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Ion beam irradiation of few-layer graphene and its application to liquid crystal cells

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ABSTRACT

Few-layer graphene was irradiated with a low-energy Ar^+ ion beam and applied to liquid crystal (LC) cells as both a transparent electrode and a homogeneous alignment enhancer. The optimum conditions for ion-beam-irradiated few-layer graphene (I-G) are 80 eV of beam energy and 1 s of irradiation time, which is confirmed by the decrease of the sheet resistance and increase of water contact angle with similar transmittance to pristine few-layer graphene. It is shown that the ion beam treatment of few-layer graphene under optimized conditions removes the surface contaminants and flattens the surface without damages. LC cells on I-G show similar device performance to that of LC cells based on indium tin oxide (ITO) with rubbing-treated polyimide. These results are very encouraging for replacing ITO electrodes with few-layer graphene in LC display applications.

1. Introduction

Graphene has received much attention in recent years because of its unique electrical, optical, and mechanical properties, such as a high mobility of charge carriers at room temperature, anomalous quantum Hall effect, ballistic transport properties, and flexibility [1–7]. These superior properties make graphene an ideal material for electronic applications such as liquid-crystal displays (LCDs) [8,9], light-emitting diodes [10,11], organic thin-film transistors [12–14], and organic photovoltaics [15–17]. Among graphene synthesis techniques, chemical vapor deposition is appropriate for obtaining large-scale graphene sheet with low sheet resistance and high transmittance [18,19]. One graphene application is to replace indium-tin oxide (ITO) transparent conducting electrodes. Although graphene is considered as a candidate for the interlayer or electrode in opto-electronic devices, the efficiency of graphene-based devices is still low compared to devices with ITO [20–22]. Therefore, many researchers have been intensely focused on graphene doping methods [23–33].

Through the optimization processes, graphene oxide and graphene layers have been applied to LCDs as electrodes and liquid crystal (LC) materials [9,34]. Anisotropic substrate surfaces are important to align LC molecules for display applications. To align the LC vertically or homogeneously, a low-energy ion beam has been irradiated onto SiO_x [35,36] or oxygen-doped SiC [37], and ultraviolet light has been applied to polyimide layers [38,39]. However, the optical transmittance of SiO_x films at visible wavelengths (70%) is lower than that of polyimide layers (90%), which may make its practical application difficult in spite of its advantages.

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Furthermore, most inorganic alignment enhancers are insulators, so conductive ITO electrodes are always needed. It is considered that graphene could overcome these weaknesses due to its transparency (>90%) and conductive properties. According to a random network model of atomic arrangement in the inorganic films, order is induced by exposure to an ion beam because planes parallel to the direction of the ion beam are favorable [40]. Few-layer graphene is not flat but wavy so that few-layer graphene has many oriented rings. Therefore, it could be assumed that ion beam irradiation could make few-layer graphene have anisotropic surface. In addition, low-energy ion beam irradiation applied to few-layer graphene could remove the surface contaminants that act as obstacles for charge transfer, increasing the conductance [41]. Therefore, it is expected that ion-beam-irradiated few-layer graphene (I-G) could be used as a transparent electrode and homogeneous alignment enhancer at the same time.

We investigated the effect of ion beam irradiation on the properties of few-layer graphene, and the use of I-G as an electrode as well as a homogeneous alignment enhancer in LCDs. Few-layer graphene films grown on copper foils were bombarded through an Ar^+ ion beam. To investigate the effect of ion beam irradiation on few-layer graphene, the electrical and optical properties were measured by 4-point probe and UV–visible spectra. The surface morphology of surfaces was determined by atomic force microscopy (AFM) in damping mode. Raman spectroscopy and X-ray photoemission spectroscopy (XPS) were used to investigate the structure ordering and surface state of I-G samples. LC cells were fabricated on I-G and rubbing-treated-polyimide/ITO (R–ITO) glass for comparison. Based on the results, the property variance of I-G and its homogeneous alignment effect in a LC cell are discussed.

2. Experimental procedures

2.1. *Few-layer graphene film preparation*

Few-layer graphene samples were grown on 25-μm-thick copper foil in a quartz tube furnace system using a chemical vapor deposition method involving methane (CH_4) and hydrogen (H_2) gas. Graphene means few-layer graphene in this experiment. Under vacuum conditions of 90 mTorr, the furnace was heated without gas flow for 30 min. Before the growth of graphene, copper foil was preheated at 950 °C for 30 min. In order to obtain a large single-crystal copper surface, H_2 gas was supplied to the furnace at 33 cm^3/min (sccm) under 150 m Torr. After the preheating step, a gas mixture of CH_4/H_2 = 200:33 sccm was supplied in ambient conditions for 10 min to synthesize the graphene. After 10 min of growth, the furnace was cooled down to room temperature at a rate of 10–15 °C/min under 33 sccm H_2 flow. After the growth of the few-layer graphene, poly[methyl methacrylate] (PMMA, 46 mg/mL in chlorobenzene) was spin-coated onto the graphene-coated copper foil. The PMMA-coated foil was placed on a hot plate heated to 180 °C for 1 min, after which O_2 plasma was used to etch the graphene on the other side of the copper foil. The sample was then immersed in a ferric chloride (1 M $FeCl_3$) bath at room temperature for 12–18 h to etch away the copper foil. After etching the copper foil, the remaining PMMA-coated graphene was carefully dipped into a DI water bath about 7–9 times to remove any residual etchant. The PMMA-coated graphene sheets were then transferred onto an arbitrary substrate. PMMA was removed by acetone bath at 50 °C for 30 min after the PMMA/graphene layer had completely adhered to the target substrate.

2.2. *Ion beam irradiation*

The few-layer graphene surfaces were bombarded with an Ar^+ ion beam. A cold hollow cathode-type ion source was used to produce the ion beam (Platar Co., Russia). The ion beam energy was calibrated by amperemeter because electron energy is correlated with electron current. The ion beam energy and exposure time were varied in the ranges of 0–200 eV and 0–10 s. The incident angle and ion beam flux density were fixed to 80° and 2.08×10^{13} Ar^+/s cm^2. The x–z plane projection of the ion beam was along the $-x$ axis of our coordinate system, as shown in Figs. SI1 and 2.

2.3. *Water contact angle measurement*

The wetting properties of the surfaces were determined by the contact angle method. The contact angle was measured by increasing and then decreasing the volume of a drop of liquid (distilled water) deposited on the sample surface. Recorded images were digitized and analyzed with software that evaluates the contact angle as the tangent at the point of contact between the drop and the surface.

2.4. *Characterization of I-G films*

The sheet resistance was measured in a standard state using a four-point probe method (Keithley 2612A multimeter, U.S.A.). UV–visible spectra were recorded on a JASCO V-740 photospectrometer with a wavelength range from 400 to 700 nm. Raman spectra of graphene were obtained with a LabRAM HR (Horiba Jobin Yvon, Japan) at an excitation wavelength of 514.54 nm. TEM (JEOL-2100F, Japan) images of the pristine graphene (P-G) and I-G films were obtained using accelerating voltage with 200 kV. XPS was conducted on a Sigma Probe model (ThermoVG, UK) operating at a base pressure of 5×10^{-10} mbar at 300 K with a nonmonochromatized Al K_α line at 1486.6 eV, a spherical sector analyzer of 180°, a mean diameter of 275 mm, an analysis area of 15–400 μm, and multichannel detectors. The results were corrected for charging effects by using C 1s as an internal reference and the Fermi edge of a gold sample. The morphology of surfaces was determined by AFM in damping mode. An ultra-lever cantilever with a spring constant of 26 N/m and a resonance frequency of 268 kHz was used for scanning.

2.5. *Fabrication of LC cells*

LC cells were prepared on I-G and R–ITO substrates. I-G glass was fabricated using alignment conditions with the ion beam energy, exposure time, incident angle, and flux density fixed to 80 eV, 1 s, 80°, and 2.08×10^{13} Ar^+/s cm^2. For the fabrication of LC cells on R–ITO substrate, ITO glass substrates were spin-coated with the polyimide RN-1702 (Nissan Chemical Co., Japan), pre-baked at 80 °C for 30 min, and cured at 230 °C for