Carbon 125 (2017) 464–471

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Three-dimensionally stacked Al_2O_3/graphene oxide for gas barrier applications

Dong-won Choi [a], Hun Park [b], Jun Hyung Lim [c], Tae Hee Han [b], [**], Jin-Seong Park [a], [*]

[a] Division of Materials Science and Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul, 04763, Republic of Korea
[b] Department of Organic and Nano Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul, 04763, Republic of Korea
[c] School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, 440–746, Republic of Korea

ARTICLE INFO

Article history:
Received 2 July 2017
Received in revised form
30 August 2017
Accepted 15 September 2017
Available online 18 September 2017

Keywords:
Atomic layer deposition
Graphene oxide
Gas barrier
Thin film encapsulation

ABSTRACT

We investigated the growth behavior of Al_2O_3 using atomic layer deposition (ALD) on the surface of chemical vapor deposition (CVD)-grown graphene and graphene oxide (GO). While selective ALD growth was observed on CVD-grown graphene along defective sites, smooth and continuous films were grown on GO without selective growth. Linear growth of Al_2O_3 on GO was observed without a nucleation region or growth selectivity. This result indicates that the ALD film growth is more suitable for GO because of the abundant and homogeneously distributed reactive sites over its basal plane. By taking advantage of GO as an ideal substrate for the ALD growth of metal oxides, highly aligned, multiple-stacked, three-dimensional Al_2O_3/GO structures were fabricated, which showed much better effective gas barrier characteristics (1.73×10^{-4} g/m^{2}day) than that exhibited by pristine single Al_2O_3 thin films of the same thickness.

1. Introduction

Defect-free single-crystal graphene is an ideal gas barrier owing to its impermeability to all gases and liquids [1–4]. However, in spite of numerous studies using graphene in gas barrier applications, a single graphene layer grown by chemical vapor deposition (CVD) has not exhibited effective gas barrier properties so far. This is due to the presence of many defects and grain boundaries on its surface. Essentially, gas permeation occurs through defect sites of graphene [3,4]. Therefore, the most promising strategy to overcome this hurdle for gas barrier applications of graphene is the prevention of gas permeation by covering the defects with a sufficient number of the graphene layers [4,5]. A potential solution could be the use of multi-layered structures because densely packed multi-layered graphene films can minimize moisture permeation [4–6]. However, even though multilayers of graphene might be one of solution for thin film encapsulation, it has never achieved for requirements for encapsulation of OLEDs [4–6].

To surpass this disadvantage, a defect-healing process, which fills defective sites with complementary materials such as metal oxides, has been attempted using various methods, such as atomic layer deposition (ALD) or the sol-gel process [7–9]. ALD is a widely known technology to deposit metal or metal oxide on graphene sheets for atomic-scale defect healing. It is based on sequential and self-limiting surface chemical reactions, and it can selectively deposit on surface-reactive sites with atomic scale [9–11]. We noted that structural defects of graphene are usually more reactive than the basal plane of graphene [12]. Therefore, the combination of two approaches (using graphene barrier materials and ALD as a defect-healing method) would be the most powerful solution for gas barrier applications. However, although the metal oxide ALD process is effective for defect healing of graphene, the gas barrier properties have not seen a large improvement as a result [6]. Multiple pairs of a metal oxide/graphene structure are required for extremely low gas permeation barriers because multilayer stacked films improve moisture barrier properties [13,14]. However, achieving such a structure using ALD has not been achieved yet because metal oxides cannot be deposited uniformly on single-crystal graphene with a large area by ALD because of its own selective film growth behavior. Therefore, an ALD process to obtain multiple pairs of highly ordered metal oxide/graphene structures should be developed for high-performance gas barriers.

Unlike CVD-grown graphene, graphene oxide (GO) has

---

[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: than@hanyang.ac.kr (T.H. Han), jsparklime@hanyang.ac.kr (J.-S. Park).

https://doi.org/10.1016/j.carbon.2017.09.061
0008-6223/

abundant reactive sites such as hydroxyl and epoxy groups on the basal plane, and carboxy, carbonyl, lactone, phenol, and quinone groups at the edges [15,16] because GO is exfoliated from graphite by introducing those oxygen functionalities on graphene. Their high reactivity allows GO to be functionalized or hybridized with various organic/inorganic materials [17,18]. Additionally, these functional groups can provide good dispersibility in many solvents. Combination of such high dispersibility and high aspect ratio leads the GO dispersion to liquid crystalline phase in which GO colloids are spontaneously ordered and assembled to macroscopically ordered materials [19,20]. Furthermore, the well-dispersed GO colloids can be easily deposited various substrates with large surface areas using solution processes [21]. Therefore, GO might be more suitable than graphene for uniform film growth and for obtaining multi-stacked structures with large areas. In this work, we have compared the growth behavior of Al_2O_3 on CVD-grown graphene and GO using ALD. Then, by repeating solution coating of GO and Al_2O_3 growth using ALD, highly aligned 3-dimensional Al_2O_3/GO hybrid structured films were successfully prepared. This highly ordered structure was more effective than single ALD Al_2O_3 thin films for gas barriers.

2. Experimental details

2.1. Synthesis of CVD-grown graphene and GO

Graphene was grown at 1000 °C under a mixed gas flow of CH_4 and H_2 on a Cu foil [22], and the Cu foil was removed using a 0.1 M ammonium persulfate ($(NH_4)_2S_2O_8$) solution; the graphene was then directly transferred to a SiO_2 substrate for Atomic Force Microscopy (AFM) and X-ray Photoelectron Spectroscopy (XPS) analysis. GO was prepared from graphite powder (Bay Carbon, SP-1) using the modified Hummers method as described elsewhere [12]. A GO solution was prepared by dispersing GO powder in a mixed solution of deionized water (DI) and MeOH (in *v*/*v* 2:1) at a 0.5 mg mL^{-1} content for spin-coating.

2.2. Growth of Al_2O_3 on graphene and GO

Al_2O_3 thin films were deposited on Si, SiO_2, and polyethylenenaphthalate (PEN) substrates at 100 °C in a handmade viscous flow reactor. Trimethylaluminum (TMA) and H_2O were kept in a stainless steel cylinder and maintained at 25 °C and were used as the precursor and reactant, respectively. A TMA (0.2 s)–N_2 purge (20 s)–H_2O (0.2 s)–N_2 purge (20 s) cycle was used for Al_2O_3 growth. In order to fabricate the Al_2O_3/GO/Al_2O_3 multi-layered structure, the surface of Al_2O_3 was plasma-treated (O_2, 40 W, 3 min, 30 sccm). 1 mL of a GO solution was deposited onto the Al_2O_3 substrate (3 cm × 3 cm, 3000 rpm for 1 min) by spin-coating. After spin-coating, the fabricated film was dried at 60 °C for 10 min using a hot plate.

2.3. Characterization of Al_2O_3 on graphene and graphene oxide

Morphologies of Al_2O_3 on graphene and GO were characterized by atomic force microscopy (AFM; Park system, XE-70) and high-resolution transmission electron microscopy (HR-TEM; JEOL, JEM-2100F). The chemical bonding states were investigated using a XPS (PHI5800). Raman spectroscopy (JASCO, NRS-3100) was performed using 514 nm laser excitation. The water vapor transmittance rate (WVTR) value was calculated by electrical Ca-test measurements using the following equation.

$$\mathrm{WVTR} = \; -n\frac{M(H_2O)}{M(Ca)}\,\delta\rho\,\frac{1}{b}\,\frac{d\left(\frac{1}{R}\right)}{dt}.$$

where n is the stoichiometric coefficient for water oxidation; M denotes the atomic mass; ρ is the density of Ca (1.55 g cm^{-3}); δ is the resistivity of the Ca film (3.4×10^{-6} Ωcm); l and b are the length and width of the Ca pad, respectively; and $1/R$ is the measured conductance. Patterned Al electrodes were deposited on the glass substrate and Ca metal was electrically connected between the Al electrodes [23]. A moisture barrier thin film was prepared on a 125-μm-thick PEN substrate and placed on the glass substrate. The edges between the gas barrier film and glass substrate were sealed with a UV-curable epoxy resin (UV resin ZNR 5570, Nagase & Co., Ltd.). To prevent the oxidation of Ca metal, all procedures were conducted in a glovebox system. The *I*–*V* characteristics of each Ca-test cell were evaluated using a Keithley 2750 multi-meter against time after fabrication. The electrical conductance of the Ca metal between the Al electrodes gradually decreased with Ca oxidation due to moisture permeation. All measurements were examined at accelerated conditions at 85 °C/85% relative humidity (R.H.) using a constant temperature and humidity chamber (TH-ME-100, Jeio Tech). The accelerated conditions at 85 °C/85% R.H. were 240 times harsher than ambient conditions (25 °C/50% R.H.) condition [6,24]. Therefore, 1 h at 85 °C/85% R.H. is equivalent to 240 h at ambient conditions.

3. Results and discussion

Al_2O_3 was deposited on both CVD-grown graphene and GO, as shown in Fig. 1. ALD film growth behavior on the two carbon materials were directly compared for various cycle numbers. As shown in Fig. 1(a), the thickness of the pristine graphene was approximately 2.5 nm. After 25 cycles of ALD operation for the deposition of Al_2O_3, growth of Al_2O_3 was observed along apparent line defect, in wrinkles, implying that the growth of Al_2O_3 preferentially occurred at specific sites, such as grain boundaries or edges, compared to that on the basal plane of graphene [9,10,25,26]. The XPS spectra clearly demonstrate the Al content for the Al_2O_3 layer obtained after 25 ALD cycles (Fig. S2 (c)). Interestingly, many Al_2O_3 nuclei were observed after 100 cycles. In many common ALD processes undertaken on CVD-grown graphene, many dot-shaped nuclei are primarily created on the basal plane of graphene and then nucleation lead to monotonous growth with increasing numbers of ALD cycles [25]. We noted that ALD film growth is based on a chemical reaction that occurs after adsorption on reactive sites on the first ALD cycle. Some clusters are formed after that over a few ALD cycles, and the clusters eventually merge after several ALD cycles. Finally, subsequent exposure leads to progressive ALD growth [27,28]. According to this ALD growth mechanism, a partially continuous film of Al_2O_3 is the result of merged clusters, and particle-like nuclei denote cluster-forming regions. In contrast with graphene, abundant oxygen functionalities are homogeneously distributed over the carbon sheets of GO [12,15,16]. These functional groups are crucial as adsorption sites for reactant gas molecules in ALD processes [9,10,25,26]. Thus, these enable uniform deposition of ALD films on the GO matrix. In order to investigate ALD film growth behavior on GO, Al_2O_3 was deposited on spin-coated GO with increasing numbers of ALD cycles. Fig. 1(b) shows the AFM image of Al_2O_3 on GO after 0, 25, and 100 cycles. The pristine GO sheet had a homogeneously smooth surface and an average thickness of 1.6 nm. Interestingly, in contrast with ALD growth on graphene, no apparent morphology change was observed with increasing ALD cycles. This result indicates the absence of any growth selectivity of Al_2O_3 on the GO matrix and