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Flexible, transparent dielectric capacitors with nanostructured electrodes

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We have prepared flexible, transparent, dielectric capacitors by spraycasting very thin networks of single walled nanotubes (SWNTs) or silver nanowires (AgNWs) onto either side of free-standing polymer films. Impedance spectroscopy showed these structures to behave as a capacitor in combination with a series resistance. Those capacitors with SWNT electrodes displayed optical transmittance between 57% and 74%, capacitances ranging from 0.4 to 1.1 μF/cm^2 and series resistances ranging 400 Ω/□-10 kΩ/□. However, using AgNW electrodes gave similar transmittance and capacitance but series resistance as low as 60 Ω/□. Finally, the properties of these capacitors were invariant under flexing. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4750059]

Transparent conducting materials[1,2] are important for a range of applications from smart windows to solar cells. Over the last decade, much work has been carried out to develop new transparent conductors. This is partly due to continuing increases in the cost of indium which, many fear, will render the most common transparent conductor, indium tin oxide (ITO), economically unviable. However, equally important is the fact that, due to its brittle nature,[3] ITO is unsuited to flexible electronic applications.

The search for materials which can be formed into thin films that combine high transparency, low sheet resistance, and flexibility has largely focused on nanostructures such as graphene,[4–7] carbon nanotubes,[8–11] or metallic nanowires.[12–16] Such materials are generally deposited from solution as disordered networks of individual nano-objects. This process is relatively cheap, scalable and can be achieved at low temperature. Alternatively, graphene monolayer films can be grown continuously by chemical vapour deposition (CVD) on meter wide rolls.[4] In the case of metallic nanowires[14,15,17] and CVD grown graphene,[4] films with transparency of >90% and sheet resistance <100 Ω/□ can routinely be achieved. A considerable advantage of these materials is that their electrical properties are remarkably stable under mechanical flexing,[12,18] making them ideal for future flexible electronics. As a result, they have been used to prepare a range of working devices including transparent supercapacitors[19,20] and batteries,[21] solar cells,[17] light emitting diodes,[22] and touch screens.[23] However, it is notable that virtually no attention has been given to demonstrating flexible, transparent versions of one of the simplest electronic component – the dielectric capacitor.

Transparent capacitors will be important for applications such as storage of energy from solar cells[24] and all-transparent circuitry[25] in applications such as head-up-displays. However, very little work has been done in this area with the vast majority of papers focusing on rigid capacitors, typically with conducting oxide electrodes.[24,26–28] Flexible, transparent capacitors will require both dielectric and electrodes to be flexible and transparent. Polymer dielectrics are well known[29] and will fulfil these criteria. Less straightforward will be the choice of electrode. However, it is likely that networks of conducting nanomaterials will be ideal candidates for flexible, transparent capacitor electrodes. In fact, one paper has described transparent, flexible capacitors with nanotube electrodes.[30] However, the dependence of properties on electrode thickness and applied frequency were not shown and no detailed analysis was given. Particularly important will be to characterise and minimise the series resistance of transparent capacitors. It is likely that this parameter will be relatively high because ultra-thin electrodes will be required to achieve high transparency. In the current work, we demonstrate flexible, transparent capacitors with polymer dielectric and both carbon nanotube and silver nanowire (AgNW) electrodes. We demonstrate how transparency, capacitance and, in particular, series resistance depend on the nature of the electrode.

To fabricate transparent, parallel electrode capacitors (Figure 1(a)), we first produced free-standing polymer dielectric films by dropcasting a solution of polyvinyl acetate (PVAc in tetrahydrofuran, THF, C = 60 mg/ml) into a Teflon tray. This was then left to dry overnight, followed by further drying in an oven at 50 °C for 8 h resulting in relatively uniform, free-standing polymer films. The film thickness was controlled by the volume of solution deposited and was varied between 35 μm and 90 μm. To deposit the electrodes, single walled nanotubes (SWNTs, produced by Iljin group) were dispersed in water with the aid of the surfactant sodium dodecyl sulphate, SDS (C_{SWNT} = 0.15 mg/ml, C_{SDS} = 10 mg/ml). This dispersion was deposited onto both sides of the polymer film by spraycasting using a Harder & Steenbeck infinity airbrush secured to a JANOME JR2300N robot.[14] Spraying was performed using a 30 psi back-pressure and a flow-rate of 2.5 mm^3/s, with the polymer film on a hotplate at 50 °C. The resulting capacitor was stored under ambient conditions for 24 h before measurements were made. We note that these components are very robust and can be handled, manipulated, and flexed without apparent damage.

Scanning electron microscopy (SEM, Figures 1(b)–1(d)) measurements (Zeiss Ultra, samples coated with a 5 nm thick

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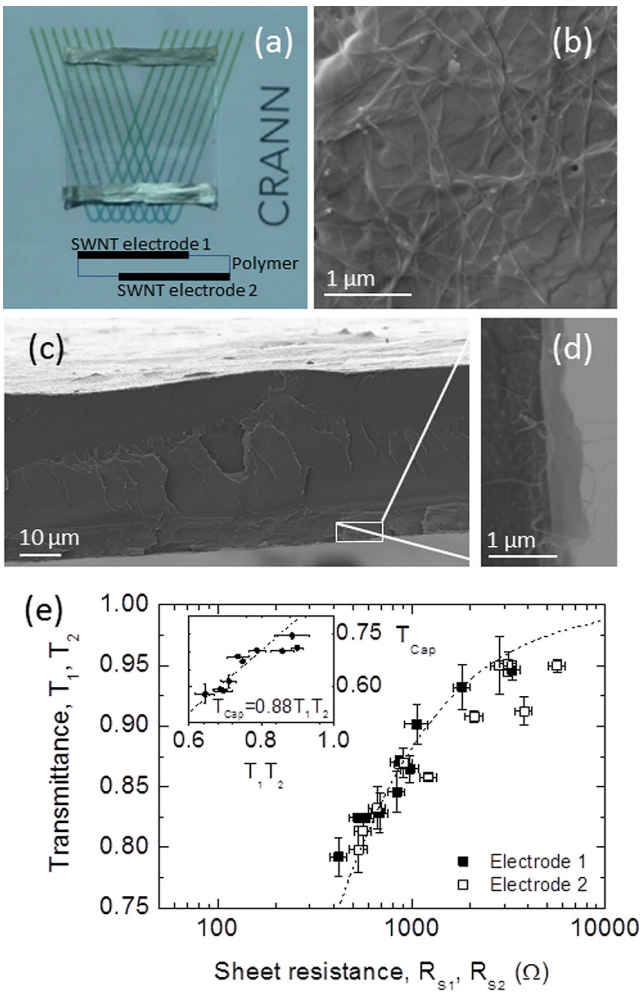

FIG. 1. (a) Photograph of a free-standing transparent capacitor ($T_{Cap} = 74\%$). The metallic bands at top and bottom are silver paint to facilitate connection to external circuitry. Inset: Schematic of the capacitor structure. (b) SEM image of a spray-coated SWNT electrode at the surface of the polymer dielectric. (c) SEM image of a fracture surface of a typical capacitor. (d) Zoomed image of the capacitor edge showing protruding nanotubes. Note, (d) had been rotated by 90° relative to (c). (e) Transmittance versus sheet resistance, R_S, for individual nanotube networks, sprayed onto PET substrates at the same times as the capacitor electrodes were deposited. Inset: Overall transmittance of capacitors as function of product of individual network transparencies.

layer of a Ti-Au alloy) show the deposited electrodes to consist of a very thin network of nanotube bundles similar to those prepared for other transparent electrode applications.[1,18,31,32] By comparison with previous work, we expect these networks to be ~5–20 nm thick.[14,19]

As the capacitor electrodes were being deposited, a piece of PET was simultaneously sprayed (one side only) with SWNTs under identical conditions to facilitate the characterisation of the electrodes individually. The transmittance of these individual networks (with PET film as reference) as well as that of the capacitors themselves (no reference) was measured using a Cary Varian 6000i spectrophotometer. Broad spectra similar to those reported previously[18] were found in all cases. The sheet resistance, R_s, of the individual electrodes was measured using a Keithley source meter. The transmittances of the individual electrodes (T_1, T_2, 550 nm) are plotted against electrode sheet resistance (R_{S1}, R_{S2}) in Figure 1(e). Here, the subscripts 1 and 2 represent individual electrodes that were sprayed concurrently with the capacitor electrodes, but on PET. Such data are well described by the expression[31,33]

$$T = \left(1 + \frac{Z_0}{R_S}\frac{\sigma_{Op}}{\sigma_{DC,B}}\right)^{-2}, \quad (1)$$

where $Z_0 = 377\ \Omega$ and in this case,[31] the electrode figure of merit is $\sigma_{DC,B}/\sigma_{Op} \sim 3$. This is significantly below the state of the art for nanostructured transparent conductors[31] but will be sufficient for this study.

We expect the transmittance of the capacitor as a whole to be given by $T_{Cap} = T_P T_1 T_2$, where T_P is the transmittance of the polymer film. This is shown to be the case in Figure 1(e) inset which predicts $T_P = 0.88$, in good agreement with measurements of PVAc films of similar thickness (45–75 μm).

Impedance (Z) spectra (Gamry 600, $V_{AC} = 25$–100 mV) were measured for a range of capacitors with various polymer and electrode thicknesses (for simplicity, the thicknesses of electrodes 1 and 2 were equal). Shown in Figure 2(a) is a typical data set showing the modulus of the impedance, |Z|, plotted as a function of angular frequency, ω, while Figure 2(b) plots the phase, ϕ, versus ω (NB $Z = Z_{Re} + iZ_{Im} = |Z|e^{i\phi}$). These curves are qualitatively as expected for a series RC combination[34] (inset Figure 2(a) inset). Such a circuit would have impedance

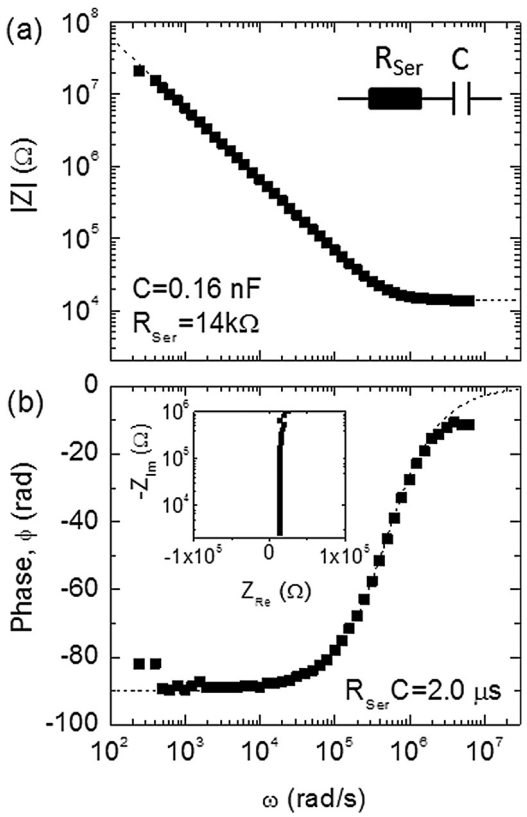

FIG. 2. Impedance data for a typical capacitor. (a) Impedance amplitude, |Z|, and (b) phase angle, ϕ, as a function of angular frequency, ω. The dashed lines represent fits to the model describing a series capacitor-resistor combination (inset in (a)). Fit constants are given in the figure. The inset in (b) represents a Cole-Cole plot of the real versus imaginary impedance. This plot shows a delta function, as expected for a series capacitor-resistor combination.

$$Z = R_{Ser} - i/\omega C, \tag{2}$$

where R_{Ser} is the series resistance and C is the capacitance. In this scenario, the impedance amplitude and phase are given by

$$|Z| = \sqrt{R_{Ser}^2 + 1/\omega^2 C^2} \tag{3}$$

and

$$\phi = \tan^{-1}(1/\omega R_{Ser} C). \tag{4}$$

Fitting these equations to the data gives very good agreement, in this case with $R_{Ser} = 14\,k\Omega$, $C = 0.16\,nF$, and $R_{Ser}C = 2\,\mu s$ (Figures 2(a) and 2(b)). Furthermore, the Cole-Cole plot exhibits a delta function, as expected for such an equivalent circuit (Inset Figure 2(b)).[34]

Similar data sets for a number of capacitors with separately varying electrode and dielectric thicknesses were analysed to give the capacitance per overlapping electrode area, C/A, and series resistance R_{Ser}. To facilitate comparison between different capacitors, we have rescaled the measured series resistances to represent square capacitors (units: Ω/□). The observed data are plotted in Figure 3(a). It is clear from this data that R_{Ser} depends solely on the electrode geometry while C/A depends solely on the polymer thickness. We can show this more clearly by noting that C/A is expected to scale with the thickness, t_{poly}, of the dielectric material as

$$C/A = \varepsilon_r \varepsilon_0 / t_{poly}. \tag{5}$$

That this is the case is shown in Figure 3(b), with this data consistent with a dielectric constant of $\varepsilon_r = 3.6$, close to the expected value for PVAc of ~3 at room temperature.[35] We note that the capacitances obtained are not particularly high. This is largely due to the relatively low dielectric constant of PVAc and the relatively high thickness of the polymer dielectric. Both of these factors should be relatively easy to improve using existing materials.[29]

It is also worth considering the relationship between T_{CAP} and both C/A and R_{Ser}, as shown in Figures 3(c) and 3(d). Varying the thickness of the polymer (open symbols) changes C/A but hardly affects T or R_{Ser}. However, changing the thickness of the SWNT network (solid symbols) does not affect C/A but has a large effect on T and R_{Ser}. Making the approximation that front and back electrodes are identical (i.e., $T_1 = T_2$, $R_{S1} = R_{S2}$, and $(\sigma_{DC,B}/\sigma_{Op})_1 = (\sigma_{DC,B}/\sigma_{Op})_2$), and assuming that the series resistance is just the sum of the electrode sheet resistances ($R_{Ser} = 2R_s$), we can relate the transmittance of the capacitor to the series resistance by the square of equation (1) (because $T_{Cap} = T_P T_1 T_2$). This curve is plotted on Figure 3(d) by the dashed line using $T_P = 0.88$ and $\sigma_{DC,B}/\sigma_{Op} = 3$ and matches the data extremely well.

Previous work has shown the electrical properties of nanotube networks to be robust under flexing.[18] Thus, we would expect the properties of our capacitors to be stable against bending. To test this, we measured the impedance spectrum of a typical capacitor in a planar arrangement (Figure 4(a)). From the fits, we extracted the series resistance and the capacitance (Figures 4(b) and 4(c)). We then bent

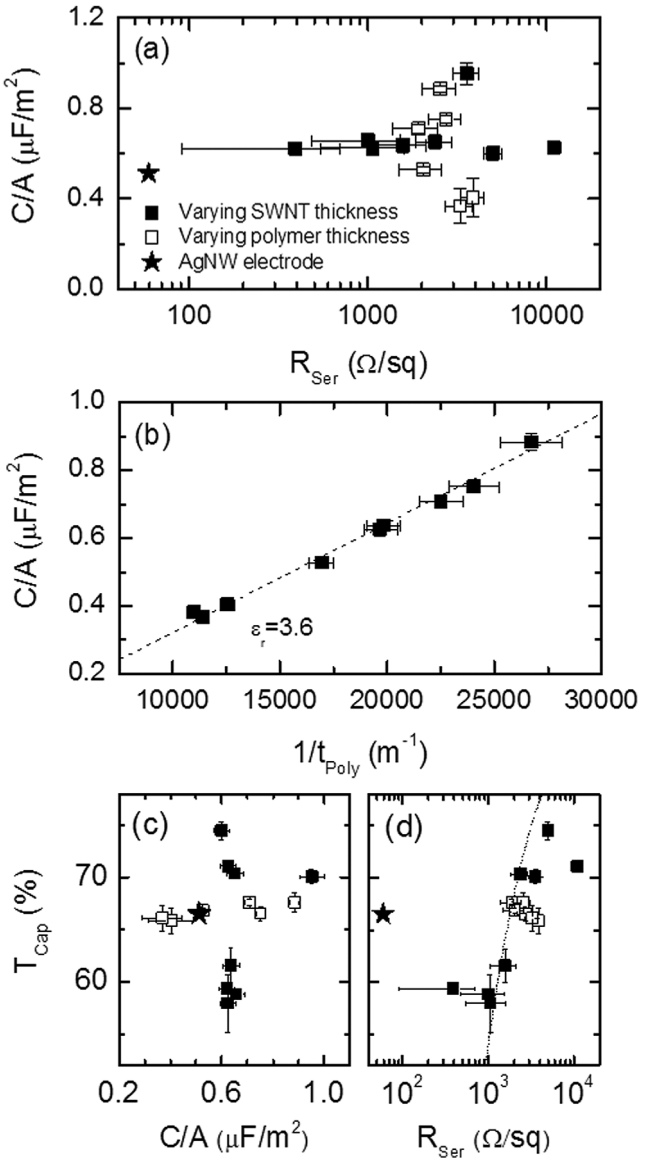

FIG. 3. Impedance data for transparent capacitors. (a) Areal capacitance plotted as a function of series resistance for capacitors with either constant electrode thickness but variable polymer thickness or vice versa. (b) Areal capacitance as a function of inverse dielectric thickness, $1/t_{poly}$. (c) and (d) Capacitor transmittance as a function of (c) areal capacitance and (d) series resistance. Data are shown for capacitors with either constant electrode thickness but variable polymer thickness or vice versa. The dashed line in (d) illustrates the behaviour expected for two identical electrodes, each described by the fit line in Figure 1(e), assuming a polymer transmittance of 0.88, $R_{Ser} = 2R_s$ and $\sigma_{DC,B}/\sigma_{Op} = 3$. NB in both (a) and (d), the series resistance has been rescaled to make it represent a square electrode and so is presented in Ω/□. NB the data for the capacitor with AgNW electrodes are shown as a star.

the capacitor to a radius of curvature of ~8 mm (Figure 4(d)), before remeasuring the impedance spectrum (Figures 4(e) and 4(f)) and extracting C and R_{Ser}. We found the properties of the capacitor to be virtually indistinguishable before and after bending, demonstrating the robustness of the structure. To confirm this robustness, we subjected a (different) capacitor to repeated bend (~8 mm radius) cycles, measuring the impedance periodically. As shown in Figures 4(g) and 4(h), both R_{Ser} and C are extremely stable under these conditions.

Finally, the capacitance per unit area for our device is quite low, ranging from 0.4 to 1.1 $\mu F/m^2$, while the series

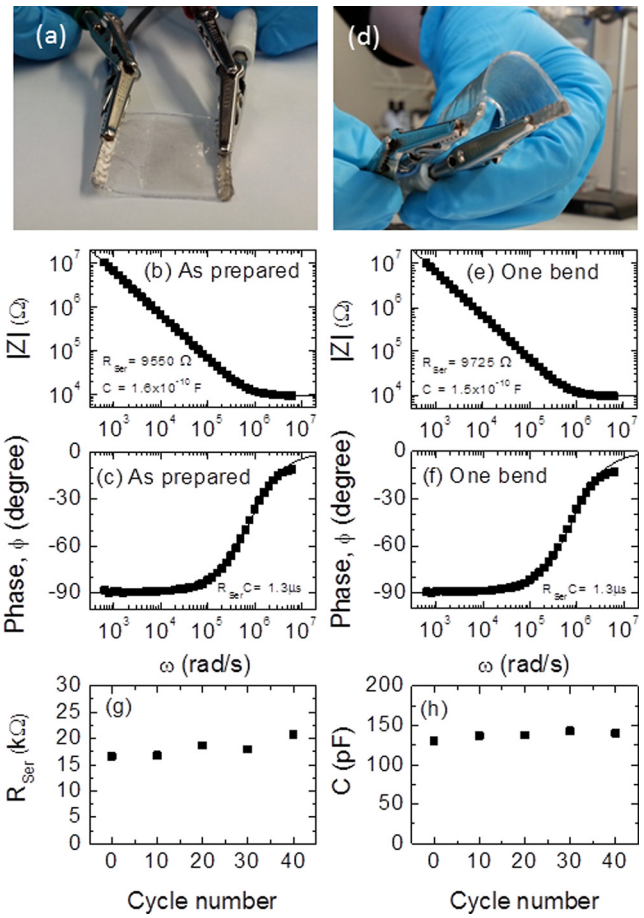

FIG. 4. (a) Capacitor in planar arrangement. (b) and (c) Modulus and phase spectra measured in planar arrangement. (d) Capacitor bent to a radius of 8 mm. (e) and (f) Modulus and phase spectra measured in bent arrangement. The series resistance, capacitance, and time constant as derived from the fits are given in the panels. (g) and (h) Series resistance and capacitance measured for a (slightly different) transparent capacitor as a function of number of bend cycles.

resistance is extremely high, with values in the range 2–10 kΩ for ~70% transmittance. As indicated above, it should be possible to increase the capacitance by using thinner polymer films and/or different dielectric materials. However, to reduce the series resistance, the conductivity of the electrode material must be increased. We propose using materials such as silver nanowires (from Kechuang Advanced Materials Ltd.),[12–14,31] which are considerably more conductive than SWNTs.[31] To test this, we prepared a capacitor as before, but with electrodes prepared by spraying[14] networks of AgNWs. Individually, these electrodes had transmittance of 90% and sheet resistances of 22–27 Ω/□, competitive with the state of the art for nanostructured transparent conductors.[14,17,31] Using this method, we achieved values of $C/A = 0.51\ \mu F/m^2$ and $T_{Cap} = 67\%$, very similar to the nanotube capacitors. However, the series resistance (rescaled to represent square electrodes) was much reduced at 60 Ω/□. While this value is low compared to that obtained from carbon nanotube electrodes, it appears high relative to commercial capacitors with metal electrodes. However, this is largely due to our requirement of transparency. To put this in context, we note that thin metal films with transparency of ~75% tend to have sheet resistances of hundreds of Ω/□.[36] This means that when such films are used to prepare transparent capacitors, series resistances of at least this can be expected. Thus, we expect AgNW networks to be the material of choice for future transparent capacitor applications.

In conclusion, we have produced transparent capacitors by spraying SWNT or AgNW networks onto both sides of PVAc thin films. These capacitors are flexible and display transmittance between 57% and 74%, capacitances ranging from 0.4 to 1.1 $\mu F/cm^2$ and series resistances ranging 60 Ω/□-10 kΩ/□. We believe these structures will be useful in a range of applications from sensors to transparent circuitry. For example, the porous nature of the electrode will make these structures ideal for capacitive gas sensing.

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