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ARTICLE TYPE

Transparent and flexible capacitor fabricated using metal wire network as transparent conducting electrode

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As transparency is becoming a desirable property even in non-optoelectronic devices, there is great impetus given to alternate materials and strategies replacing the conventional ITO. Here we have used transparent Au wire networks as electrodes, obtained from a crackle template method, in a capacitor where an ion-gel serves as the dielectric. The transparent capacitor thus fabricated with flexible PET as substrate showed a capacitance of 20 μF/cm^2 at 1 Hz with average transmittance of ~ 68% and was stable after many bending cycles. Such a performance is made possible due to high transmittance (~86%) and low sheet resistance (~ 4.2 Ω/sq) of the Au wire network. A ITO-free, flexible organic solar cell has also been fabricated using the Ag wire network.

1. Introduction

Transparent conductor (TC) is an unavoidable component of any optoelectronic device be it a display,[1] touchscreen,[2] organic LED[3] or solar cell.[4, 5] TC serves as one of the electrodes (TCE) while light interacts with the active layer beneath. In many instances, for example in organic or dye sensitized solar cells,[6] the active layer at its optimized thickness is reasonably transparent to visible light which has prompted fabrication of transparent solar cells,[7, 8] which as window panels or as curtains, not only save space but are also attractive.[9] Considering such advantages, there is a recent trend worldwide of extending these features even to non-optoelectronic devices. For instance, there have been reports on fabrication of transparent capacitors,[10, 11] transparent strain sensors,[12, 13] transparent speakers,[14] transparent batteries[15] and transparent gas sensors[16] Such fabrication of course, demands for more usage of the TCE as well as for additional attributes in a TCE such as flexibility.

Indium tin oxide (ITO) is being used extensively as transparent conductor, but its continued usage in optoelectronics is challenged mainly due to indium scarcity besides that the oxide is too brittle to be used in flexible devices. Many other oxide formulations have been tried out but only to find relatively inferior performance compared to ITO.[17, 18] The new generation TCs includes CNT networks,[19, 20] metal nanowire networks,[21, 22] graphene,[2, 23] conducting polymers[24] as well as their combinations in the form of hybrid electrodes.[5, 25] While graphene and conducting polymers find applications in specific devices, in general, nanowire networks particularly of Ag[26, 27] and Cu[28, 29] have gained much importance in the recent past. In networks, optical transparency and electrical conductivity are made independent of each other as light bends around and easily gets transmitted through the void regions in between. This being an advantage with the network structures, there are several issues too, to deal with, such as percolation below a threshold density,[30] non-uniform, sparse distribution of the wires,[31] high resistance at the wire junctions,[32] and importantly, roughness arising from out-of-plane nanowires, the latter causing electrical shorts in thin film devices.[33] Many remedial recipes have been developed to achieve uniform wire coverage,[34] to reduce junction resistance[35] and to restrict wires to the film thickness.[36] Needless to mention in detail, such measures in general increase the number of process steps, energy and material inputs adding further to the fabrication cost.

Fabrication of metal network in the form of a mesh has recently emerged out as a new approach to overcome these issues.[25, 37,38] Recently, grain boundary lithography[39] has been employed for the fabrication of random nanostructured Au mesh. Growth patterns of sodium carbonate crystals have been used as template for the fabrication of Ag metal network.[40] Similarly, self-assembled surfactant bubbles have served as template for Ag mesh based TCE.[41] Unfortunately, realizing large area TCE using these methods is rather difficult due to limited extension of the templates. In this work, we have employed a crack template method developed recently by us[42, 43] and Han et al.[44] that allows fabrication of large area TCEs. Although the quality of a TCE is ascertained with a set of parameters- transmittance, sheet resistance, roughness, flexibility etc., its actual performance will not be properly known until it is assembled in a device. Here we report, the fabrication of a transparent capacitor with both top and bottom electrodes made of Au mesh TCEs obtained from the crack template method and a transparent polymer ion gel as the dielectric. The fabricated capacitor is not only transparent in the visible range (68%) and is also flexible. Additionally, an unoptimized fabrication of working organic solar cell using Ag mesh TCEs is also demonstrated.

2. Experimental Section

2.1 Fabrication of crack template

A commercially available crack nail polish (Ming Ni Cosmetics Co., Guangzhou, China) consisting of acrylic emulsion was dispersed in diluter (0.5 g/ml) and rigorously ultrasonicated for 30 min and left overnight in an air-tight bottle. The suspended solution was spin coated at 500 - 2000 rpm on clean PET substrate for 120 s. Upon drying, a crack network formed spontaneously in the coated layer. Physical vapour deposition system (Hind High Vacuum Co., India) was used for Au deposition. In the final step of lift-off, the crack layer was dissolved by rinsing in chloroform.

2.2 Characterization

AFM measurements were performed using di Innova (Bruker, USA) in contact mode. Standard Si cantilevers were used for normal topography imaging. Wyko NT9100 Optical Profiling System (Bruker, USA) was used for height and depth measurements. Transmittance spectra were taken using a Perkin−Elmer Lambda 900 UV/visible/near-IR spectrophotometer with a white light source coupled with a monochromator and detected using integrating sphere and silicon photodiode. Sheet resistance was measured using a 4-Point Probe Station (Techno Science Instruments, India). Image-J software was used to perform FFT analysis of the metal network. The C-V measurements were performed using Keithley 4200 semiconductor parameter analyzer for all frequencies. The voltage was scanned from -2 to 2 V.

2.3 Fabrication of capacitor

Capacitor devices were fabricated by spin coating the electrolyte gel onto two identical Au wire network electrodes, each of 3 × 1 cm^2 area. An electrolyte gel comprising of PMMA and 1-ethyl-2-methylimidazolium bis(trifluoromethanesulfonyl)imide[45] was spin coated at 1000 rpm onto both electrodes. The two electrodes were placed on top of each other and the devices were encapsulated using pressure sensitive adhesive (3M 467MP).

3. Results and discussion

The metal wire electrode was fabricated following the crackle template method developed by us recently.[43] Briefly, commercially available crackle precursor in diluter is used for the formation of a crackle pattern (see Figure 1a). During spin coating, firstly, the film thinning occurs due to the radial outflow of the crackle dispersion till the dried solid becomes immobile due to fast solvent evaporation. This results in a uniformly cracked polymer film, referred to as the crackle template, where the cracks run down to the substrate (i.e. crackle), important to serve as a template (see ESI Figure S1). In this method, the crack width, the cell size can be easily tuned by varying the spin

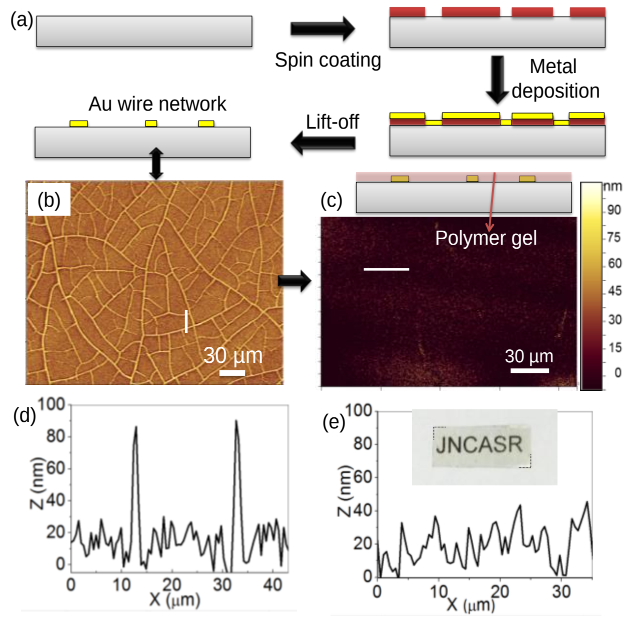

Figure 1: (a) Schematic showing the fabrication of Au wire network using crackle template. (b) Optical profilometry image Au wire network (b) before and (c) after polymer-gel coating, (d) and (e) are corresponding height profiles along the lines marked in 'b' and 'c', inset in 'e' is the photograph of the Au wire network coated with the polymer-gel.

coating conditions (see ESI Figure S2). Au is vacuum deposited in the crackle grooves as well as on flat regions sparing groove wall which is nearly vertical. The crack precursor is removed by thoroughly rinsing in chloroform and Au from flat regions is lifted off neatly (which can be recovered) without disturbing the metal in the grooves. This process is so trustworthy and reproducible that Au wire mesh could be realized over tens of cm^2 areas.[42, 43] Thus produced Au mesh is very well connected across the area without any defects as revealed by the optical profilometry image (Figure 1b). The metal appears to adhere well on the PET substrate. The sheet resistance (R_S) of the TCE was ~ 4.2 Ω/sq. A line profile in Figure 1b shows Au wire width to be ~ 2 µm and thickness ~ 70 nm, the latter being also the peak-to-valley roughness of the mesh. Using this method, wire networks of different widths could be easily made (see ESI Figure S3). The estimated surface roughness of the wire mesh was of ~ 20 nm, which may arise due to residual precursor along with some contribution from the inherent roughness of the PET substrate.

Transparent and flexible capacitor is an important device for realization of new generation transparent and bendable circuitry in displays and in energy storage particularly in combination with solar cells. This study is focused on fabricating transparent capacitors using the metal wire network based TCEs as parallel plate electrodes. As shown in Figure 1c, the polymer-gel was spin coated to a thickness of ~20 µm when the surface became smooth (~ 10 nm roughness). The line profiles taken before and after coating the polymer-gel clearly demonstrate that the metal network got buried (compare Figures 1d and e). The electrode coated with the polymer-gel appeared quite transparent as shown in photograph in the inset of Figure 1e.

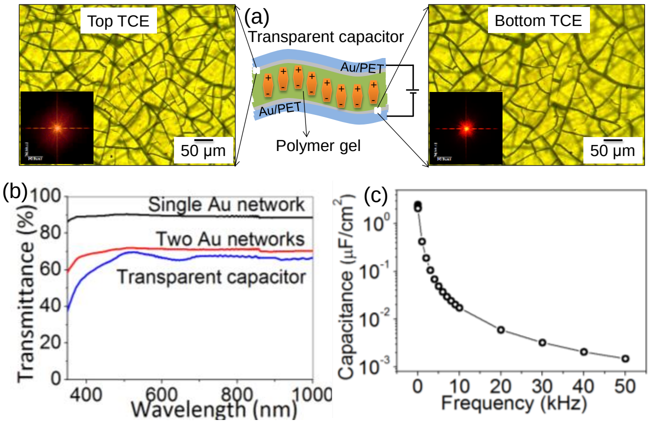

Figure 2: (a) Schematic illustration (middle) and optical micrographs of the fabricated transparent capacitor, with top (left) or bottom (right) TCE is held in focus. Corresponding FFT patterns are shown in the insets. (b) Diffusive transmittance spectrum of an encapsulated transparent capacitor along with those of Au wire mesh based TCEs, single and two together. (c) Capacitance as a function of frequency from 1 Hz to 50 kHz.

A parallel electrode capacitor was fabricated using two similar Au wire mesh TCEs coated with the polymer ion gel and assembled as shown in Figure 2a. The optical microscope images collected focusing on top and bottom TCEs show the two wire networks, one in focus and the other out-of-focus (see either sides of schematic in Figure 2a. Since each TCE is a random network of wires, stacking two of them did not produce any shadowed regions. The corresponding FFTs shown in the insets are free of any moire diffraction patterns, which are considered in general detrimental to display. From Figure 2b, we see that the transmittance of a single TCE is ~ 89% which gets reduced to 69% for the integrated capacitor device. This value is only slightly less compared to that from the stack of two TCEs, the difference being due to the polymer gel and the encapsulant. The active area of the transparent capacitor was 1 cm^2 though the metal occupied only 15% of the total area (metal fill factor). Therefore, the effective capacitor area is just 0.15 cm^2, which is contributing for the total capacitance of the device. The obtained C-V curves are shown in ESI Figure S4. From Figure 2c, we see that the capacitance decreases with frequency, from 2 $\mu F/cm^2$ at

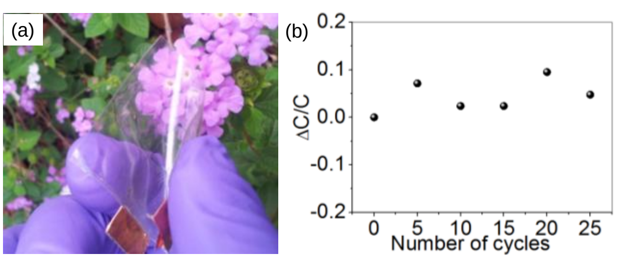

Figure 3: (a) Photograph of the transparent capacitor when it is bent. (b) Relative change in the capacitance as a function of bending cycles. Every fifth cycle, the capacitance was measured.

1 Hz to 0.001 $\mu F/cm^2$ at 50 kHz, due to the limited polarization of ions at higher frequencies. The other two devices fabricated in a similar way, exhibited 2 and 20 $\mu F/cm^2$ at 1 Hz, respectively. The metal electrode wall width and fill factor variations can bring in such changes in capacitance which has not been studied in this study. It may be noted that the capacitance values mentioned here refer to the total area and not just the metal filled area. Moreover, as a polymer ion gel electrolyte was used, it is essentially an electric double layer capacitor.[46] To our knowledge, this is the first time that an ion gel has been used in a transparent capacitor, although it has been used in normal (opaque) capacitors exhibiting similar capacitance values.[47,48] Our transparent capacitor may be compared with literature results (See ESI, Table S1). The high capacitance values obtained in this study owe much to the ion gel dielectric.

In order to determine the flexibility, the transparent capacitor is bent as shown in the Figure 3a. Since the PET substrate and the polymer dielectric, both are flexible in nature, the resulting capacitor is also flexible (Figure 3a). The capacitance was monitored under flexing cycles and it was found to be almost unaffected even after several bending cycles (Figure 3b). The capacitor was stable ever after 30 days without any degradation in the performance. Thus, the fabricated capacitor with metal wire network is not only transparent but also flexible. Such transparent capacitors find applications in the integration of solar cells for window panels.[11]

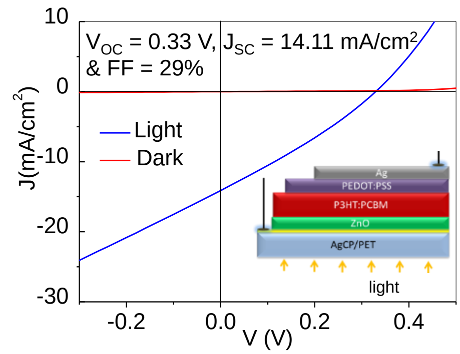

Figure 4: J-V characteristics and schematic of an unoptimized Ag wire network TCE based organic solar cell.

Having successfully fabricated transparent capacitor, we have made a preliminary attempt to fabricate a conventional organic solar cell[49] but using our TCEs (Figure 4). On Ag wire network serving as TCE (T, 86% and sheet resistance, 5 Ω/sq), several layers - ZnO (50 nm), P3HT: PCBM (300 nm), PEDOT:PSS (100 nm) were deposited by spin-coating with intermittent annealing, followed by Ag deposition as top electrode (see inset of Figure 4). It may be noted that here, ZnO nanoparticle layer was coated directly on Ag wire network without a conducting PEDOT layer in between; the latter is normally employed in the case of wire networks.[49] Our first attempt produced a cell with power conversion efficiency of 1.2% under AM 1.5 illumination, typical of non-ITO based solar cells.[50] As typical efficiencies of 3.6% are obtained with standard ITO electrodes,[51] further optimization is clearly required in the present case to improve the performance.

Nonetheless, this experiment demonstrates the possibility of using our wire network based TCEs for ITO-free solar cell fabrication.

Conclusions

In conclusion, the study has dealt with the fabrication of a transparent capacitor using Au wire network based transparent conductors as electrodes. Here, capacitor as a device was chosen as an example to demonstrate the capability of the wire electrodes. The devices showed capacitance in the range of 2-20 $\mu F/cm^2$ at 1 Hz frequency and were highly flexible. This is truly because of the remarkable properties for the wire network electrodes, which can probably be considered as a substitute in all ITO based applications, optoelectronic as well as non-optoelectronic. It is envisaged that transparent energy storage devices such as one shown above may find niche applications in combination with solar cells.[11] In this regard, we made an attempt to fabricate polymer solar cell with our Ag wire network, which showed good promise. The demonstration of a working capacitor and a solar cell provides evidence that the electrodes can be easily adapted in successful integration of devices.

Notes and references

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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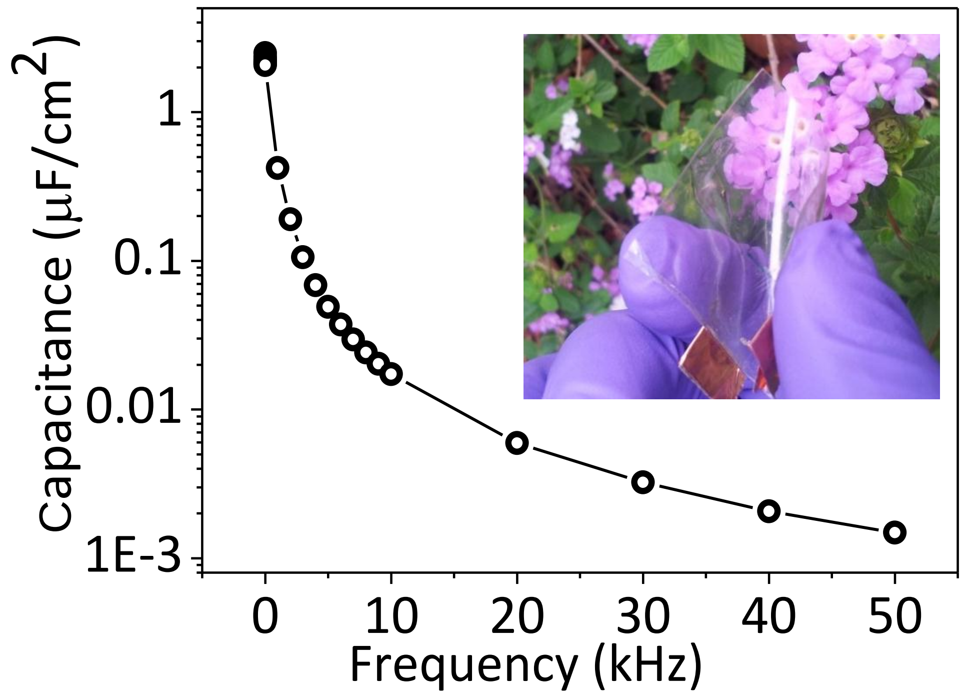
Table of content



A bendable transparent capacitor made of Au wire network electrodes on PET with an ion gel as dielectric shows a typical frequency response. The wire width and network cell size being in µm range, the wire network is invisible to eye.