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Modifications and multiple roles of graphene film in SIS structural solar cells

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Abstract

In this report, large area and high-quality graphene films were synthesized under 1000 °C by chemical vapor deposition technique. Their structure, optical and electronic properties have been characterized by Raman spectroscopy, Ultraviolet–visible spectrophotometry and Hall Effect measurement system, respectively. The films were found to be perfect sp^2 bonding form of graphene with a maximum size of 9 cm^2. By contrasting the current–voltage feature of ITO/SiO_x/Si, G/ITO/SiO_x/Si and ITO/G/SiO_x/Si configurations, the different roles of graphene layer to the heterojunction solar cells were discussed. The results showed that an energy conversion efficiency of 7.54% is obtained with the structure of G/ITO/SiO_x/Si. The improved solar cell performance was attributed to the roles of graphene in SIS structures, such as improvement of light transmission and current flow, reduction of interfacial states and removal of Fermi pinning effect at the hetero-junctions between graphene films and oxides. The interfacial region between ITO, Graphene and Silicon was analyzed by transmission electron microscope image and X-ray photoelectron spectroscopy. It was found that the a-SiO_x layer does exist between ITO film and Si substrate even without intentional oxidation treatment. The surface passivation and defect-assisted tunneling effect of the ultra-thin oxide layers was reflected by the device performance.

Keywords: Graphene film; Modification roles; Solar cell structure; Interface states; Fermi pinning effect

1. Introduction

Graphene, a unique two-dimensional (2D) monoatomic planar membrane of carbon, has emerged as a revolutionary breakthrough in material technology. It is well known that graphene has the potential properties with the both metal and semiconductor characteristics for charge transport in a functional device, either in electronic or in optical applications (Novoselov et al., 2012; Li et al., 2009; Phan et al., 2012; Geim and Novoselov, 2007). Graphene and graphene based materials promise potential applications across many fields (Su'ait et al., 2015; Brus et al., 2014; Pumera, 2011; Chen et al., 2015; Guo et al., 2011; Fang et al., 2011), such as photodetector, graphene transistors, electrochemical sensors, graphene photonics and optoelectronics, applications of graphene in energy production and storage, and biosensing applications. CVD graphene is a promising material for optoelectronic applications (Mattevi et al., 2011; Hong Guai et al., 2012; Guermoune et al., 2011; Li et al., 2010 and Li et al., 2013; Du et al.,

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2015). For instance, Zhu's group (2010 and 2013) demonstrated that graphene sheet films can be combined with Si to form Schottky junctions and efficient solar cells. They constructed a C/Si heterojunction solar cell with a relative low efficiency of 1.5%. For traditional crystalline silicon solar cells, as an excellent transparent conducting film, the ITO films have been successively applied to easy manufacturing process and low production cost TCO-SiO_x-Si (SIS) heterojunction structures photovoltaic (PV) devices. Du et al. (2015) discussed the role of interfacial oxide produced at the interface between ITO and Si in a structure of ITO/SiO_x/n-Si heterojunction. However, both of these structures reported in past literature reveal some shortcomings. The most of the Graphene/Silicon heterojunction is Schottky junction, which possesses far lower potential barrier than silicon p-n junction. Although the work function can be adjusted to some extent by doping or using few-layer graphene, the effective barrier height remains low. This case restricts the effectively transport and collect of electron–hole pairs, which result in greater leakage current and poor conversion efficiency. Wherever, there usually exist interface states (Q_{IS}) and Fermi pinning (Q_{FP}) effect between the ITO film and Si substrate, which presents a transport barrier for photogenerated electron–hole pairs. Both of these limiting factors cause serious recombination and bring about reduced open-circuit voltage.

To improve the performance of solar cell, most of the works in this area are focused on exploiting new materials or optimizing preparation processes (Li et al., 2010 and Li et al., 2013; Du et al., 2015). In this work, efforts were tried to change the structure of solar cells. To combine the characteristics and advantage of both crystalline silicon solar cells and carbon based solar cells, large-area (9 cm^2) single layer graphene films were synthesized by CVD and were inserted into ITO/SiO_x/n-Si structure. And, the modification function and its impact on carrier transport of graphene film in heterojunction devices were emphatically discussed by contrasting the different structures of solar cells. Meanwhile, the action ways of interfacial ultrathin oxide layer in ITO/Si heterojunction solar cells were further testified by comparing different oxidation manner. As a whole, the device structure for solar cells in this work is simpler, less expensive and much more accessible, which make this work demonstrate a new class of graphene-based solar cells.

2. Experimental section

2.1. Graphene film synthesis and characterization

Graphene films were synthesized on copper foils by chemical vapor deposition (CVD) at temperatures of 1000 °C using a mixture of methane and hydrogen as the precursor. Copper foil (25 μm in thickness, Alfa Aesar) was chosen as substrate and was gradually heated to 1000 °C in an H_2 (50 standard cubic centimeters per minute (sccm)) flow for 60 min. The carbon source (methane) was imported with a gas flow rate of 1 sccm for 10 min. Next, turn off the methane and aerate 50 sccm of hydrogen into 100 sccm of Argon for another 60 min to cool down the substrates to 300 °C with a high cooling rate. Finally, graphene films were formed on the copper foils. A graphene film with maximum size of 9 cm^2 is obtained in this work. The structure characteristics of graphene films were performed by confocal Raman spectroscopy. Here, the confocal Raman spectrometer (INVIA, Renishaw PLC, England) emitted a typical laser wavelength at 633 nm. The laser beam was focused on the sample with a spot size of 2.0–3.0 μm in diameter.

2.2. Transfer and photoelectric properties of graphene films

Electronic application of graphene based device requires graphene to be integrated in silicon device. So, the obtained as-grown graphene film needs to be separated from metal substrates and transfer to insulating substrates for further evaluation and various electronic device processing (Du et al., 2015; Yu et al., 2008). A detailed transfer process is described by a flow diagram Fig. 1(a). At first, the copper foil with graphene film was cut into smaller samples with area of 1 cm^2. Polymethyl methacrylate (PMMA) (MicroChem 950 PMMA A9) was diluted in anisole with a liquid–solid ratio concentration of 30 mg/mL. Then, this mixture was spin-cast on the as-grown graphene of the foil at 6000 rpm for a minute with thick of 200 nm. The PMMA coated samples were baked at 150 °C for 10 min. Next, the copper foil was etched away by soaking in 0.5 mol/L $FeCl_3$ solution. Then, the graphene film with PMMA (illustrations in Fig. 1(c)) was rinsed with deionized water three times. Target substrate, such as silicon, was pre-prepared to fish the graphene–PMMA film up. Similarly, they were baked at 150 °C for 10 min. Finally, the PMMA–graphene–Si samples were soaked in acetone for over 6 h to dissolve the PMMA. By this way, the graphene can be easily transferred to alternative substrates, such as SiO_2/Si or glass (photo illustrations in Fig. 1(b)).

Ultraviolet–visible spectrophotometry was used to measure the absolutely transmittance of different layer graphene films transferred to the glass. In this work, the Persee TU-1901 double beam mode UV-spectrophotometry is produced by Beijing Purkinje General Instrument Limited Company. The range of spectrum is 300–850 nm, and spectral bandwidth is 1 nm. The electrical properties, such as carrier concentration, carrier mobility and resistivity of graphene transferred to SiO_2/Si substrate were tested by Crosstech HMS300 Hall Effect Test System, which was manufactured by ACCEAT OPTICAL Company from England.

2.3. Configuration of solar cells

To confirm the action ways of interfacial oxide in ITO/Graphene/Silicon solar cells, three different oxidization ways to silicon wafers were carried out as comparative study: (1) Without additional oxidization; (2) thermally