Fabrication of ATO/Graphene Multi-layered Transparent Conducting Thin Films

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Abstract. A novel transparent conducting oxide based on the ATO/graphene multi-layered thin films has been developed to satisfy the application of transparent conductive electrode in solar cells. The ATO thin films are prepared by pulsed laser deposition method with high quality, namely the sheet resistance of 49.5 $\Omega$/sq and average transmittance of 81.9 %. The prepared graphene sheet is well reduced and shows atomically thin, spotty distributed appearance on the top of the ATO thin films. The XRD and optical micrographs are used to confirm the successfully preparation of the ATO/graphene multi-layered thin films. The Hall measurements and UV-Vis spectrophotometer are conducted to evaluate the sheet resistance and optical transmittance of the innovative structure. It is found that graphene can improve the electrical properties of the ATO thin films with little influence on the optical transmittance.

1.Introduction

Indium doped tin oxide (ITO) is the dominant material used in transparent conducting oxides (TCOs) which have a wide range of applications as transparent electrodes\cite{1-3}. In spite of the excellent optoelectronic properties, ITO suffers from the rare abundance and toxic sources making the application of ITO nonstainable. As an alternative, antimony doped tin oxide (ATO) have attracted vast interests due to prominent advantages as abundant, chemical stability, thermal stability, nontoxic, mechanical durability and especially for the low cost\cite{4-6}. However, the electrical and optical properties of ATO are inferior to ITO, especially for the electrical properties.

Recent researches have focused on the development of thin layers of highly transparent conductive films. Graphene is an exciting material which has a high intrinsic mobility (200000 cm$^2$\textit{v}$^{-1}$s$^{-1}$) and high optical transmittance ($\sim 97.7$ %)\cite{7-9}. However, the high cost for the preparation of the large area, high performance graphene restricts the application of graphene at present. Therefore, the concept of using the ATO/graphene multi-layered thin
films is extraordinarily useful for a substitute of ITO to further improve the properties of transparent conducting oxide films. Moreover, the designable ATO/graphene multi-layered structures as metamaterials have the potential to enhance the optical absorption to improve the photoelectric conversion efficiency for thin film solar cell. Various methods to make graphene have been developed such as mechanical exfoliation from graphite, chemically converted graphene from solution-phase graphene oxide and chemical vapor deposition [7,10-11]. Chemical reduction method has attracted much attention due to the simple experimental condition, easily controlled system, high quality and yield of graphene.

In this paper, we prepare the ATO/graphene multi-layered thin films by spin-coating experimental setup using the graphene produced from the chemical reduction method. The structural, electrical and optical properties of the ATO/graphene multi-layered thin films have been investigated in details.

2. Experimental procedures

Graphite oxide (GO) was prepared from purified natural graphite (30 μm nominal particle size, Shanghai colloid chemical Inc.) by the modified Hummers method. The phase compositions were analyzed using X-ray diffraction (XRD, Rigaku Ultima III) with Cu Kα radiation. Surface morphology analysis was performed with a transmission electron microscope (JEM-2100F STEM/EDS, Japan) and optical microscope. Raman spectra were recorded from 200 to 2000 cm⁻¹ on a INVIA Raman Microprobe (INVIA, England). The electrical resistivities were determined with a conventional four-probe instrument. The Hall measurements were made with Van der Pauw techniques. The optical transparency was performed with a Shimadzu UV-2550 spectrophotometer.

Graphite oxide (GO) was prepared from a modified Hummers method using 1.0 g of graphite powder (30 μm nominal particle size, Shanghai colloid chemical Inc.) dispersed in 23 mL of H₂SO₄ kept at 0 °C. Next, 0.5 g of NaNO₃ and 3 g of KMnO₄ were slowly added. After keeping the reaction for 3 h, the solution was transferred to a 35 °C water bath and stirred for 0.5 h. Then 140 mL of H₂O was added and the temperature was raised to 90 °C. The solution changed to a light brown color during the addition of 10 mL of 30% H₂O₂. Then the prepared GO dispersion was ultrasonicated until it became clear. NaBH₄ (200 mg) was added and the solution was heated in an oil bath at 95 °C for 5 h over which the reduced GO gradually precipitated out as a black solid.

The ATO/graphene multi-layered thin films were prepared by spin-coating experimental setup. The ATO thin films were grown on quartz glass substrate by pulsed laser deposition method at 550 °C in oxygen partial pressure of 8 Pa with Sb doping ratio of 12 at.%. Next, the graphene powder was dissolved in N,N-dimethyl formamide (DMF) and ethanol respectively at a concentration of 0.5 mg/L and the solution was spin coated onto the ATO thin films. The ATO/graphene multi-layered thin films were allowed spin at 3000 rpm and then dried at 100 °C inside a drying oven.

3. Results and discussion

The phase compositions and microstructure of the graphene oxide and graphene have been further investigated. The reduction of graphene oxide to graphene should result in structural change, especially the distance between the layers [12]. Fig. 1 shows the XRD patterns of
natural graphite, prepared graphene oxide and graphene. It can be seen that the main peak of natural graphite appears at 2θ=26.5° corresponding to the (002) diffraction. The interlayer spacing between atomic planes of (002) diffraction is 0.34 nm \[13\]. However, the main peak becomes wider and shifts to lower angles of 2θ=10.1° corresponding to an interlayer spacing of 0.94 nm for graphene oxide \[14\]. The oxygen containing functional groups, such as C=O, C-OH and –COOH, introduced into the layers of graphite by the function of strong oxidizer result in the increase of the interlayer spacing. After the graphene oxide is reduced to graphene, it is observed that all the peaks are disappeared, indicating that the crystallinity is degraded and the graphene is efficiently exfoliated to sheet structure.

Fig. 1 The XRD patterns of natural graphite, prepared graphene oxide and graphene

Fig. 2 Raman spectra of natural graphite, prepared graphene oxide and graphene

The chemical structures of natural graphite, prepared graphene oxide and graphene are further studied by Raman spectroscopy. As shown in Fig. 2, there exits two peaks for graphene oxide, which is G band locating at 1600 cm\(^{-1}\) and D band locating at 1349 cm\(^{-1}\). After the reduction of graphene oxide, the peaks for G band and D band both shift to lower wave numbers. The G band moves to 1586 cm\(^{-1}\), which equals the value of natural graphite (1586 cm\(^{-1}\)), indicating the reduction of the graphene oxide. However, a notable increase of the intensity of D band for graphene is observed which is compared with the natural graphite, reflecting the existence of large amounts of unrepaird defects on the graphene surface due to the removal of oxygen containing groups \[15\].

Optical microscope is used to analyze the surface morphology of the ATO/graphene multi-layered thin films. The obtained graphene are dissolved in DMF and ethanol respectively and the dispersion is spin coated onto the ATO thin films. Fig. 3(a-c) shows the optical micrographs of the ATO thin films, the ATO thin films coated with graphene dispersion in DMF and the ATO thin films coated with graphene dispersion in ethanol. The images illustrate that the graphene exhibits a black, spotty distributed appearance and the graphene sheets are scattered across the surface of the ATO thin films. It is observed that more graphene sheets are densely clustered for the ATO thin films coated with graphene dispersion in ethanol. Fig. 3(d) shows a TEM image of a partially folded ethanol-soluble graphene sheet. The graphene sheet appears transparent and is folded over on one edge with other graphene on its surface. The results reveal that the graphene is very thin with high optical transmittance and the obtained graphene is of the order of micrometres in size.
Sheet resistance and optical transmittance are the main factors to evaluate the quality of transparent conducting oxide films. Table 1 compares the sheet resistance and average transmittance of the ATO thin films and the ATO/graphene multi-layered thin films. The average transmittance is calculated in the visible range of 300 nm ～ 800 nm. As can be seen, the graphene can improve the electrical properties of the ATO thin films. Especially for the ATO thin films coated with graphene dispersion in ethanol, the sheet resistance is decreased by 15 %.

Table 1 Comparison of sheet resistance and average transmittance of the ATO thin films and the ATO/graphene multi-layered thin films

|                     | Sheet resistance (Ω/sq) | Average transmittance (%) |
|---------------------|-------------------------|---------------------------|
| ATO                 | 49.5                    | 81.9                      |
| ATO/graphene (DMF)  | 47.5                    | 81.8                      |
| ATO/graphene (Ethanol) | 40.6                   | 80.5                      |

The enhancement of the electrical properties for the ATO/graphene multi-layered thin films may result from the increase of electron moving in the whole system. However, spotty
distributed graphene instead of the structure of the continuous large size will restrict the maximum electrical performance of the ATO/graphene multi-layered thin films. Nevertheless, the thin layer structure of the prepared graphene sheet can ensure less optical absorption which has a slight influence on the average transmittance of the ATO thin films. The optical transmittance is determined by the amount and dispersion of graphene across the surface of the ATO thin films. It is clearly that the ATO thin films coated with graphene dispersion in ethanol show lower average transmittance (80.5 %) due to the more densely clustered graphene sheet as shown in Fig. 3. The ATO/graphene multi-layered thin films provide a new method to further improve the electrical properties without the cost of transmittance for transparent conducting oxide films.

4. Conclusions

We fabricate the ATO/graphene multi-layered thin films by a spin-coating method. The graphene sheet is well reduced from the graphene oxide prepared by a modified Hummers method. The obtained graphene sheet shows good transmittance with thin layer structure. The graphene can improve the electrical properties of the ATO thin films. Especially for the ATO thin films coated with graphene dispersion in ethanol, the sheet resistance is decreased by 15 % from 49.5 Ω/sq to 40.6 Ω/sq. Moreover, the ATO/graphene multi-layered thin films exhibit atomically thin, spotty distributed appearance with less optical absorption to avoid the deterioration of transmittance. It provides a promising way to produce the transparent conducting oxide films with lower resistance, without lowering the transmittance.

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References

[1] Kwark D J, Park M W. and Sung Y M 2008 Vaccum 83 113.
[2] Tak Y H, Kim K B and H.G. Park 2002 Thin Solid Films 411 12.
[3] Fortunato E, Ginley D and Hosono H 2007 MRS Bull 32 242.
[4] Montero J, Herrero J and Guillen C 2010 Sol. Energ. Mat. Sol. C. 94 612.
[5] Ma J, Hao X T and Ma H L 2003 Appl. Surf. Sci. 214 208.
[6] Marcel C, Hedge M S and Rougier A 2001 Electrochim. Acta. 46 2097.
[7] Geim A K and Novoselov K S 2008 Solid State Commun. 146 351.
[8] Morozo S V, Novoselov K S and Katsnelson M I 2008 Phys. Rev. Lett. 100 016602.
[9] Tung V C, Allen M J and Yang Y 2009 Nature Nanotechnol. 4 25.
[10] Bae S, Kim H K and Lee Y B.2010 Nature Nanotechnol. 5 574.
[11] Chen W F and Yan L F 2010 Nanoscale. 2 559.
[12] Wang G X and Yang J Park J 2008 J. Phys. Chem. C. 211 8192.
[13] Boukhvalov D W and Katsnelson M I 2008 J. Am. Chem. Soc. 130 10697.
[14] Zhou Y, Bao Q Land Tang L A L 2009. Chem. Mater. 21 2950.