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ZnO Thin Film Grown on Graphene on Insulator by Chemical Vapor Deposition using Catalytically Produced High-Temperature Water

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Abstract

The characteristics of ZnO films grown on graphene, i.e. single-layer (SLG) and multi-layer graphene (MLG), on insulators at 500°C using a reaction between dimethylzinc and high-temperature H_2O generated by a catalytic reaction on Pt nanoparticles were investigated. The growth rate of continuous ZnO layer on MLG (0.07 µm/min) grown for 1 hr was almost 10 times higher than that of SLG (0.007 µm/min). XRD patterns for the ZnO films exhibited an intense diffraction peak associated with (0002) plane and small ones associated with (10-10) and (10-11) planes, suggesting the grown hexagonal wurtzite ZnO is not perfectly along c-axis direction due to the nature of the used graphene structures. The photoluminescence at room temperature exhibited strong emission peak at 3.28 eV with no significant level of green emission indicating negligible defect density in the grown ZnO films.

1. Introduction

ZnO is a promising candidate for the fabrication of several kinds of devices due to its unique electronic and optical properties such as wide bandgap and large exciton energy. A hybrid structure of the ZnO nanostructure and thin film on graphene shall lead to several device applications not only on Si substrate but also on other transparent insulating substrates such as glass and flexible plastic due to the high transparency of ZnO and graphene.

We have studied the growth of ZnO directly on graphene using chemical vapor deposition (CVD) technique in this paper. Here, we have developed a new CVD method that utilizes high temperature water (H_2O) to effectively hydrolyze metalorganic source gases. In this process, high temperature H_2O molecules are generated from the exothermic reaction between hydrogen and oxygen on platinum (Pt) nanoparticles inside a catalytic cell and subsequently effuse through a de Laval nozzle, a device that has been widely used for the generation of cluster and ion cluster beams after which they effectively hydrolyze metalorganic gas molecules. In this paper, we report the direct growth of ZnO films on graphene with excellent morphological, structural and optical properties, based on the reaction between dimethylzinc (DMZn) and high temperature H_2O produced by a Pt-catalyzed H_2–O_2 reaction.

2. Experimental

Fig. 1 shows a schematic diagram of the CVD apparatus used in this study [1]. H_2 and O_2 gases were admitted into a catalyst cell containing a Pt-dispersed zirconia (ZrO_2) catalyst. The catalyst temperature increased rapidly to over 1300 K within a minute. This is due to the exothermic reaction between H_2 and O_2 on the catalyst. The resulting high-temperature H_2O molecules were ejected from a fine nozzle into the reaction zone where they collided with DMZn ejected from another fine nozzle. The distance between the H_2O nozzle and the substrate was 50 mm, while the distance between the DMZn nozzle and the substrate is 10 mm. A skimmer cone was placed between the H_2O nozzle and the substrate to select high-velocity H_2O molecules and direct them to the substrate. ZnO films were grown directly on SLG/glass (Graphene Laboratories, USA) and MLG/SiO_2/Si Graphene Laboratories, USA) substrates at substrate temperatures of 500°C for 1 h and 2 hrs. The substrates were degreased using methanol and acetone, and rinsed with ultrapure water. The H_2 and O_2 gas flow rates were set 300 and 100 sccm, respectively. DMZn gas flow rate was monitored by the pressure and its typical value was 2.0-4.1x10^{-3} Pa. The reaction gas pressure in the chamber during deposition was 0.6-0.8 Pa.

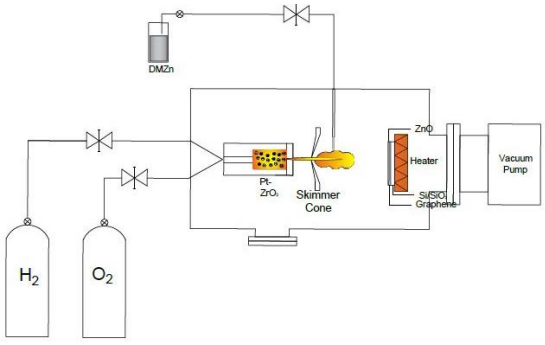

Fig. 1. Schematic diagram of CVD set up

3. Result and Discussion

Fig. 2a and **2b** show the examples of FE-SEM images (top view and cross-sectional view), AFM images and EDX spectra of the ZnO films grown on SLG/glass (2 hrs) and MLG/SiO_2/Si (1 hr), respectively. As can be seen, all grown samples show continuous layers with rough top surfaces. Here, top surfaces were formed by dense hilly structures with multi-crystalline facets. This indicates that the film growth direction is not sole along the c-axis. The EDX spectra show

the major elements detected in both samples, which consist of Zn, O and carbon (C) with no other impurity detected.

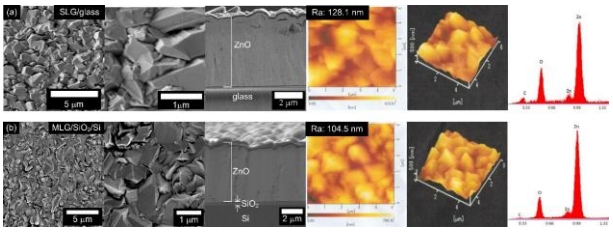

Fig. 2. The examples of FE-SEM images (top view and cross-sectional view), AFM images and EDX spectrum of the ZnO films grown on **(a)** SLG/glass (2 hrs) and **(b)** MLG/SiO_2/Si (1 hr).

Fig. 3 shows XRD patterns for the grown ZnO thin films on SLG/glass and MLG/SiO_2/Si at temperature of 500°C. Sample MLG/SiO_2/Si and SLG/glass show high intensity of ZnO (0002) peak at 2θ =34.57° and 34.65° and other weak two peaks associated with (10–10) plane at 2θ =31.80° and 31.89°, and with (10–11) plane at 2θ =36.50° and 36.58°, respectively. This suggests that the grown hexagonal wurtzite ZnO is not in perfectly c-axis direction. This is due to the nature structure of the used graphene, which contains grain boundaries and steps. Such morphologies will lead to the nucleation and subsequent growth of ZnO in the multi directions. As mentioned above, the ZnO (0002) diffraction peak for the grown samples appeared at 2θ values in the range of 34.57–34.65°, which were slightly larger than those for bulk ZnO crystals (2θ =34.41–34.42°) [2].

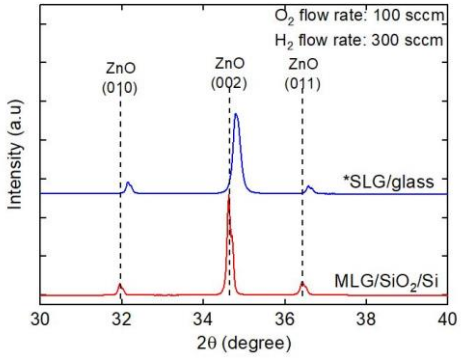

Fig. 3. XRD patterns for the grown ZnO thin films on SLG/glass and MLG/SiO_2/Si at temperature of 500°C. Asterisk shows that the intensity has been amplified by 10 times.

This suggests that the ZnO/graphene films grown by the proposed method on different substrates contain a small amount of residual tensile stress, and lattice and thermal coefficient mismatch of substrate surface. The full width at half maximum (FWHM) values of the 2θ for the ZnO (0002) peaks were estimated to be in the range of 0.173°-0.213° for SLG/glass, while 0.146°-0.152° for MLG/SiO_2/Si substrates.

Fig. 4 shows the PL spectra of the as-grown ZnO films grown on SLG/glass and MLG/SiO_2/Si, measured at room temperature (RT). The PL spectra of both samples show sharp peaks at 3.28 eV with a FWHM range of 0.1151-0.1381 eV. This peak can be assigned to band edge emission. Green luminescence from deeper levels is hardly observed: its intensity is as low as 1-2% of the band edge emission intensity.

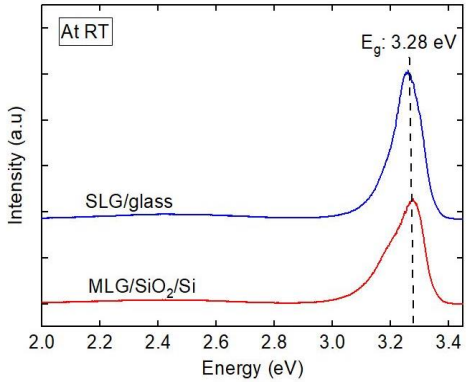

Fig. 4. PL spectra of the as-grown ZnO films grown on SLG/glass and MLG/SiO_2/Si, measured at room temperature (RT).

This clearly indicates that the defect density is negligible. The defect densities of ZnO films grown on graphene by thermal evaporation [3] and electrochemical deposition [4] are found to be very high where very significant level of green luminescence has been observed: its intensity can reach around 70% of the band edge emission intensity.

4. Conclusions

The growth of ZnO films on graphene on insulators at low temperature of 500°C using a reaction between dimethylzinc and high-temperature water generated by a catalytic reaction on Pt nanoparticles was performed for the first time. The growth rate of continuous ZnO layer on MLG grown for 1 hr was almost 10 times higher than that of on SLG. Intense (0002) peak and weak (10-10) and (10-11) peaks were observed, suggesting the grown hexagonal wurtzite ZnO is not perfectly in c-axis direction due to the nature of the used graphene structures. The FWHM values of the 2θ for ZnO (0002) were relatively small for ZnO grown on both SLG and MLG. A strong emission peak at 3.28 eV was observed with no significant level of green emission indicating negligible defect density in the grown ZnO films.

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