the dielectric constant was obtained in a self-passivated Al filled polymer composites. However, the dielectric constant of the composite is only around 100 at an high loading level of Al (90wt%). The insulating Al<sub>2</sub>O<sub>3</sub> layer with a thickness larger than 40nm makes the composite more similar to that with ceramic loading.

In this work, a three phase epoxy-based composite was developed which consisted randomly dispersed Cu@SiO<sub>2</sub> core-shell structure nanoparticles of 100~150 nm in diameter for the core and 5~10 nm in thickness for the shell and 100 nm BT particles. In order to explore the percolation behaviors of the Cu@SiO<sub>2</sub> filled composites, the BaTiO<sub>3</sub>-epoxy composite is considered as a high-dielectric-constant host material. Similar to the metal polymer composites, the electrical properties of the metal-ceramic-polymer three phase composites substantially change near the  $f_c$ , which is usually explained with the percolation theory [12], as described in the equation:

$$\varepsilon_{eff} = \varepsilon_1 \left| (f_c - f) / f_c \right|^{-q} \quad (1)$$

where  $\varepsilon_{eff}$  is the effective dielectric constant of the composite,  $\varepsilon_1$  is the dielectric constant of the matrix,

$f_c$  is the percolation threshold,  $f$  is the filler volume fraction, and  $q$  is a critical exponent of about 1.

The highest dielectric constant that has been achieved in this study is 880, which is about 40 times larger than that of the BaTiO<sub>3</sub>-epoxy matrix. The microstructure of the Cu@SiO<sub>2</sub> particles and the effect of SiO<sub>2</sub> on the dielectric performance of the Cu@SiO<sub>2</sub>-BaTiO<sub>3</sub>-epoxy composite film were investigated.

## 2. Experimental

To prepare Cu@SiO<sub>2</sub> nano particles, the CuCl<sub>2</sub> (Guoyao Chemical Co. China) was used as a precursor of Cu. Hydrazine hydrate (H<sub>4</sub>N<sub>2</sub>•H<sub>2</sub>O) and tetraethoxysilane (TEOS) (both from Tianjin Damao Chemical Co. China) were employed as the reducing and capping agent, respectively. The Cu core was obtained by reducing CuCl<sub>2</sub> (200ml, 0.1M) with H<sub>4</sub>N<sub>2</sub>•H<sub>2</sub>O (200ml, 0.5M). The tetraethyl orthosilicate (TEOS, 100ml, 0.02M) was dissolved in absolute alcohol and added to the above solution. Throughout the experimental process, the temperature was kept at 60°C. The reactant was cleaned by redistilled water and alcohol three times and dried in a vacuum oven at 40°C for 12h. Finally the Cu@SiO<sub>2</sub> particles were obtained. Nano-sized BaTiO<sub>3</sub> particles with a mean diameter of 100 nm (Guangdong Fenghua Advanced Technology Co. China) were used as the ceramic fillers.

The bisphenol-A epoxy (E-51, Wuxi Resin Factory Blue Star New Chemical Materials Co., Ltd), tetraethylenepentamine and 2-butanone were used as the polymer matrix, curing agent and solvent, respectively. The Cu@SiO<sub>2</sub>-BaTiO<sub>3</sub>-epoxy composites were prepared by mixing the epoxy resin, BaTiO<sub>3</sub>, and Cu@SiO<sub>2</sub> in 2-butanone. The prepared slurry was coated on copper foil with a bar coating method and heat-treated at 90 °C for 30min. Two pieces were laminated face to face and cured at 150 °C for 30min to form a prototype capacitor. The thickness of the dielectric film is about 20 μm.

The morphology of the Cu@SiO<sub>2</sub> particles and composites was investigated with scanning electron microscope (FE-SEM, HITACHI S-

4800). To determine the elemental composition of the particles, an energy dispersive X-ray (EDX) detector from EDAX was used together with the FE-SEM. The microstructure of the Cu@SiO<sub>2</sub> particles was further examined with transmission electron microscopy (TEM, JEM-100CX II). The dielectric properties were measured by Agilent 4294 Impedance analyzer in the frequency range of 1 kHz~10 MHz.

## 3. Results and Discussion

### 3.1 Microstructure of Cu@SiO<sub>2</sub> particles and Cu@SiO<sub>2</sub>-BaTiO<sub>3</sub>-epoxy composite

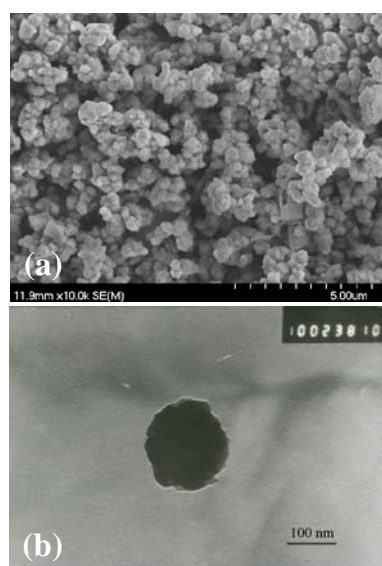


Fig.1. Morphology of Cu@SiO<sub>2</sub>, (a) powders under SEM and (b) a single granular under TEM.

For the freshly prepared Cu particles, some hydroxyl groups may adhere to the surface by chemisorption. As a result, amorphous SiO<sub>2</sub> layer can be formed through the process of hydrolysis and condensation of TEOS, as taught by C. Graf et al [13] and thus a core-shell structured Cu@SiO<sub>2</sub> particles were obtained.

Fig. 1 presents the SEM image of Cu@SiO<sub>2</sub> powders (a) and a single particle under TEM (b). The grains with the size of 100~150nm are clearly seen in Fig.1(a). A bright thin layer with a thickness of 5~10nm around the Cu core can be observed, as shown in Fig. (b), which is attributed to the SiO<sub>2</sub> coating. The coverage of the Cu particles with a silica layer has been further proven by analyzing the elementary

composition of the colloids with EDX. The weight ratio of O:Si:Cu is 6.09:7.44:86.48.

Fig.2 shows the cross-section morphology of the Cu@SiO<sub>2</sub>-BaTiO<sub>3</sub>-epoxy composite film with 20.0vol% Cu@SiO<sub>2</sub> and 40vol% BaTiO<sub>3</sub>, observed under optical microscope and SEM, respectively. The thickness of the composite dielectric film is about 20 μm with good adhesion to the copper foil, as shown in Fig.2(a). Due to the large particles content, both Cu@SiO<sub>2</sub> and BaTiO<sub>3</sub> are tightly embedded in the epoxy matrix, with some clusters and holes being observed (Fig.2(b)).

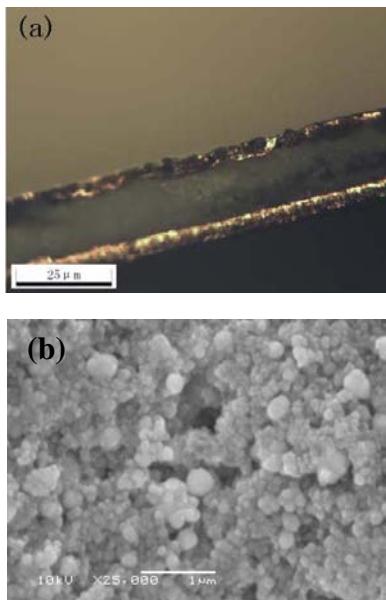


Fig.2. Cross-section morphology of Cu@SiO<sub>2</sub>/BaTiO<sub>3</sub>/epoxy composite film with 20.0vol% Cu@SiO<sub>2</sub> and 40vol% BaTiO<sub>3</sub>, observed with (a) optical microscope and (b) SEM.

### 3.2 Dielectric performance of the Cu@SiO<sub>2</sub>-BaTiO<sub>3</sub>-epoxy composite film

Fig.3 shows the dielectric constant and loss of the Cu@SiO<sub>2</sub>-BaTiO<sub>3</sub>-epoxy composite films with various volume fractions of Cu@SiO<sub>2</sub>. The dielectric constant  $\epsilon_r$  of the BaTiO<sub>3</sub>-epoxy composite is 22.9, which is considered as the matrix for filling the Cu@SiO<sub>2</sub> particles. As shown in the figure, the  $\epsilon_r$  of the composites improves from 22.9 to 193 when the Cu@SiO<sub>2</sub> content increases from 0 to 15vol%. A

dramatically increased value of 880 is obtained while the Cu@SiO<sub>2</sub> is further increased to 20vol%, which is nearly 40 times larger than of the BaTiO<sub>3</sub>-epoxy matrix, indicating a percolation effect. The dielectric loss  $\tan\delta$  of the composites gradually increases with Cu@SiO<sub>2</sub> loading amount. However,  $\tan\delta$  does not show a rapid increase when the volume fraction of Cu@SiO<sub>2</sub> approaches the percolation threshold. It increases from 0.04 to 0.29 with the addition amount of Cu@SiO<sub>2</sub> increased from 0 to 20vol%, improved by about 7 times. Compared with the results of dielectric constant, the increase of  $\tan\delta$  is moderate. The dielectric behavior of the composite is different from the typical percolate material, in which a dramatic increase of both dielectric constant and loss are observed at the percolation threshold, and the system undergoes a transition from insulator to conductor. The untypical behavior of the composite in this study should be ascribed to the insulating SiO<sub>2</sub> layer on the surface of Cu, as well as the BaTiO<sub>3</sub> particles, which act as a barrier around Cu@SiO<sub>2</sub> and separate Cu@SiO<sub>2</sub> from each other to some degree. As a result, it is difficult to form electron tunneling in the system. Furthermore, even if the conducting networks were formed, they could only develop into some island-shaped regions over the whole composite but could not contact the two electrodes due to BaTiO<sub>3</sub> barriers, as illustrated in Fig. 4.

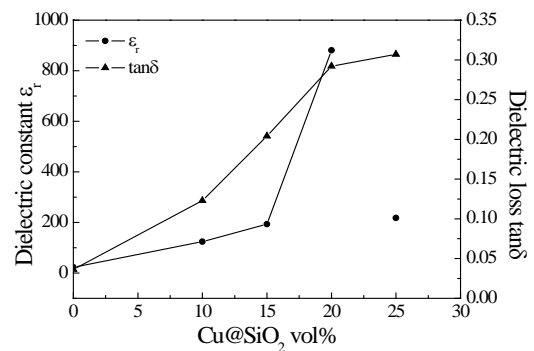


Fig.3. Dielectric behavior of Cu@SiO<sub>2</sub>-BaTiO<sub>3</sub>-epoxy composites with 30vol% BaTiO<sub>3</sub> and various fractions of Cu@SiO<sub>2</sub>, measured at 1 kHz.

The dielectric constant suddenly decreases to 200 when the Cu@SiO<sub>2</sub> loading is increased to 25vol%, which could be caused by the

inhomogeneity due to the formation of some clusters and conducting islands in the system.

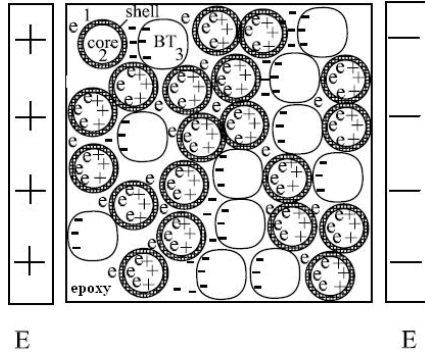


Fig. 4. Schematic diagram of the filler distribution in the Cu@SiO<sub>2</sub>-BaTiO<sub>3</sub>-epoxy composite. (1: interface between SiO<sub>2</sub> layer and epoxy, 2: interface between Cu and SiO<sub>2</sub> layer, 3: interface between BaTiO<sub>3</sub> and epoxy)

Fig.5 presents the dependence of the dielectric constant  $\epsilon_r$  and the loss  $\tan\delta$  of the three-phase Cu@SiO<sub>2</sub>-BaTiO<sub>3</sub>-epoxy composite films on frequency. As shown in Fig. 5(a),  $\epsilon_r$  is nearly independent on the whole measured frequency range for the BaTiO<sub>3</sub>-epoxy composite. As for the composites containing Cu@SiO<sub>2</sub>,  $\epsilon_r$  shows a slight drop with increasing frequency for the composite with lower Cu@SiO<sub>2</sub> loading (10vol% and 15vol%). When Cu@SiO<sub>2</sub> content reaches the percolation threshold of 20vol%,  $\epsilon_r$  reduces rapidly with frequency, e.g. from 880 at 1 kHz to 355 at 1MHz. According to the percolation theory [12], as

$$f_{Cu@SiO_2} \rightarrow f_c$$

$$\epsilon \propto \omega^{u-1} \quad (2)$$

Where  $\omega = 2\pi f$  and  $u$  is a critical exponent. The data for  $f_{Cu@SiO_2} = 0.20$  give  $u = 0.838$  which is close to the normal value from the percolation theory [12].

The above results indicate that the dielectric property is determined by BaTiO<sub>3</sub>/PVDF matrix as the filler concentration is low. With increasing the Cu@SiO<sub>2</sub> loading level, the effect of Cu@SiO<sub>2</sub> particles on the dielectric behavior of the composites becomes remarkable. The noticeable drop of dielectric constant with increasing frequency implies the existence of interfacial polarization generated by inclusions. The enhancement in dielectric constant is

mainly attributed to the interfacial polarization, also referred to as the Maxwell-Wagner-Sillars (MWS) effect [14].

The dielectric loss  $\tan\delta$  versus frequency shows a similar tendency as the dielectric constant  $\epsilon_r$ , as shown in Fig. 5(b). For the composite containing only BaTiO<sub>3</sub> particles,  $\tan\delta$  changes little over frequency.  $\tan\delta$  shows a dependence on the frequency in the composites containing Cu@SiO<sub>2</sub> particles, which becomes apparent when Cu@SiO<sub>2</sub> reaches 20 vol%, especially at low frequencies. The maximum  $\tan\delta$  is 0.29, indicating that no conducting path is formed in the whole system and SiO<sub>2</sub> layer should play a key role in suppressing the movement of space charges.

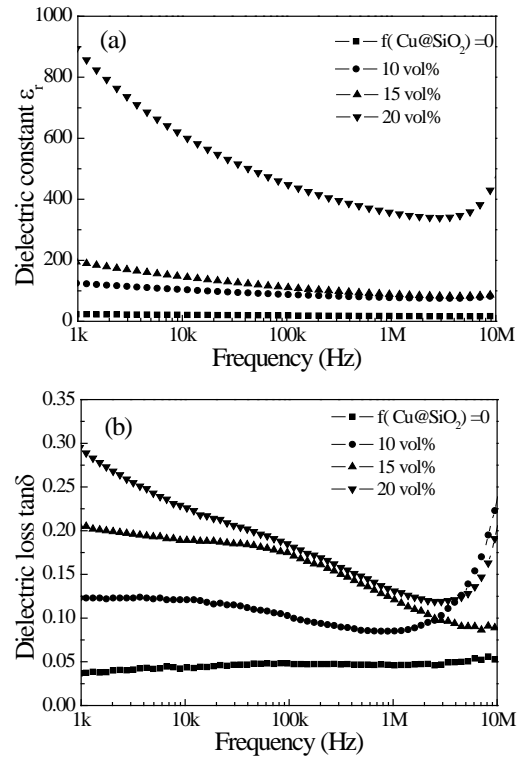


Fig.5 Dependence of dielectric constant (a) and loss (b) of the Cu@SiO<sub>2</sub>-BaTiO<sub>3</sub>-epoxy composite films on frequency with 30 vol% BaTiO<sub>3</sub> and different volume fractions of Cu@SiO<sub>2</sub> at room temperature.

As discussed above, for the three-phase Cu@SiO<sub>2</sub>-BaTiO<sub>3</sub>-epoxy composites, it is due to the insulating SiO<sub>2</sub> layer on the surface of Ag and BaTiO<sub>3</sub> as barriers between Cu@SiO<sub>2</sub> powders that



no typical percolation effect has been observed in the system. A high dielectric constant  $\epsilon_r$  of 880 and a relatively low loss  $\tan \delta$  of 0.29 were obtained in the system with 20vol% Cu@SiO<sub>2</sub>. Both of the interfacial polarization induced by nano-sized BaTiO<sub>3</sub> and intrinsic electric dipole moment in ferroelectric ceramic BaTiO<sub>3</sub> contribute to the high dielectric constant.

#### 4. Conclusions

In this paper, Cu particles were prepared through a simple wet chemical reduction and modified with TEOS to form Cu@SiO<sub>2</sub> core-shell structure. Cu@SiO<sub>2</sub>-BaTiO<sub>3</sub>-epoxy composite films with Cu foil as electrodes were prepared via a simple coating and face to face laminating technique. The typical percolation phenomenon of the “conductor-insulator” system has not been observed in the composite film due to the SiO<sub>2</sub> barrier layer and BaTiO<sub>3</sub> particles around Ag@SiO<sub>2</sub>. A maximum dielectric constant of 880 has been obtained which results from the huge interfacial polarization induced by nano-sized Cu@SiO<sub>2</sub> and BaTiO<sub>3</sub> fillers and the intrinsic electric dipole moment in the ferroelectric BaTiO<sub>3</sub>. The relative low loss of less than 0.30 should be attributed to the SiO<sub>2</sub> layer which to some extent acts as internal electron barrier and restricted electrons to transfer between Cu cores. Besides, BaTiO<sub>3</sub> particles further isolate Cu@SiO<sub>2</sub> particles and make the tunneling more difficult to occur. Such a three-phase polymer matrix composite with tunable dielectric properties is a promising candidate material for embedded capacitors and energy storage device applications.

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