The fabrication of Cu nanowire/graphene/Al doped ZnO transparent conductive film on PET substrate with high flexibility and air stability

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ABSTRACT

The fabricating of transparent conductive films with low resistance, high transparency, flexibility and air stability is significant in the study of flexible electronics. In this work, Cu nanowire/Graphene/Al doped ZnO (Cu/Gra/AZO) composite transparent conductive films were fabricated on PET substrate at room temperature. It is found that this composite film has a high transmittance of 74% at 550 nm, a low sheet resistance of 9.40 Ω/sq and good air stability. In this sandwich structure electrode, Cu nanowires (NWs) play an important role for ensuring the low resistance of the composite film, and the addition of graphene further reduces the resistance plus protects Cu NWs from oxidation. Moreover, the top layer AZO can protect the graphene layer from external damage and improve its stability.

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1. Introduction

Flexible transparent conductive film is a key material in many fields, including folding electronic screen, flexible solar cell, and etc. In the past, materials like indium tin oxide (ITO) [1,2], AZO [3–5], metal NWs (Cu NWs [6,7], Ag NWs [8].), are widely used for the preparation of transparent conductive films. However, being as ceramic materials, ITO and AZO would be easily fractured during deformation, resulting in a rapid resistance increase. Although metal NWs own good bending ability, they are easily oxidized, and their resistances will quickly increase when exposed in the air. Thus the fabricating of transparent conductive films combined with low resistance, high transmittance, flexibility and air stability is always a goal in the study of flexible electronics.

Recently, it is found that graphene is an excellent material for the preparing of flexibly transparent conductive materials. Kobayashi et al. reported that the graphene transparent conductive film fabricated by roll-to-roll chemical vapor deposition (CVD) synthesis, exhibited a high transparency, good flexibility and low resistance of 150 Ω/sq [9]. Jin et al. fabricated transparent conductive thin film by using monolayer rGO, which displayed a low resistance of 200 Ω/sq [10].

Although the ideal graphene film is supposed to own the lowest resistance, in real, its resistance is usually higher than the metal NWs. Meanwhile, due to the ultra-thin structure of graphene, its stability is much worse than the traditional ITO and AZO films. It is found that each material including ITO, AZO, metal NWs and graphene owns its special strengths and weaknesses.

Therefore, in this work, we designed and fabricated a Cu/Gra/AZO three-layer composite transparent conductive film on the flexible PET substrate. It is expected that this three-layer structure combined the excellent electrical, flexible and stability properties together in this composite film. In the experiment, Cu NWs were first deposited on the PET substrate, providing good deformability and low resistance. And then, graphene film was followed deposited on the surface of Cu NWs, protect them from oxidation and guarantee the low resistance during deformation process. In the end AZO was deposited, ensuring the air stability of the entire transparent conductive film.

2. Experimental

In a standard synthesis of Cu NWs, 0.197 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 1.44 g hexadecylamine, and 0.4 g glucose were dissolved in 80 mL water, then the solution was magnetically stirred at room temperature for

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Fig. 1. (a) The schematic illustration of Cu/Gra/AZO multilayer film deposited on the PET substrate. (b–g) The TEM image and diffraction pattern of Cu NWs (b, c), graphene (d, e), AZO (f, g).

Fig. 2. The transmission spectra of Cu, Cu/Gra, and the Cu/Gra/AZO multilayer. The inset shows the optical image of the multilayer sample.

over 5 h to get a homogeneous distribution. At last the Cu NWs were fabricated by using hydrothermal method at 130 °C for 6 h [11]. Graphene used in this study was synthesized by CVD method with copper foil as a substrate [12]. The substrate was placed

inside a quartz tube and then heated to 1000 °C under argon atmosphere. After flowing reaction gas mixtures ($\text{CH}_4:\text{H}_2:\text{Ar} = 30:30:200$ sccm), the sample was cooled to room temperature using flowing argon. The AZO target was fabricated compressing ZnO (99.99%) and Al (99.99%) powders with an atomic ratio of Zn:Al of 0.96:0.04, followed by sintering at 1000 °C for 2 h in air. AZO film were deposited using pulsed laser deposition (PLD) [13], and the energy density of excimer laser beam at the target surface was maintained at 1 J/cm^2 . SiC single crystal was used for heating substrate and temperature was varied in the range from room temperature to 1000 °C. According to XPS data, the actual Al content is $\sim 1.34 \text{ at.}\%$.

The optical transmission through the film was measured by a Varian Cary-300 spectrophotometer. Surface morphologies were identified by using FEI Tecnai G2 F20 transmission electron microscopy (TEM). The uniaxial tensile testing was performed by using a Micro-Force Test system (MTS) microtensile tester. The standard tensile sample used has a gauge length of 20 mm, a gauge width of 3 mm. Samples were strained sequentially in 2.5% increase with a running speed of $10 \mu\text{m/s}$. The electrical properties of the

Fig. 3. (a) The sheet resistance of AZO and the Cu/Gra/AZO multilayer versus strain. (b) The resistance increase versus bending cycles.

multilayer during deformation were in situ recorded by using a four-probe resistivity/square-resistance tester.

3. Results and discussion

Fig. 1a shows the fabrication process of the PET/Cu/Gra/AZO multilayer. In this experiment, Cu NWs were firstly fabricated by using a hydrothermal method, then they were coated onto the PET substrate. The graphene film was prepared by CVD synthesis and transferred by PMMA on the Cu NWs subsequently. Finally, AZO film was deposited on graphene by PLD, and the entire composite transparent conductive film was totally prepared. According to AFM data, the thicknesses of AZO, Cu NWs and graphene are 42 ± 5 nm, 165 ± 20 nm and 2 ± 0.3 nm respectively.

Fig. 1(b–g) show the TEM images and related diffraction patterns of the layers applied respectively. We find that Cu NW prepared by hydrothermal method is straight with a diameter of ~ 50 nm (Fig. 1b). The sharp diffraction points (Fig. 1c) confirm a good crystal quality and typical single crystal structure. Fig. 1d shows the TEM image of as-prepared graphene film, and the layer number is six. Fig. 1e manifests the good crystal quality of graphene, which is further confirmed by Raman spectra (Fig. S1). Fig. 1f shows the high resolution TEM image of AZO, which confirms that it was composited by nanoparticles. The diffraction pattern of AZO (Fig. 1g) confirms the polycrystalline structure. After combining these three layers together, the film looks flat and we could find the traces of NW (Fig. S2).

As a typical transparent electrode, the transparency is one of its most significant properties. Fig. 2 compares the transmission spectra of Cu, Cu/Gra, and Cu/Gra/AZO multilayer in the wavelength ranging from 400 to 750 nm. It is found that the transparency of pristine Cu NWs is the highest (78% at 550 nm), and it slightly decreases to 77% after the addition of graphene. The macroscopic image of Cu/Gra/AZO is shown in the inset, and it is found that the transparency of this multilayer still remains over 74% at 550 nm. The decrease of transparency may be due to two reasons. Firstly, the introducing of graphene greatly increases the electron concentration, more electrons attend the excitation which affects its transparency, and it is similar to the effect of metal layer intermediated in the traditional TCO/metal/TCO system [14]. Moreover, since Cu NWs, graphene and AZO formed a multilayer structure, the scattering loss increases greatly, which also decreases the transparency [15].

Since the motivation for preparing the Cu/Gra/AZO multilayer film is to be used under flexible condition, it's significant to explore its electrical and mechanical feature changes upon deformation. The in-situ stretching experiment was carried out on the samples and the sheet resistance changes were measured. The resistances upon elongation deformation experiments are shown in Fig. 3a. It is observed that the initial resistance of our multilayer can be as low as $9.40 \Omega/\text{sq}$ before deformation, which is far lower than the samples without Cu NWs. Also, as tensile strain increases, its resistance increasing speed is the smallest, which can be explained by the strong malleability of Cu NWs [16] and graphene. When the strain reaches 20%, the sheet resistance of the PET/Cu/Gra/AZO sample reaches $\sim 3 \text{ k}\Omega/\text{sq}$, which is similar to the performance of PET/Gra/AZO fabricated in our pervious study [15]. Referring to the traditional PET/AZO, its resistance already increased to $\sim 30 \text{ k}\Omega/\text{sq}$. Another superiority property of the PET/Cu/Gra/AZO is that it can remain good resistance stability after bending test. Fig. 3b compares the resistance changes of PET/AZO and PET/Cu/Gra/AZO upon repeated bending. It is found that PET/Cu/Gra/AZO can remain a low resistance of $9.55 \Omega/\text{sq}$ after 50 cycles bending test, which is far better than PET/AZO ($0.59 \text{ k}\Omega/\text{sq}$). Moreover, PET/Cu/Gra/AZO keeps a high air stability, which increases from 9.40 to $11.62 \Omega/\text{sq}$ after storage in the air for 30 days. Each layer in our sandwich structure film is indispensable (Table S1), which contributes its superiority performance than other transparent conductive films (Table S2).

4. Conclusion

In summary, a Cu/Gra/AZO three-layer composite film was successfully fabricated on PET substrate via a three-step method. Compared with traditional transparent conductive films, our film shows a much lower resistance of $9.40 \Omega/\text{sq}$. Additionally, good transmittance (74% at 550 nm), high flexibility (good stability upon deformation) and good air stability (for more than 30 days) are obtained together, indicating the potential application in flexible electronic products. In the future, more efforts are needed to improve the transparency of the film and further decreases its resistance.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.matlet.2017.07.048>.

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