High Dielectric Constant SU8 Composite Photoresist for Embedded Capacitors

Jianwen Xu, C.P. Wong

School of Materials Science and Engineering, National Science Foundation Microsystems Packaging Research Center, Georgia Institute of Technology, Atlanta, Georgia 30332-0245

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ABSTRACT: A novel, photodefinable, high dielectric constant (high-k) nanocomposite material was developed for embedded capacitor applications. It consists of SU8 as the polymer matrix and barium titanate (BT) nanoparticles as the filler. The UV absorption characteristics of BT nanoparticles were studied with a UV-Vis spectrophotometer. The effects of BT nanoparticle size, filler loading, and UV irradiation dose on SU8 photopolymerization were systematically investigated. The dielectric properties of the photodefined SU8 nanocomposites were characterized. Embedded capacitors using the novel high dielectric constant SU8 composite photoresist were demonstrated on a flexible polyimide substrate by the UV lithography method. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1523–1528, 2007

Key words: SU8 epoxy; barium titanate; nanocomposite; photoresists; embedded capacitors

INTRODUCTION

Printed circuit boards (PCBs) are the backbone of all electronic devices. Conventionally discrete passive components like capacitors, resistors, and inductors are surface-mounted on top of the PCBs by a soldering process. These discrete passives take up a large PCB surface area. The ever-increasing demands of miniaturization, cost reduction, and fast speed in the microelectronic industry call for innovations in PCB technology. One promising approach, which may match these demands, is to integrate passive components into the board structure during the PCB manufacturing instead of mounting them in a later production phase. Because they are embedded inside multilayer PCBs, such components are called embedded passives. An example of an embedded capacitor, which is buried in the PCB board right beneath the integrated circuits (ICs), is shown in Figure 1.

Embedded capacitors require the use of high dielectric constant (high-k) materials because of the limited space inside the PCB substrate. Many dielectric materials have been investigated, and particularly polymer–ceramic composites have been extensively studied as the candidate for embedded capacitors because the combination of polymer and filler may give the composites advantages from both components.[1–5] However, the conventional polymer–ceramic composites are not photosensitive and cannot be directly patterned into the desired geometry by the photolithography method, which is a standard process used in the manufacture of PCB board. In addition, via openings in the embedded capacitor layer are often required to make interconnects in the PCB board, as shown in Figure 1. An expensive and time-consuming laser drilling process has to be used to the open via in conventional polymer–ceramic composites. On the other hand, a photodefinable high-k composite can be easily patterned into the desired shape so that it can save the substrate area and save the time needed for laser drilling of via openings as in conventional high-k composites. Therefore, successful development of such a photodefinable high-k polymer composite will lead to embedded capacitors with low cost, great design flexibility, as well as great versatility in applications.

We present here a study on the novel, photodefinable, high dielectric constant composite material for embedded capacitor applications. It consists of SU8 as the polymer matrix and barium titanate (BT) nanoparticles as the filler. UV lithography was used to pattern the SU8 composite photoresist on a variety of substrates, i.e., rigid glass substrate, Cu-coated rigid glass substrate, and polyimide flexible substrate. The UV absorption characteristics of BT nanoparticles were studied with a UV-Vis spectrophotometer. The effects of BT nanoparticle size, filler loading, and UV irradiation dose on the SU8 photopolymerization were systematically investigated. The dielectric properties of

Correspondence to: C. P. Wong (cp.wong@mse.gatech.edu).

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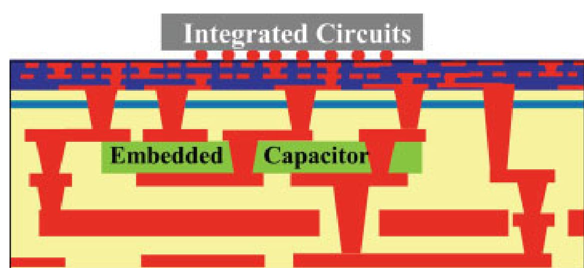

Figure 1 Embedded capacitor in the PCB board. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the photodefined SU8 nanocomposites were characterized by an LCR meter.

EXPERIMENTAL

Materials and composite photoresist formulation

The SU8 (Epon Resin SU-8) was obtained from Hexion Specialty Chemicals (Columbus, OH). SU8 is an epoxy-type, negative, near-UV (365 nm) photoresist that has high optical transparency and is well suited for applications where it is imaged and permanently left in place. Figure 2 shows the chemical structure of SU8. Because the resist has a high functionality, a high degree of crosslinking can be achieved, resulting in a high aspect ratio and straight sidewall structure in lithographic applications. SU8 has been extensively used to fabricate high-aspect ratio structures such as micro-electro-mechanical systems (MEMS), micro fluidic devices, etc.[6–10] Triarylsulfonium (TAS) salt (Aldrich, Milwaukee, WI), with a fixed concentration of 10 wt%, was used as the photosensitive compound to initiate the cationic polymerization of SU8 epoxide ring. γ-Butyrolactone (GBL) and propylene glycol monomethylether acetate (PGMEA) were used as the solvent and developer, respectively. Two BT nanopowders, with average particle sizes of 65 nm (small nanoparticles) and 590 nm (large nanoparticles), respectively, were used in the SU8 composite photoresist in order to increase its dielectric constant.

The high dielectric constant composite photoresist was obtained by a two-step mixing procedure. The formulations were first ultrasonicated for 1 h, then ball-milled with yttrium-stabilized zirconia beads at a rate of 220 rpm for 24 h.

UV-Vis spectroscopy characterization of BT nanoparticles

The UV-Vis spectroscopies of small and large BT nanoparticles were characterized by a UV-Vis spectrophotometer (DU520, Beckman, Fullerton, CA), from a wavelength of 300–800 nm. The particles were dispersed in GBL, which has almost no UV absorption in this range.

Microfabrication process and characterization

To study the effects of BT nanoparticle size, filler concentration, and UV irradiation dose on the photopolymerization of the composite photoresist, glass substrates were used to fabricate the testing structure. First, the glass substrates were cleaned by oxygen plasma in a reactive ion etcher (RIE, Plasma Therm, St. Petersburg, FL). The conditions were as follows: power 300 W, flow rate 30 sccm, pressure 150 mTorr, and time 10 min. Oxygen plasma cleaning can effectively improve the adhesion of composite photoresist on glass substrates. Because spin coating cannot produce very thick composite films uniformly, we used a bar coating method instead to deposit composite photoresist of about 50 μm thickness. The composite photoresist was then prebaked at 95°C for 1 h to evaporate solvent GBL. To study the photopolymerized thicknesses, back-side UV exposure was utilized to initiate the crosslinking of SU8 photoresist, as this can guarantee good adhesion of a polymerized structure on the substrate. The back side of composite-coated glass substrate was exposed to a UV source through quartz masks by a UV Mask Aligner (MA-6, Karl Suss, Waterbury Center, VT). The exposure was at I line, with a wavelength of 365 nm. The exposed composite photoresist was then postbaked at 95°C for 30 min in order to complete the acid-catalyzed cationic polymerization. Then the patterned structure was developed in PGMEA to remove unexposed composite photoresist. Ultrasonication for a few minutes was required to obtain a good and clear structure. Isopropyl alcohol (IPA) was used to rinse the developed high dielectric constant composite photoresist. The

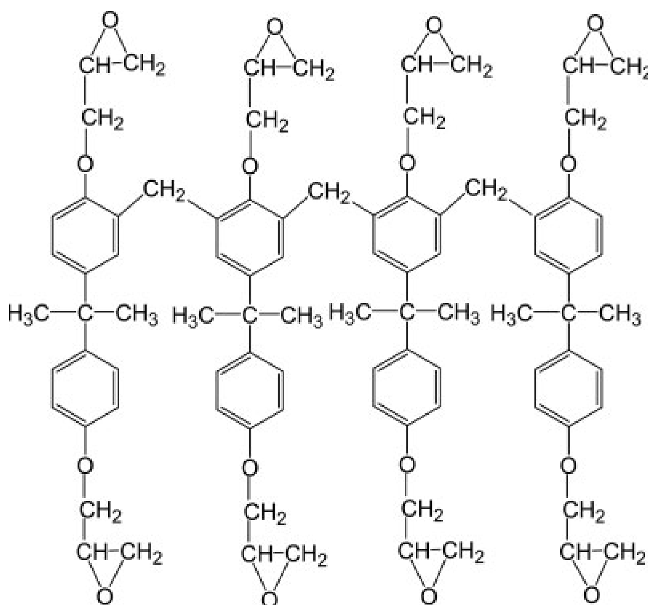

Figure 2 Chemical structure of SU8.

thicknesses of photopolymerized structure were then measured by a profilometer (KLA-Tencor P15). Figure 3 shows the photodefined pattern of SU8 composite photoresist containing 40 vol% small BT nanoparticles. The exposure dose was 1200 mJ/cm^{-2} and the polymerized thickness was $\sim$ 1.52 μm.

To measure the dielectric properties of composite photoresist, parallel plate capacitors were fabricated on Cu-coated glass substrates. First, a thin layer of titanium (200 Å) and copper (3000 Å) was deposited on the glass substrate as the bottom electrode of capacitors by a DC sputterer (CVC Products, Rochester, NY). Then the SU8 composite photoresist was spin-coated onto the Cu-coated glass substrate. The next processing steps were similar to the previously described method for processing SU8. The only difference is that the sample was exposed to 365 nm UV light in the front-side mode. Finally, the DC sputterer was used to deposit another layer of copper (3000 Å) as the top electrode onto the material through a shadow mask. The capacitance and dissipation factor of the capacitor were then measured with an HP 4263A LCR meter at a frequency of 10 KHz to 10 MHz. Figure 4 shows an example of parallel plate capacitors fabricated with SU8 composite photoresist containing 40 vol% small BT nanoparticles.

Embedded capacitors were demonstrated on a flexible polyimide substrate. Interdigitated electrodes were prefabricated on the flexible polyimide film. Then the high dielectric constant composite photoresist was spin-coated on the substrate and patterned with the same processing method as described above for SU8.

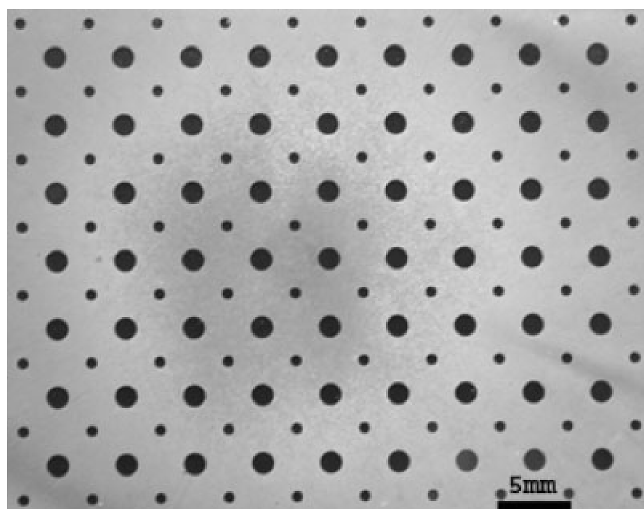

Figure 3 Photodefined pattern of SU8 composite photoresist containing 40 vol% small BT nanoparticles. The exposure dose was 1200 mJ/cm^{-2} and the polymerized thickness was about 1.52 μm.

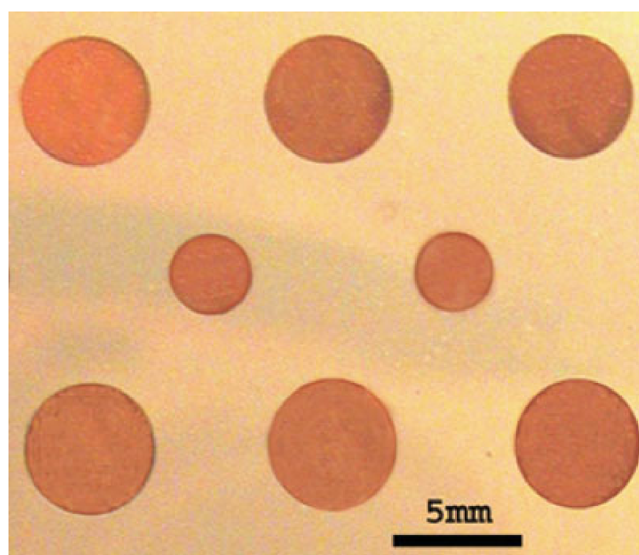

Figure 4 Parallel plate capacitor fabricated with SU8 composite photoresist containing 40 vol% small BT nanoparticles. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSIONS

In polymer-ceramic high-k composites, polymer matrices are used to provide the low temperature processing compatibility in line with the organic PCB (mostly epoxy-based) manufacturing processes. Epoxy has often been used as the polymer matrix in conventional high-k polymer-ceramic composites. Because SU8 is a high functionality epoxy, using SU8 as the matrix for high-k composite photoresist can ensure good compatibility with the PCB manufacturing.

SU8 photoepoxy can be polymerized by cationic photopolymerization, which is typically induced by Lewis acid. In our system, the Lewis acid was generated by exposing triarylsulfonium salt to the UV source. The photogenerated acid can catalyze epoxy ring opening reaction, and thereby initiate the cationic crosslinking of SU8. BT nanoparticles are used to provide high dielectric constant in the nanocomposites. However, BT nanoparticles can absorb UV light, which has a strong effect on the photopolymerization behavior of the SU8 composite photoresist. Figure 5 shows the UV-Vis spectroscopy of 0.01 wt% small (65 nm) and large (590 nm) BT nanoparticles in solvent GBL. GBL has very little UV absorption in the measurement wavelength range and was used as the reference. As shown in Figure 5, small and large BT nanoparticles show different UV-Vis absorption behaviors. The large BT nanoparticles show a high and almost constant UV absorbance in the whole measurement wavelength range from 300–800 nm. On the other hand, the UV absorption intensity of small nanoparticles decreases dramatically as the UV wavelength increases. When the wavelength is above 441

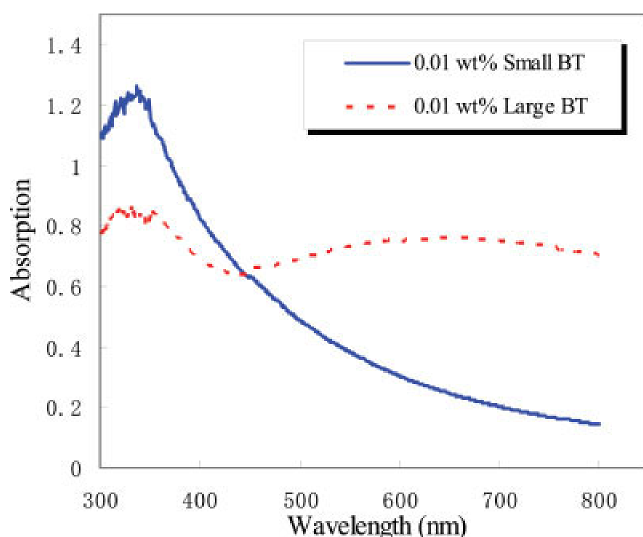

Figure 5 UV-Vis spectroscopy of small and large BT nanoparticles in solvent. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

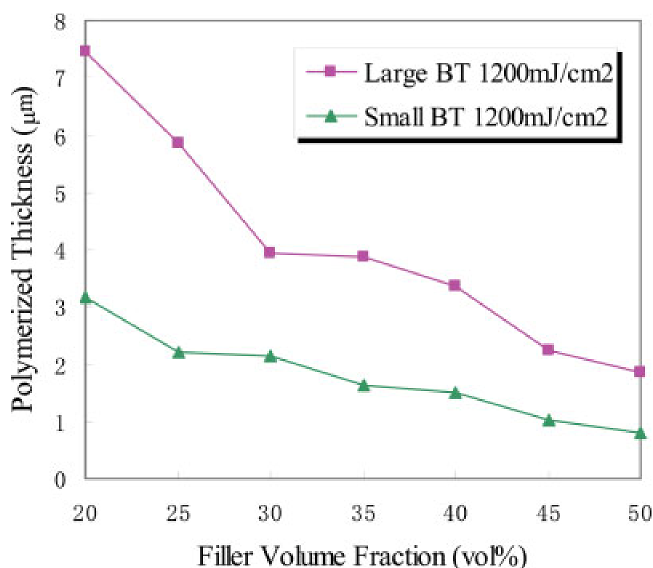

Figure 6 Photopolymerized thickness versus BT filler loading in the SU8 composite photoresist. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

nm, the large BT nanoparticles have stronger absorption than the small BT nanoparticles. In this wavelength range, the size of large BT particles is comparable to the UV wavelength. However, when the wavelength is below 441 nm, the small BT particles show stronger UV absorption. SU8 photoresist is typically exposed at 365 nm. At this wavelength, the UV absorbance of small BT particles is much stronger than the large BT particles. Overall, the BT nanoparticles have quite strong UV absorption, which can significantly hinder the generation of Lewis acid during UV exposure and thereby affect the photopolymerization reaction of SU8 composite photoresist.

In order to study the effect of BT nanoparticle inclusion on SU8 photopolymerization thicknesses, SU8 composite photoresist was deposited on glass substrates and then exposed in the back-side mode. For neat SU8, an exposure dose of 300 mJ/cm^{-2} can polymerize SU8 of ~ 100 μm thick. However, even after 400 mJ/cm^{-2} irradiation the composite photoresist cannot be adequately polymerized to form dielectric film. Figure 6 shows the photopolymerized thickness after 1200mJ/cm^{-2} irradiation versus BT filler loading in the SU8 composite photoresist. The polymerized thicknesses decrease with the inclusion of more BT nanoparticles. The inclusion of small BT nanoparticles leads to a much smaller polymerized thickness when compared with the inclusion of large BT nanoparticles at the same filler loading. This change is associated with the UV absorbance of the BT nanoparticles. Small BT particles have stronger absorbance at the 365 nm exposure wavelength, which reduces the depth that the UV light can penetrate through in the SU8 composite photoresist. Therefore, the polymerized thickness is smaller with the inclusion of small BT nanoparticles.

The photopolymerized thickness of composite photoresist also depends on the irradiation dose. A higher polymerized thickness can be obtained by increasing the exposure dose. As illustrated in Figure 7, for a composite containing 40 vol% large BT nanoparticles the polymerized layer thickness increased from 3.35 μm to 5.08 μm when the exposure dose increases from 1200 to 1800 mJ/cm^{-2}. The dotted trend lines in Figure 7 indicate that the photopolymerization in composite photoresist follows a logarithmic rule. Based on the Beer-Lambert law, the photopolymerization model predicts that the photopolymerized thickness

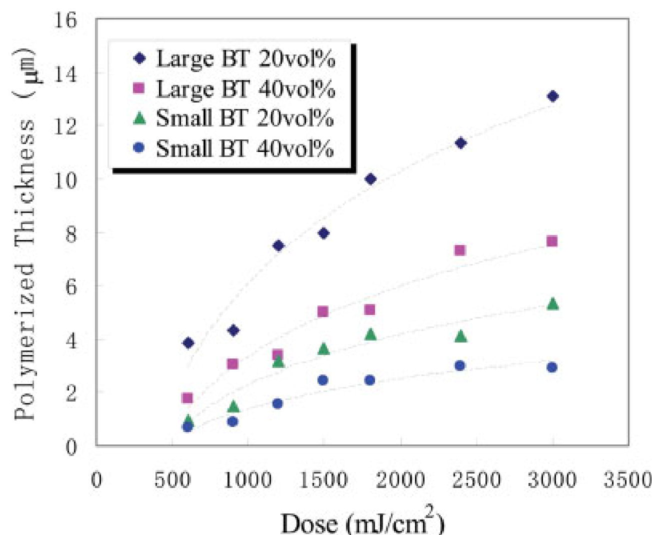

Figure 7 Photopolymerized thickness as a function of irradiation dose. The dotted trend lines are calculated according to logarithmic rule. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(T_p) is proportional to the penetration depth (P_d) and logarithm of exposure dosage (D)[11,12]:

$$T_p = P_d \ \mathrm{In}(D/D_c) \quad (1)$$

where D_c is the threshold dosage required to start the photopolymerization.

Table I shows a comparison of the penetration depth and threshold dosage calculated based on Equation 1. The penetration depth, P_d, is determined by the BT nanoparticle size as well as the filler loading. Large BT nanoparticles, which have less UV irradiation absorbance at 365 nm, result in a larger penetration depth. For the same size BT nanoparticles, a higher filler loading leads to a smaller penetration depth. Similarly, the threshold dosage D_c is also related to the BT nanoparticle size as well as the filler loading. However, the dependency is not as strong as for P_d, and all of the threshold dosage values are close to 400 mJ/cm^{-2}. The threshold dosage is slightly larger for composite photoresist filled with small BT nanoparticles because of the stronger UV absorbance of small BT nanoparticles at 365 nm. Table I also shows a higher threshold dosage is required at a higher BT loading.

The dielectric constant of SU8 composite photoresist can be improved by the inclusion of BT nanoparticles. For neat SU8, the dielectric constant is about 3.5. With the addition of 50 vol% BT nanoparticles, the dielectric constant (@10 KHz) can be enhanced to 44 and 46 for small and large BT, respectively, as shown in Figure 8. The dielectric constant and dissipation factor of SU8 composite photoresist are almost same for large and small BT at the same filler loading. A modified Lichteneker equation is often used to predict the dielectric constant of composites that have high volume fraction of ceramic and also a larger difference in the value of relative permittivity of ceramic and polymer.[3]

$$\log \varepsilon = \log \varepsilon_1 + v_2(1-k)\log\left(\frac{\varepsilon_2}{\varepsilon_1}\right) \quad (2)$$

where k is a fitting factor, which is typically 0.3 for well dispersed suspensions; ε_1 is the dielectric constant of the polymer matrix; ε_2 is the dielectric constant of the filler. According to the above equation, the dielectric constant of composite is dependent on the dielectric constant of ceramic phase as well as on

TABLE 1
Comparison of the Penetration Depth and Threshold Dosage of SU8 Composite Photoresist

BT Size	Vol. Fraciton (vol%)	P_d (μm)	D_c (mJ/cm^{-2})
Large	20	6.06	348
Large	40	3.81	416
Small	20	2.72	430
Small	40	1.64	432

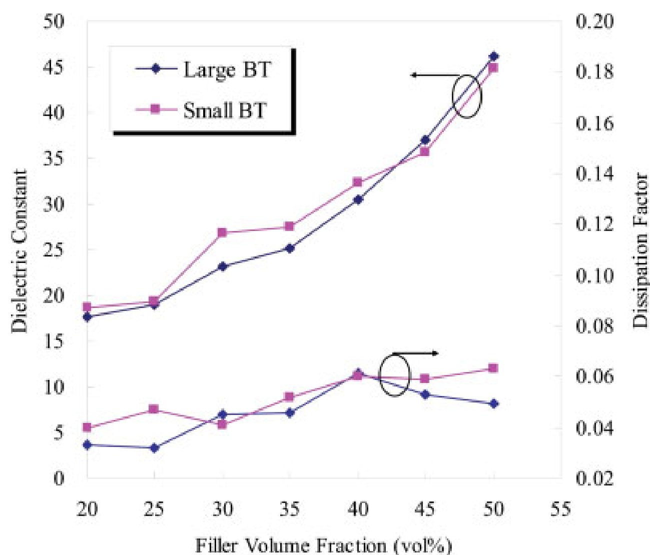

Figure 8 Dielectric constant and dissipation factor of SU8 composite photoresist versus the BT nanoparticles volume fraction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the polymer phase. It is reported that the dielectric properties of BT nanoparticles have very strong size dependency. The dielectric constant of 590 nm BT nanoparticles is above 3000; however, it is less than 1000 for 65 nm particles.[13] From our results, such a difference in the dielectric constant of BT nanoparticles does not yield significant differences in the dielectric properties of the SU8-BT nanocomposites. This suggests that as long as the dielectric constant of the filler is high enough, there will not be dramatic differences in the dielectric constant of its composites even if the dielectric constant of filler is quite different. Because by using smaller particles one can obtain

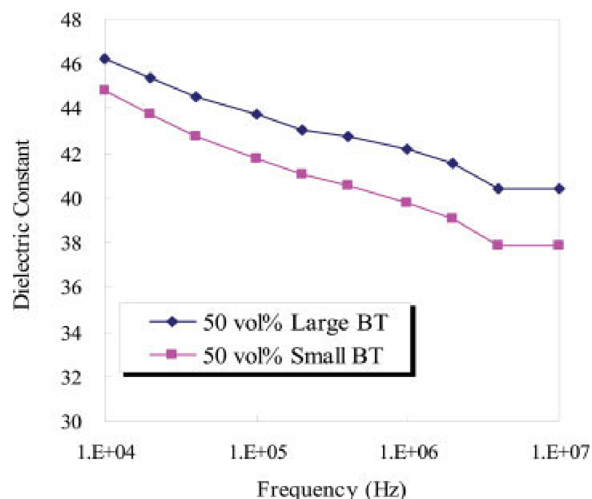

Figure 9 Frequency responses of the dielectric constant of SU8 composites photoresist. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

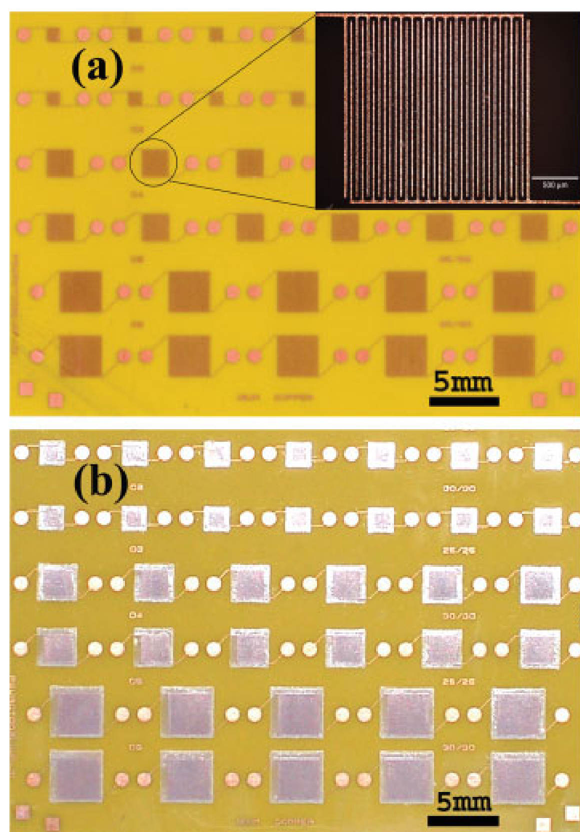

Figure 10 Image of (a) a test coupon with interdigitated capacitor electrodes on a flexible polyimide substrate and (b) embedded capacitors fabricated on the flexible polyimide substrate. The inset in (a) shows the detailed structure of interdigitated electrodes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

a thinner layer of dielectric coating and thereby higher capacitance density, smaller particles are recommended for embedded capacitors when applicable.

The frequency responses of the dielectric constant of SU8 composites photoresist are shown in Figure 9. The dielectric constant of SU8 composite photoresist decreases slightly when the frequency increases.

The SU8 composite photoresist shows a high dielectric constant at high filler loadings, and it can be processed by a straightforward photolithography method. Therefore, SU8 composite photoresist is suitable for embedded capacitors on organic substrates. Figure 10(a) shows the image of a test coupon with interdigitated capacitor electrodes fabricated on a flexible polyimide substrate. The inset shows the detailed structure of electrodes. The thickness of Cu electrodes is 12 μm. Figure 10(b) shows the embedded capacitors fabricated on the flexible polyimide substrate by the photolithography method. The dielectric is SU8 composite photoresist filled with 40 vol% large BT nanoparticles. Because the electrode thickness is large (12 μm), a dose of 4500 mJ/cm^{-2} was used to ensure complete polymerization of the composite photoresist that covered the whole depth of the electrodes. The dielectric constant was measured to be about 31, which is similar to the value from parallel plate capacitor measurement.

CONCLUSIONS

A novel, photodefinable, high dielectric constant composite material was developed. It consisted of SU8 as the polymer matrix and barium titanate (BT) nanoparticles as the filler. It was found that the smaller BT nanoparticles had stronger UV absorbance at the exposure wavelength, and thereby led to smaller photopolymerization thicknesses in the composite photoresist. As the BT filler loading increased, the photopolymerization thickness decreased as well because of the absorption of BT nanoparticles. The SU8 composite photoresist showed a high dielectric constant at high BT filler loadings. The BT nanoparticle size does not have a significant effect on the dielectric properties of composite photoresist. Embedded capacitors using the novel high dielectric constant SU8 composite photoresist were demonstrated on a flexible polyimide substrate by UV lithography method.

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