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Dielectric Properties of Multi-layer High-K Polymer Composite Films

Wataru Sakai and C. K. Chiang
Polymers Division, National Institute of Standards and Technology
Gaithersburg, Maryland 20899-8541, US

ABSTRACT

The electrical properties of thin polymer films are key parameters in the design of both smaller and faster circuit devices in the microelectronics industry. In this study, we made a three-layer film structure, ABA', to investigate the dielectric interaction between two high-K dielectric polymer thin films, A and A', as a function of the thickness of the middle B layer. The Cole-Cole plot showed clear changes with the thickness of the middle B layer. The total capacitances were evaluated with a simple serial three capacitances model. This ABA' structure is thought to be very useful for studying mechanical and thermal properties of thin polymer film system.

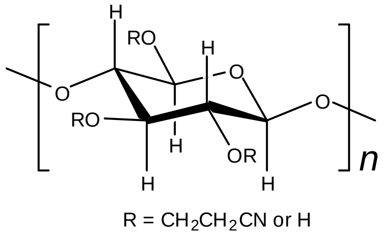
INTRODUCTION

High dielectric constant (high-K) polymer films are crucial for the development of high-speed wireless communication equipment. High-K insulating films are particularly useful for distributing and storing the electric energy in the vicinity of devices operated at high frequencies (low RC time constant). Recently, Popielarz et al showed an empirical logarithmic mixing rule for two-phase composite materials in which high-K ceramic fillers are dispersed in a polymer matrix [1]. As the volume concentration of the high-K filler increased, the effective dielectric constant increased in the frequency region, 10^2 Hz to 10^{10}Hz. These phenomena were explained by sum of serial or parallel capacitance model and the rule has not been elucidated clearly. It is thought that the design and modify of interfacial interaction between these high-K particles may help in promote the dielectric constant of advanced polymer composites. [2].

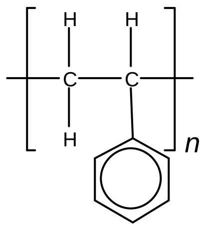
In this study, we made a simple three-layered structure, ABA', to investigate the dielectric interaction between two high-K dielectric polymer thin films using broad band dielectric measurement from 10^{-3} Hz to 10^7 Hz. The middle B layer of low-K polymer served as an interface layer to control the distance. Experimental results were also compared with the theoretical simulation and discussed. Since multi-layered polymer films are also a basic structure for many device applications, this study is also useful to understand the fundamental material science that occurs at thin film interfaces [3].

MATERIALS

The high-K polymer for layer A and A' was a cyanide resin (CR-S, Shin Etsu Chemical Co. Ltd) while low-K B layer was poly(styrene) (PSt, NIST SRM, No.705a) [4]. These polymers were used as received, without further purification. The dielectric constants for CR-S and PSt were 20 and 2.5 at 1 kHz at 25°C, respectively.



1. CR-S



2. PSt

EXPERIMENTS

Sample Preparation

Figure 1 shows the layer structure of sample. First, the bottom aluminum electrode was put on the glass substrate by vacuum deposition. Second, the first CR-S layer (A) was deposited by solvent casting from an acetone solution. Third, the middle PSt layer (B) was deposited by spin coating, with various concentrations of PSt in a toluene solution to control the film thickness. Fourth, the top CR-S layer (A') was deposited by spin coating method: Finally, the top circular electrode was applied by vacuum deposition. The sample was dried at 100°C for 3 h between each deposition of a polymer layer to remove the residual solvent. Because CR-S is not soluble in toluene and likewise for PSt in acetone, the polymer layers should not intermix significantly during the sample preparation. The thickness of both electrodes was 300 nm, and the diameter of top electrode was 2 mm.

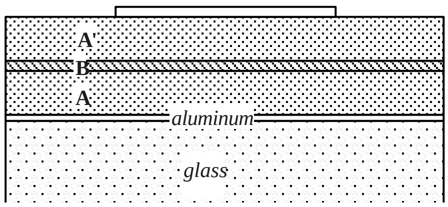


Figure 1. Sample structure of three-layer polymer composite.

Measurements

The thickness of each polymer layer was measured using laser scanning confocal microscope (LSCM, Carl Zeiss, LSM-512 system) with 50X and NA = 0.80 objective at 543 nm wavelength. Dielectric measurements were done on a Hewlett-Packard 4194A analyzer for the frequencies from 10^2 Hz to 10^7 Hz, and a Gamry Framework system from 10^{-3} Hz to 10^4 Hz. The data from these two instruments are usually in good agreement in the overlapping frequency region. The combined standard uncertainties of these data were about 10 % of the measured values.

RESULTS AND DISCUSSION

Sample Structure

Table I shows the thickness of each polymer layer in the sample measured by a confocal microscope. The resolution for this measurement was ~50 nm. The distance from the bottom electrode and the polymer surface was measured each time a polymer layer was deposited and dried, and the layer thickness is then obtained by subtraction . This is because the reflected intensity from the interface between CR-S and PSt layers was much weaker than the interfaces with aluminum electrodes. The difference of refractive index between CR-S (n_{633nm} = 1.50) and PSt (n_{633nm} = 1.58) are too small to resolve this interface. In this study, however, the thickness of the middle PSt layer for TL5 and TL6 were not available because of the resolution limit. Thus, B

Table I Thickness of each polymer layer in three-layer polymer composite

Films	A (CR-S) (μm)	B (PSt) (μm)	A' (CR-S) (μm)
TL1	1.00	3.20	0.70
TL2	1.00	1.00	0.90
TL3	0.80	0.50	0.80
TL4	1.20	0.20	0.75
TL5	0.85	(0.10)*	1.25
TL6	0.90	(0.05)*	0.70
averaged	0.98		0.79

* The thickness of PSt for TL5 and TL6 were unavailable but estimated fromthe solution concentration used for spin coating.

layer thickness in TL5 and TL6 was tentatively estimated from the concentration-thickness curve for PSt spin coating, which was separately measured using various concentrations of PSt toluene solutions and approximately extended to smaller thickness region.

Dielectric Measurements

Figure 2 shows the frequency dependencies on the real and the imaginary capacitances of TL4 sample, which has 0.20 μm PSt layer. The measurements were done from higher to lower frequency. There seems large increases in the low frequency region below 1 Hz for both the real and the imaginary curves. At this time, there is no clear evidence but these phenomena are maybe due to the conductive property of sample.

The inset in Figure 2 shows the Cole-Cole plot obtained from the frequency dependence data in Figure 2. As shown in the inset, the curve can be divided into two regions at about 1 kHz. The right side of the curve continues going up with decreasing frequency, which maybe related to the electrode and CR-S layer in the sample. On the other hand, the left side of the curve shows a part of the semi-circle as shown by dashed line in the inset. This semi-circle should come from the capacitance of the PSt polymer layers in the sample.

Figure 3 shows Cole-Cole plots in log-log scale for all TL samples. As the thickness of the middle PSt layer decrease from TL1 to TL6, the real capacitance became much larger. Moreover, the size of the semi-circle, which can be seen at the left side of each curve, became much larger in a linear scale. This size change of semi-circle is related to the change of capacitance property of the middle PSt layer. Qualitatively, we observed the capacitance increased with decreasing the thickness of PSt film as we expected. In addition, we also observed the increase of the minimum point of the dielectric loss as the thickness of the PSt film decreased.

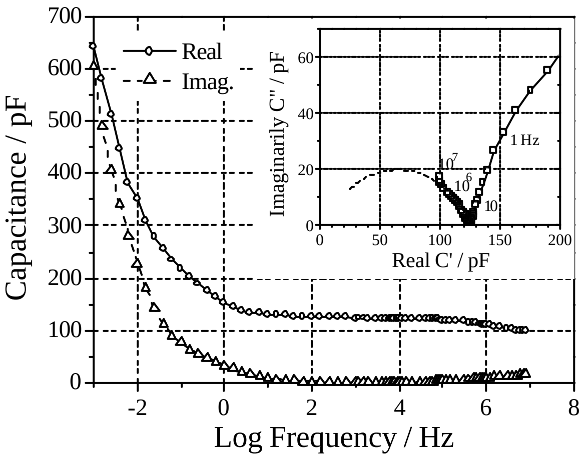


Figure 2. Frequency dependences on real and imaginarily capacitances for TL4 sample. The inset shows Cole-Cole plot from the same data.

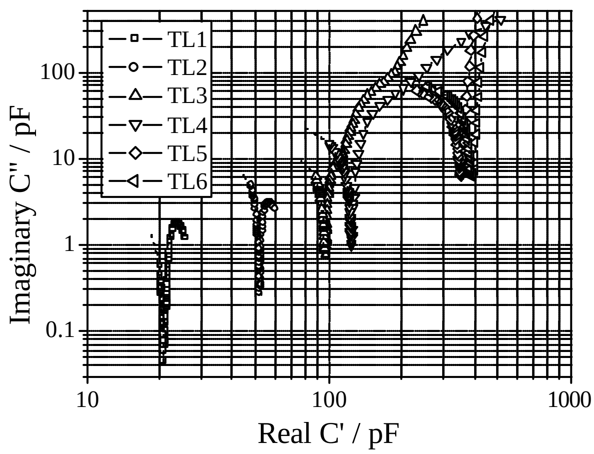


Figure 3. Cole-Cole plots in log-log scale for all TL samples. The dashed lines indicate part of semi-circle.

Model Simulation

In this study, we applied a simple serial circuit model to the three-layer polymer composite to simulate the total capacitance. The circuit is made of three polymer film capacitances, A, B, and A', without any interfacial interactions, as shown in Figure 4. The total capacitance is calculated as following,

$$\frac{1}{C_{total}} = \frac{1}{C_A} + \frac{1}{C_B} + \frac{1}{C_{A'}} \quad (1)$$

where C_n is a capacitance of n layer. For example, if it is assumed that the thickness of A layer and A' layer are 0.98 μm and 0.79 μm, respectively, as shown in Table I, the total capacitance of the three-layer composite at 1 kHz is shown by the dashed curve in Figure 5.

Each predicted point for each sample was calculated using the equation above and each layer thickness measured as shown in Table I and indicated in Figure 5 with triangle symbol. The experimental capacitances for sample TL1 to TL6 at 1 kHz are plotted as black circles. For the samples TL1 to TL4, the experimental data agree well with the predicted points. This indicates that the serial model in Figure 4 is very good model to describe the dielectric property of three-layered composite and that there are no significant interfacial interaction between layers. However, as for TL5 and TL6 that have nano-film at the middle layer, the experimental results are higher than both the simulated and calculated. It appears that the dielectric constant has been enhanced. However, we were not able to determine the thickness of these samples precise enough to confirm those discrepancies. Further investigation of the nanometer range films will help to establish the effect.

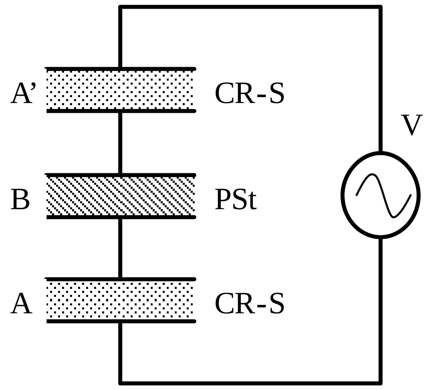


Figure 4. Serial circuit model for three-layer polymer composite.

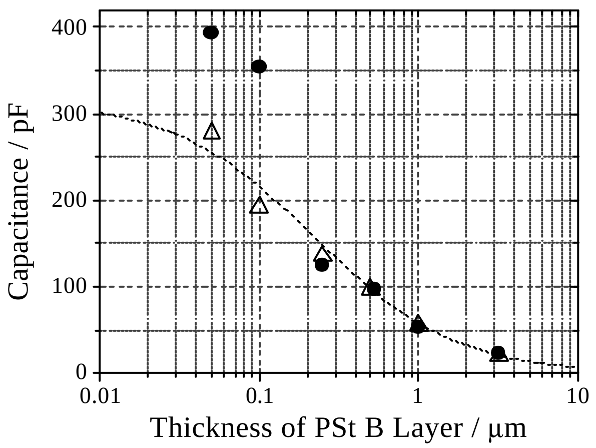


Figure 5 Thickness dependence on total capacitance for three-layer structure: -- - -, calculated curve using thickness A = 0.98 μm and A' = 0.79 μm; ●, experimental data; and △, predicted using those thickness data in Table I. The calculation was done using simple serial model shown in figure 4.

SUMMARY

The dielectric properties of three-layer polymer thin-film system were investigated to understand the electrical interactions between thin polymer films in the frequency range from 10^{-3} to 10^{7} frequency. The system consisted high-K CR-S polymer for the first and the third layer, and low-K PSt for the middle layer. When the thickness of middle PSt layer was decreased, the total capacitance also increased. Moreover, the higher frequency arc from the dielectric property of thin polymer layers became larger. The thickness change of the middle layer was simulated using a simple circuit model made of three serial capacitances. In this study, the multiplayer film system with the thickness of the middle layer down to 1 micron obeys a simple RC model. We were not able to conclude the effect when the middle layer film reaches nanometer size. For the further study more precise polymer thin film structural analysis are need.

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4. Certain instruments and materials identified in this paper are to adequately specify experimental details. In no case does it imply endorsement by NIST or that those are necessarily the best for the purposes specified.