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Chen, Cheng; Stiens, Johan; Hauffman, Tom; Revilla, Reynier I.; Pletincx, Sven

Published in:
Applied Surface Science

DOI:
https://doi.org/10.1016/j.apsusc.2019.144169

Publication date:
2019

Document Version:
Final published version

Citation for published version (APA):
Full Length Article

Exploration and mechanism analysis: The maximum ultraviolet luminescence limits of ZnO/few-layer graphene composite films

Cheng Chen, Lu Kou, Tom Hauffman, Zhiyong Zhang, Sven Pletinck, Junfeng Yan, Reynier I. Revilla, Wu Zhao, Jiangni Yun, Johan Stiens

Abstract

In this paper, ZnO films were deposited on the surface of few-layer graphene films by RF magnetron sputtering and its photoluminescence performance was studied. Large-area few-layer graphene films were prepared on a Cu substrate by CVD. To improve the crystalline quality and c-axis preferred growth orientation of ZnO films, we systematically optimized the process parameters (RF power, working pressure, substrate temperature, the sputtering time) to make the composite films have the strongest UV emission performance with the lowest visible range.

1. Introduction

Zinc oxide (ZnO) as a third-generation semiconductor is excellent in UV-excited emission at room temperature [1]. It has attracted much attention owing to its outstanding optoelectronic device applications, such as ultraviolet light emitters [2], solar cells [3], luminescent screens [4], etc. Several techniques, such as sputtering, sol-gel, hydrothermal method, etc. are used for the synthesis of ZnO films [5]. Among them, sputtering is a more effective and safe method for the preparation of ZnO films. As is well-known ZnO is one of the most ideal materials for preparing semiconductor lasers because of its exciton binding energy which is much higher than that of room temperature thermal energy [6]. Graphene is a two-dimensional monolayer of sp2-hybridized carbon atoms. It has been widely investigated for diverse applications such as transistors, sensors, actuators, flexible and transparent [7]. Many approaches have been used to fabricate graphene including mechanical cleavage, chemical vapor deposition (CVD) and graphite oxide reduction, etc. [8]. The CVD technique has proven its success in the experimental and commercial production of graphene. Numerous studies have found that graphene is an ideal hybrid material because of its excellent chemical and physical properties [9–11]. The study on the properties of ZnO/graphene composites is of great significance to promote the application of ZnO based optoelectronic semiconductor devices.

In general, ZnO yields photoluminescence (PL) output in two spectrally distinct regions: ultraviolet (UV) emission and visible emission; the former is caused by excitonic recombination and the latter by deep level defects [12,13]. Generally, ZnO thin film has strong UV emission because of its stable structure, especially when the film is annealed, this effect will be more obvious; for one-dimensional (1D) or zero-dimensional (0D) ZnO, such as nanorods, nanowires or quantum dots, a large number of defects on its surface and inside lead to strong visible emission, and the colors of visible emission, such as red light, green light or yellow light, is determined by the types of its major defects [14–16]. According to the literature, ZnO has six kinds of defects: Zn vacancy (VZn), O interstitials (Zni), O antisite (OZn), O vacancy (VO), O interstitials (Oi), and O antisite (ZnO) [17,18]. Among them, VO defect is the main defect in ZnO body-phase, which has a strong inhibiting effect on UV emission characteristics [19]. Therefore, to obtain ZnO with excellent UV emission performance, the first problem to be solved is to...
optimize the preparation process of ZnO to improve its crystal quality and reduce defects as much as possible. ZnO has a variety of morphological structures (0D, 1D, 2D) [20–22]. Graphene is generally divided into two categories: graphene nanosheets, nanoparticle powders; graphene films [23,24]. Therefore, the composite forms of these two materials are miscellaneous, and different composite forms can be exploited in different fields. ZnO and carbon nanocomposites gaining interests due to their distinctive optical properties. These composite structures yield an enhanced UV to visible emission ratio owing to improved surface-plasmon-mediated emission and a new defect emission mechanism [25–27]. To optimize the preparation process to improve the crystalline quality of ZnO and graphene composite film will be beneficial to improve its UV emission.

In this paper, the ZnO/graphene composite films were prepared by CVD and magnetron sputtering method. The technological parameters of ZnO film growing on the surface of the few-layer graphene films are optimized by the single-factor optimization method. Also, the influence of flow ratio of Ar and O2 on ZnO crystal quality in the sputtering process and the reinforcement effect of graphene on the UV emission of ZnO in composite film structure are reported. Finally, to obtain the ZnO/graphene composite film with an excellent performance UV emission, the influence of the sputtering time on the PL properties of the composite structure was studied.

2. Experimental work

2.1. The preparation of ZnO/graphene composite films

The graphene film was fabricated by CVD on a polished polycrystalline Cu substrate. During the deposition process, the surface temperature TS was 1050 °C, and two different gasses, Ar (600 SCCM) and the hydrocarbon mixture of C2H2/H2 (15 SCCM/75 SCCM) were passed into the airway for 600 s. ZnO films were deposited on graphene films by RF-magnetron sputtering. During the sputtering process, the working pressure, RF power, and TS were maintained at 0.5 Pa, 200 W, and 150 °C, respectively, and the gas flow rate of Ar and O2 was 35 and 5 SCCM, respectively.

2.2. Characterisation

The surface morphology of few-layer graphene films was characterized by Metallo-microscope (Nikon Eclips ME6000), scanning electron microscopy (SEM-EDS, Phenom ProX), and atomic force microscopy (AFM, Park-AFM XE-100). The crystalline quality and thickness of graphene films were characterized by Raman spectroscopy (LabRAM HR Evolution (HORIBA Scientific)) and AFM line-scan. The phase analysis, qualitative analysis and surface relative quantitative analysis (Xat%) of ZnO/graphene composite films were characterized by X-ray film diffractometry (XRD, Shimadzu 6100) and X-ray photoelectron spectroscopy (XPS, HPI-5600ci). The atomic percentage and energy dispersive spectroscopy of ZnO/graphene samples were characterized by SEM-EDS. The PL performance of ZnO/graphene sample was characterization a fluorescence spectrophotometer (HORIVA Fluoro Max-4p).

3. Result and discussion

3.1. The preparation of graphene films

CH4 will be decomposed during the CVD deposition process, and the carbon atoms will deposit and continuously disperse on the substrate surface at high temperature. Then, the carbon atoms will crystallize to form the graphene film during the cooling stage. As the thermal expansion coefficient of Cu is larger than that of graphene, the lattice contraction of the substrate surface will cause the graphene film to shrink and generate wrinkles in the cooling process. Fig. 1a–c show the changes of the Cu substrate surface after polishing and deposition. The folds of the graphene film can be seen in Fig. 1d. As shown in Fig. 1f, we randomly scanned 10 points on the substrate surface along a straight line. The Raman scanning results in this figure can prove that the graphene films have excellent coverage and integrity. From the AFM image and line-scan curve in Fig. 1e and g, the thickness of few-layer graphene are between 0.5 and 1 nm.

The reasons why we chose to prepare a few layers of graphene as the bottom layer are as follows: (1) Inevitably, there are lattice defects on the top surface of the Cu substrate, which lead to uneven degree of surface contraction in the cooling process, and monolayer graphene may be prone to fracture during this process, thus affecting the integrity of the film. (2) The preparation cost of mono-layer graphene film is relatively high, and it needs to be completed on the surface of the monocrystalline Cu substrate. However, the price (€) of polished (1 0 0) monocrystalline Cu substrate is more than 5 times that of the poly-crystalline Cu substrate. (3) To obtain samples featuring very similar properties, it is easier and more reliable to prepare a batch of few-layer graphene films with similar thickness than a batch of monolayer graphene film. The value of tFl/tG values of the ten curves in Fig. 1f were all-around 1.31. 4) The process is more stable than the preparation of monolayer graphene film.

3.2. Effect of Ar/O2 flow ratio on the crystal quality of the ZnO/graphene sample

In the RF magnetron sputtering process, four main technological parameters affect the growth of ZnO: RF power [28], TS [29], deposition pressure [30], and the flow ratio of Ar and O2 [31]. Numerous relevant studies have concluded that: (1) The RF power will affect the density of Ar+ ions produced by the ionization of Ar gas and influence the kinetic energy of Zn2+ and O2+ particles during deposition; (2) TS is an important factor influencing the crystallization quality of ZnO. On the one hand, heating the substrate to a certain temperature in a vacuum can induce the decomposition of pollutants adsorbed on the substrate surface; on the other hand, the proper increase of TS can improve the migration rate of target particles and make them have sufficient kinetic energy to reach the optimal energy site. Meanwhile, the TS also affects the nucleation and growth of particles on the substrate surface; (3) Working pressure can influence the deposition rate effectively. A high concentration of gas molecules will result in the reduction of the average free path of Ar+ and the energy carried, which further leads to the reduction of the energy of argon ions hitting the target. Therefore, choosing the right working pressure is vitally important for the ZnO growth. (4) The sputtering efficiency of Zn atoms is higher than that of O atoms during the sputtering process. This phenomenon will lead to the occurrence of defects such as O vacancy, Zn interstitial atom or O antisite in ZnO body phase after deposition. To improve this problem, pure O2 and Ar gas are mixed into the chamber in a certain proportion during sputtering. RF power, working pressure, and TS can effectively influence the crystal quality of ZnO. The selection of proper flow ratio of Ar and O2 not only affects the crystal quality of ZnO films but also determines the content of Zn and O atoms in the ZnO films after deposition. Through systematic experiments of single-factor method and analysis of the SEM image and the characteristic parameters (Full width at half maximum (FWHM), Intensity of diffraction peaks) of ZnO XRD spectrum, the optimal process parameters of RF power, working pressure and TS are determined (Supplementary Material, Figs. S1–S6, Tables S1–S3).

As mentioned above, the visible emission of ZnO is attributed to its intrinsic and extrinsic defects and these defects will inhibit the UV emission. According to the optimization results of process parameters (Supporting Information), the sum of Ar and O2 flow was determined to be 40 SCCM. Four levels of this factor were selected within the experimental range (SCCM): Ar:O2 = (a) 38 to 2, (b) 35 to 5, (c) 30 to 10, (d) 25 to 15. As shown in Fig. 2, by comparing the XRD spectrum in
Fig. 2a to d with the standard PDF card (JCPDS Card No.36-1451) of ZnO, the diffraction peaks with the 2θ angle of 34.4° (0 0 2) and 36.2° (1 0 3) are all included in these four pictures. The curve in Fig. 2d also contains two non-polar diffraction peaks: (1 0 0) and (1 0 1), which are located at 31.8° and 36.3°, respectively. As shown in Fig. 2e to h, the granular clusters with different sizes appeared on the surface of these samples. It can be preliminarily concluded from SEM images that the particle clusters on the sample surface in Fig. 6f are the smallest and evenly distributed. Fig. 2i shows Eat% results of different ZnO/graphene samples. It can be seen that the ratio of O atoms in Eat% (b) is higher than in (a), (c) and (d), and a small number of Cu atoms have been scanned in these three samples, which also indicates that the coverage of ZnO on the corresponding sample surface of Eat% (b) is better than (a), (c) and (d).

As shown in Table 1. Through comparison, when the flow ratio of Ar and O2 (SCCM) are 38 to 2, the lack of O2 during sputtering will increase the content of O vacancy defects in the crystal of ZnO due to the lack of O atoms. When Ar and O2 flows are 35 and 5 SCCM, the (0 0 2) diffraction peak of the ZnO/graphene sample is maximum and sharpest, and the ratio of peak intensity to FWHM is maximum, coinciding with the best crystallization. When the flow ratio of Ar and O2 (SCCM) is set at 25 to 15, the crystallinity of ZnO further deteriorated. As shown in Fig. 2d, two non-polar peaks (1 0 0) and (1 0 1) appeared near the (0 0 2) diffraction peak in the XRD curve, which indicates the c-axis preferred orientation of the ZnO change for the worse. Therefore, the O2 flow in the deposition process should be neither too low nor too high.

3.3. Reinforcement effect of graphene on the UV emission of ZnO

Graphene is a zero-gap conductor, and ZnO is a wide-bandgap semiconductor material. When the two materials are combined, photocarriers in ZnO can be introduced into the graphene side during the PL test. Besides, the hexagonal honeycomb structure of graphene improves the crystal quality of ZnO with a hexagonal wurtzite structure in the growth stage. For comparison, we directly used the optimized growth parameter to deposit the ZnO films on Cu substrate. As shown in Fig. 3a, six diffraction peaks of ZnO and Cu are identified by the XRD standard PDF card (PDF#04-0836Cu and PDF#36-1451ZnO). For the ZnO film, two diffraction peaks with the 2θ angle of 34.4° (0 0 2), 36.2° (1 0 3) and a non-polar diffraction peak at 36.3° (1 0 1) are all shown in Fig. 3a. Through calculation, the value of intensity/FWHM of (0 0 2) peak in Fig. 3a is only 1.419. The surface morphology of the ZnO/Cu sample is obviously granular in Fig. 3b. As shown in Fig. 3c, the Raman characteristic peak signal of graphene was weakened, and the positions of the three characteristic peaks were red-shifted. The Raman result shows that: (a) Although the ZnO films have an excellent transparency, it still absorbs part of the laser signal during the Raman test, which weakens the characteristic signal of graphene in the Raman spectrum; (b) In general, crystal lattice distortion, stress change or temperature change of external environment will cause redshift of the Raman peak. Comparing with graphene, the crystal structure of ZnO is not laminated,
which causes the redshift of Raman peak of graphene; (c) The Raman characteristic peaks of ZnO were at 438 cm$^{-1}$ and 579 cm$^{-1}$, respectively. According to literature, the wavelength of UV emission of ZnO is in the 365–385 nm range$^{[32]}$, and the visible emission basically includes blue emission (420–460 nm) and green emission (490–535 nm) which are attributed to Zni and VO, respectively$^{[33,34]}$. The visible emission of ZnO also includes red emission and yellow emission which are due to Oi defects and double ionized VO defect respectively$^{[35,36]}$. The PL spectra of two samples in Fig. 3d were measured with an excitation wavelength of 325 nm, which show the UV emission peaks at 367 nm. The PL spectra of the ZnO/graphene sample exhibits stronger UV emission than the ZnO/Cu sample, the intensity of visible emission peak of ZnO/graphene sample in the wavelength range of 410–500 nm is also lower than that of ZnO/Cu sample. Theoretical research shows that the graphene layer acts as lattice matching with ZnO, resulting in high electron mobility and PL intensity of ZnO film$^{[37,38]}$. Comparing with Fig. 2f and 3b, under the same sputtering process parameters, the ZnO films grown on graphene substrate are flatter. As the seed crystal of ZnO growth, graphene can greatly improve the crystal quality of ZnO.

### Table 1

<table>
<thead>
<tr>
<th>The ratio of Ar to O₂ (SCCM)</th>
<th>FWHM</th>
<th>Intensity</th>
<th>Intensity/FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>38 to 2</td>
<td>0.473</td>
<td>2657</td>
<td>5617.3</td>
</tr>
<tr>
<td>35 to 5</td>
<td>0.452</td>
<td>3463</td>
<td>7661.5</td>
</tr>
<tr>
<td>30 to 10</td>
<td>0.456</td>
<td>1996</td>
<td>4032.3</td>
</tr>
<tr>
<td>25 to 15</td>
<td>0.776</td>
<td>1226</td>
<td>1579.7</td>
</tr>
</tbody>
</table>

To obtain the ZnO/graphene sample with the strongest UV emission, the sputtering time of ZnO was studied systematically. From the theoretical, in case the ZnO layer is too thick, the electrons provided by the graphene layer will be captured by defects in the ZnO body during the PL test, eventually eliminating the contribution of graphene in the luminescence spectra of the ZnO surface. Table 2 shows the XRD characteristic values of the (0 0 2) diffraction peak of the ZnO/graphene.

As can be seen from Table 2, for a longer sputtering time, the FWHM and intensity of (0 0 2) peaks were increased and decreased, respectively. This demonstrates that the crystal quality of the ZnO layer was improved with the thickness. Mechanism analysis: the XRD spectra in Fig. 5a and b only contain the (0 0 2) peak of ZnO, which indicates that ZnO on the surface of these samples have excellent c-axis preferred orientation. This phenomenon is attributed to the fact that graphene...
film as a seed crystal layer of ZnO promotes the preferred orientation of ZnO. However, the FWHM value of the ZnO peak (0 0 2) in Fig. 4a and b are relatively large, which indicates the existence of lattice defects. The defects were caused by the so-called island growth mode of ZnO prepared by the sputtering method. The changes from SEM images in Figs. 4e–h and 2f also prove this point. For short sputtering times, the morphology of ZnO on the surface of graphene film exists in discrete island form. This structure is not stable, and numerous defects are distributed on its surface. As the thickness of the ZnO layer increases, the effect of the graphene film on the growth of ZnO becomes less and less. As shown in Figs. 4c and d, 20 diffraction peaks of 36.3 (1 0 1), 47.5 (1 0 2) and 62.9 (1 0 3) appear, which indicates that the preferred orientation of ZnO becomes worse. However, according to the XRD curve of the sample in Fig. 2b, a good preferred orientation is shown at the (0 0 2) diffraction peak. This indicates that when the sputtering time reaches 2 h, the ZnO layer reached a critical thickness and formed a relatively stable film structure, which improves the preferred orientation of ZnO. The reason for good orientation has nothing to do with graphene at this point.

3.5. PL properties of graphene/ZnO samples after optimization

As shown in Fig. 5a, the intensity of the UV emission peak decreases with increased sputtering time. In the same way, all the PL spectra in this figure were measured with an excitation wavelength of 325 nm. It can be found that the sample sputtered for 20 min has almost the same UV emission intensity as the sample sputtered for 30 min. However, Fig. 5b shows that in the visible range the broad emission peak for short sputtering times is much larger than for longer sputtering times. The visible emission peak is due to deep level defects, which will restrain the intensity of UV emission. This indicates that the reinforcement effect of graphene on UV emission for the ZnO with 20 min of sputtering is stronger than that of 30 min of sputtering. Mechanism analysis: combining Fig. 5a and b, it can be found that the thinner the thickness of ZnO is, the stronger the UV emission of the composite material is. In the PL test, the testing depth of pump light is related to the absorption coefficient of the material to the light source. The penetration depth of the excitation light source for direct bandgap semiconductor materials such as ZnO is generally tens to hundreds of nanometers, while the penetration depth for indirect bandgap semiconductor materials is up to the micron level. Therefore, the thicker the ZnO layer, the less obvious the enhanced effect of graphene on UV emission of composites. Finally, the composite material featured the best UV emission performance when the sputtering time of ZnO is 30 min.

On the other hand, the ratio of UV emission peak intensity (I_UV) and visible emission peak intensity (I_VIS) was used to judge the optical quality of the samples. As shown in Fig. 5e to f (Supplementary Material), The value of I_UV/I_VIS of each PL spectrum in Fig. 5 from 20 to 120 min is 28.90, 52.51, 137.05, 45.16, 15.47, respectively. These results show that the optical quality of the sample sputtered for 60 min is
Fig. 4. XRD spectrum of ZnO/graphene samples with different sputtering times: (a) 15 min; (b) 30 min; (c) 60 min; (d) 90 min. SEM images of ZnO/graphene samples with different sputtering time: (e) 15 min; (f) 30 min; (g) 60 min; (h) 90 min.
In the previous section, it has been proven that, within a certain range, the crystalline quality of ZnO layer improved with the increase of thickness, while the reinforcement effect of the few-layer graphene films on the UV luminescence and growth quality of ZnO decreased with the increase of the thickness of ZnO layer. Therefore, the intensity of UV emission of samples which sputtered for 20 and 30 min is very strong and close in Fig. 5a. However, when the sputtering time increased to 60 min, the intensity of UV emission peak of this sample decreased significantly compared with the first two samples. When the sputtering time is further increased, the UV emission of the samples decreases again. For example, PL spectra of the samples sputtered for 90 and 120 min, are very close with only small differences in UV emission. At this time, it can be judged that the reinforcement effect of graphene on the UV emission of the sample surface basically does not exist anymore.

The XPS full spectrum in Fig. 6a shows the diffraction peak of C1s, O1s, and Zn2p. The diffraction peaks of Zn2p3/2 and Zn2p1/2 were located at 1021.3 and 1044.4 eV in Fig. 6b. Four fitting peaks and their location are calculated by Gaussian method in Fig. 6c. Fig. 6d shows the diffraction peak of O1s and two fitting peaks are calculated by Gaussian method in this figure. The measured result of the full spectrum shows the Xat% of O, C, and Zn is 20.05%, 72.98%, and 6.97%, respectively. It’s different from the Eat% results in Figs. 2i and 3b, which show the Eat% value of Zn is larger than that of O. Therefore, we cannot directly estimate the content of defects from EDS analysis alone. According to the literature, XPS is a way of detecting at depths of several atomic...


