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Full Length Article

Temperature-time dependent transmittance, sheet resistance and bonding energy of reduced graphene oxide on soda lime glass

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ABSTRACT

Reduced graphene oxide coated soda lime glass can act as an alternative transparent/conducting electrode for many opto-electronic applications. However, bonding between the deposited reduced graphene oxide film and the glass substrate is important for achieving better stability of the coating and an extended device lifetime. In the present study, delamination energy of reduced graphene oxide on soda lime glass was quantified by using nanoscratch technique. Graphene oxide was deposited on soda lime glass by dip coating technique and was thermally reduced at different temperatures (100 °C, 200 °C, 300 °C, 400 °C and 500 °C) and treatment time (2 h, 3 h, 4 h, 5 h and 10 h) in Ar (95%) with H_2 (5%) atmosphere. An inverse behavior of delamination energy with temperature and treatment time was observed, which could be correlated with the removal of oxygen functional groups. Sheet resistance of the film demonstrated a steady decay with increasing temperature and treatment time. Functional groups attached to the graphene planes have more influence on conductivity than groups attached to the edges. Removal of functional groups could also be related to optical transmittance of the samples. Knowledge generated in this study with respect to delamination energy, sheet resistance and optical transmittance could be extensively used for various opto-electronic applications.

1. Introduction

Two-dimensional (2D) materials like graphene have found great attention in a myriad of device applications. With high conductivity, strength, transparency and catalytic behavior, graphene stands in the list of most-sought materials used in sensors, energy conversion and storage, electronic displays etc. [1]. Hexagonally arrayed, sp^2 hybridized graphene is the thinnest material (a single atomic dimension layer) with high carrier mobility, excellent optical transparency, good thermal conductivity, high Young's modulus and large specific area. Due to high conductivity and large specific area, graphene has low charge transfer resistance [2].

Graphene can be synthesized by various methods including mechanical exfoliation, epitaxial growth, chemical vapor deposition and graphene oxide reduction. While the first three processes yield relatively perfect structure and better electronic properties, the last technique is popular as a low cost and high yield method, producing less perfect structure of graphene. Graphene oxide (GO) forms stable aqueous colloidal suspension, owing to its hydrophilic property. Reduction of graphene oxide by different method partly restores graphene structure and property. Properties of reduced graphene oxide (rGO) strongly depend on the efficiency of the reduction methods, directly influencing performance of the device in which rGO is used [3].

One of the ways to reduce GO is to thermally reduce graphene oxide under reducing and/or inert gas atmosphere. Thermal reduction can be performed in two ways: 1) rapid heating and 2) slow heating. During rapid heating, oxygen containing functional groups create high pressure between the layers by decomposing of CO

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and CO_2 gases and their sudden expansion causes mechanical exfoliation of the structure. The dual effects of thermal reduction, exfoliation and reduction, make it a good method to produce graphene in bulk quantity. However, structural defect and small size are the main problem of rapid heating. During rapid heating, decomposed functional groups also remove carbon atoms from the structure due to the high energy provided by decomposition carbon dioxide, which creates distortion in the carbon planes, leading to breakage of graphene sheets into smaller sizes. Thus, rapid heating provides small sized, wrinkled and structurally damaged graphene sheet. On the other hand, slow heating during reduction helps graphene to retain its structure by preventing rapid expansion of the sheets. However, slow heating is a time consuming process [3].

Studies have shown that reduction of graphene oxide can be performed at high temperature [4–6]. But, if the rGO film is to be used on low melting substrates, e.g. glass and polymers, then in-situ reduction at high temperature becomes difficult. Thus, graphene oxide can be reduced in a reducing atmosphere with or without inert gas. Hydrogen has high reducing ability at lower temperature due to which graphene oxide can be reduced at low temperature in hydrogen atmosphere [3].

Apart from the reduction of the GO film, bonding between the film and the substrate is another important factor which decides life of a device. A loosely bonded film will be peeled-off easily leading to damage of the device. Quantification of the delaminating energy of thin films with substrates creates interest for understanding the bonding mechanism which can be linked to the thin film deposition process and the reduction mechanism. Delamination energy can be measured popularly by two methods: 1) Double Cantilever Beam (DCB) method and 2) Nano Scratch technique. Among these two methods, DCB has few limitations [7]. DCB is generally applicable to the 3-D micro/macro materials; not to 2-D thin materials. Further, DCB provides insufficient information about homogeneity of the delamination energy throughout the substrate. On the other hand, nano scratch technique can be applied on 1-D materials (carbon nanotube), 2-D materials (graphene) and a single biological cell [8] also. This sophisticated technique is very consistent and straightforward with presumption during calculation. In this technique, delamination energy of the film with substrate is measured by using a nano-indenter. A lateral force is applied through the interface of the film and the substrate and delaminating energy was measured by calculating the area of the lateral force-lateral displacement curve [9,10].

In the present study, GO film on soda lime glass was reduced at different temperature and treatment time combinations and their optical transmittance, electrical resistance and adhesion energy was quantified to understand the effectiveness of the reduction process. Previous study [11] showed that graphene film could be peeled-off easily from fluorine doped tin oxide (FTO) substrate, if reduced above 400 °C, due to burning out of the organic binder (e.g. terpineol and cellulose). However, no quantification was performed in this perspective. Annealing temperature and treatment time play important roles in the quality of the deposited film. There were a number of studies, on deposition/reduction of graphene oxide on different substrate using different methods; but no quantitative study on predicting the quality of the film was performed. In one of our previous studies [12], rGO based transparent conducting electrode was prepared and de-bonding energy of rGO film with soda lime glass was measured for one processing parameter. However, it was felt that the exciting properties of rGO based transparent conducting electrodes (TCEs), i.e., resistance, transmittance and de-bonding energy, could well be related to the processing conditions. Thus, in this study, nanoscratch technique was used to understand the adhesion of graphene oxide film on soda lime glass at different temperature and treatment time conditions; for optimizing adhesion of the film with substrate for better life of the device. Simultaneously, resistance and transmittance of the films were also characterized in order to generate a comprehensive idea about the TCE application of rGO films on soda lime glass. To the best of our knowledge, this is the first study to quantify the delamination energy, resistance and transmittance of reduced graphene oxide film, reduced at different temperature and treatment time combinations, deposited on soda lime glass.

2. Materials and methods

Graphite powder (average particle size ~100 μm) was purchased from S D Fine Chem Limited. Potassium permanganate ($KMnO_4$, 99%), sulfuric acid (H_2SO_4, 98%), phosphoric acid (H_3PO_4, 88%), hydrogen chloride (HCl, 35.4%) and hydrogen peroxide (H_2O_2, 30%) were purchased from Rankem. All the chemicals were of analytical reagent grade. Soda lime glass slides (thickness 1.1 mm) were purchased from AICIL LAB (I) Pvt. Ltd. (India).

Graphene oxide was synthesized by modified Hummer's method [12–14]. GO was deposited on soda lime glass with concentration of 1.25 mg/ml by dip coating method with 10 times dip cycles (thickness ~260 nm). After deposition, samples were put in a controlled atmosphere furnace for thermal reduction at 100 °C, 200 °C, 300 °C, 400 °C and 500 °C with heating rate of 5 °C/min. Further, reduction was performed for selected samples for 2 h, 3 h, 4 h, 5 h and 10 h at 200 °C, in Ar + H_2 (95% + 5%) atmosphere. Cooling was done in Ar atmosphere only.

X-ray diffraction patterns were taken in thin film X-ray diffractometer (D8 Advance, Bruker, Germany) with Cu Kα radiation (of wavelength 1.5405 Å). XRD, having Ni filter, was operated at 40 kV and 30 mA. XRD patterns were recorded in the range of 5–50° with a scan rate of 1°/min. Hitachi UH5300 UV–vis-NIR Spectrometer was used to study the transmittance of the films in visible range (380–700 nm). TEM images and SAED patterns were taken from transmission electron microscope (model: FEI TECHNAI G2). Sheet resistance was measured by two point probe method with Keithley 4200 Semiconductor Characterization System. Hysitron Triboindentor TI950 (Hysitron Inc., Minneapolis, USA) was used to study the delamination energy of the film with the substrate, by using a Berkovich diamond tip with radius of ~100 nm. 20 μm long scratches were made by the tip at a speed of 0.5 μm/s and 10 μN normal force.

X-ray photoelectron spectroscopy (XPS) of GO and heat-treated rGO samples were recorded with a Thermo Scientific Multilab 2000 spectrometer using non-monochromatic AlKα radiation (1486.6 eV) at 15 kV and 10 mA as X-ray source. The binding energies reported here were calculated with reference to C1s peak at 284.6 eV. For XPS analysis, samples were mounted on the sample holders and were placed into a load-lock chamber with an ultra-high vacuum (UHV) of 8×10^{-8} mbar for 5 h in order to desorb any volatile species present on the surface. After 5 h, samples were transferred into the analyzing chamber with UHV of 5×10^{-10} mbar one by one. All the spectra were obtained here in the digital mode on a computer with 25 eV pass energy across the hemispheres of the electron analyzer and 0.05 eV step increment.

3. Results and discussion

Reduction of graphene oxide was confirmed by XRD (Fig. 1(a)). The single prominent peak of GO (002) at 10.14° with d-spacing of 8.71 Å was observed to be absent at different reduction temperatures. The peaks of thermally reduced graphene oxide at different temperatures of 100–500 °C were observed between 24.17°–24.57° with d-spacing in the range of 3.67 Å–3.61 Å. This reduction in d-spacing (from 8.71 Å in GO to 3.61 Å in rGO) was occurred due to the removal of oxygen functional groups as well as water molecules