



Defect-curing function of self-limiting Al₂O₃ thin films in graphene materials

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Abstract

Impedance spectroscopy was applied to 2-dimensional graphene materials that were thermally grown on copper substrates to quantitatively monitor the quality of the as-grown graphene materials without the subsequent transfer process. The presence of the graphene layer prevents the dissolution of the metallic copper elements in the corrosive electrolyte and provides an interface between the ionic electrolyte and electronic graphene/copper materials. The highest impedance appears at the graphene/electrolyte to be associated with electrochemically robust graphene materials, i.e., the as-grown graphene materials subjected to atomic layer deposition of Al₂O₃. Such an effect is attributed to the anti-corrosive protection of graphene materials and the defect-curing function of Al₂O₃ in graphene materials. The impedance-based information can be exploited in-situ without the use of any destructive approaches to evaluate the electrical perfectness vulnerable to preparation environments.

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1. Introduction

Graphene, which is a monolayer of sp²-bonded carbon atoms, has been gaining extensive academic/industrial attention because of its unprecedented electrical [1,2], mechanical [3], optical [4], chemical properties [5,6], and superior thermal conductivity [7]. Additionally, several approaches such as the mechanical exfoliation of graphite, chemical reduction of graphene oxide, and chemical vapor deposition (CVD) on metal substrates have been reported [8–10]. The wide range of interesting properties and development of mass-production in graphene materials have allowed for numerous applications in

electrochemical sensors, energy storage devices, and nano/microelectronics involving active devices [11–16].

The CVD of graphene layers has been widely employed in addition to the mechanical exfoliation of graphite and chemical reduction of graphite oxides [8–10]. Despite a wealth of synthesis and fabrication research, the corresponding monitoring tools in graphene materials have been limited to atomic force microscopy (AFM), scanning tunneling microscopy (STM), optical microscopy, X-ray diffraction (XRD), Raman spectroscopy, Hall measurements, and transmission/scanning electron microscopy [6,17–22]. To demonstrate the presence of graphene in single and/or multi-layers and to estimate the quality of as-grown graphene materials, Raman spectroscopy has been recognized as a major tool despite the local sampling area. In addition, optical microscopy and Hall measurements have been employed in the characterization of these materials. Another point of interest is that the graphene should be transferred onto appropriate substrates, typically thermally-

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grown SiO₂ on Si wafers. In other words, the graphene materials can encounter undesired defects resulting from the transfer process, in the form of wrinkles, cracks, etc. The resulting data may be associated with the process defects in the transferring process. Although the established protocols have been successfully applied to the materials, the number of graphene layers is identified through the relative comparison of the intensity of 2D- and G-bands observed in Raman spectra. The graphene synthesis process is vulnerable to the experimental surroundings and the graphene transfers are still sensitive to the experimenter's skill in addition to the lengthy and time-consuming steps and reproducibility concerns. The qualitative and/or quantitative monitoring should be required in graphene-based materials.

Impedance spectroscopy offers unique features due to the frequency-dependent impedance information: (i) simultaneous measurements of conductivity and dielectric constants, (ii) discernable separation of electrical origins e.g., bulk, interfacial, and electrode-associated effects, and (iii) electrical homogeneity of non-bulk responses from grain boundaries and/or electrode-related behaviors. Impedance spectroscopy has been applied to various materials, i.e., ionic conductors and electrochemical reactions in solid-oxide fuel cells, grain-boundary-controlled ceramics, positive temperature coefficient resistors, and corrosion phenomena in metallic materials [22–26]. Electrochemical characterizations have been attempted for graphene-associated phenomena, i.e., graphene for corrosion protection, biological monitoring, and energy-based applications [12,27–30].

The current study places its main emphasis on the quality of graphene materials synthesized on metallic materials using electrochemical impedance spectroscopy in combination with electrode-polarization between electronic electrodes and ionic electrolytes: electrochemical monitoring is attempted at the interfaces between the ionically conducting liquids and the electrically conducting metals, mostly copper. The perfectness or quality control is demonstrated for optimized graphene synthesis.

2. Experimental procedures

The graphene layers were grown via thermal CVD (TCVD) on 2 cm × 2 cm Cu substrates (Cu-113213, 20-μm thickness, 99.9%, Nilaco Corporation, Japan). The gas atmosphere was controlled with the aim of depleting oxygen involvement using hydrogen in growing the graphene layers. The processing chamber was raised to 950 °C at a heating rate of 10 °C/min along with a continuous flow of hydrogen and kept at 950 °C for 0.5–2 h along with the injection of methane into the synthesis chamber, where hydrogen and methane were kept at a ratio of 3 to 1. The chamber was then cooled to ambient conditions through either furnace cooling or rapid cooling, where the hydrogen was supplied until the chamber temperature reached room temperature. After growing the graphene materials onto copper substrates, Al₂O₃ was deposited onto the graphene materials using atomic layer deposition, in which trimethyl aluminum (TMA) and water were employed as

sources for aluminum and oxygen, respectively at 150 °C. The ALD cycles were fixed at 100 cycles with a pulse time of 0.5 s in TMA and water, leading to the thickness of approximately 10 nm.

The as-grown graphene materials were subjected to electrochemical impedance spectroscopy tests. The impedance spectra were acquired in the three-point electrode configuration, where a Ag/AgCl electrode was employed as a reference electrode. The impedance information was acquired using an electrochemical impedance analyzer (SP-300, Biologic, France) between 1 MHz and 10 mHz with 10 points per decade, and the oscillating amplitude was fixed at 25 mV. For the corrosive media, 0.1 M aqueous sodium sulfate (Na₂SO₄) was selected with a high concentration of ionic compounds in the electrochemical impedance spectroscopy and potentiodynamic polarization measurements. The scan rate was set to 60 mV/min, and the open cell voltage was varied from –50 mV to 1.5 V. Through a transfer process involving FeCl₃ as the etchant, the transferred graphene materials were monitored using Raman spectroscopy (Micro-Raman, Reinshaw, UK).

3. Results and discussion

Electrochemical impedance spectroscopy was applied to two types of graphene materials prepared on Cu foils in addition to the pristine Cu foils. One of the materials was as-grown graphene on a Cu substrate using TCVD, and the other was as-grown graphene subjected to the ALD of Al₂O₃. As demonstrated in Fig. 1, the corresponding impedance spectra are divided into two regimes, i.e., ionic contribution and electrode-based responses, as a function of frequency, where the frequency decreases from the left to the right portion in the Nyquist plots. The ionic contribution reflects the ionic transport in the concentrated ionic solution employed in this work, i.e., Na₂SO₄. The 3-point impedance spectroscopy allows for the interfacial features occurring between the ionic solution and graphene materials grown on the Cu sheets functioning as

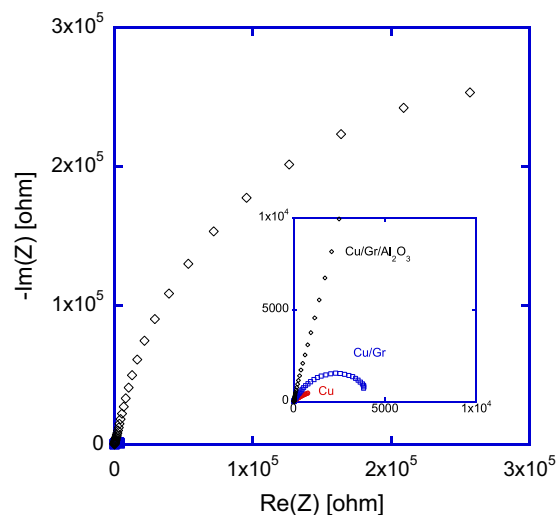


Fig. 1. Impedance spectra of bare Cu substrates, as-grown graphene materials on Cu substrates, and as-grown and Al₂O₃ deposited graphene materials.

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