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Growth mechanism of novel scaly CNFs@ZnO nanofibers structure and its photoluminescence property

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\textbf{ABSTRACT}

Zinc oxide (ZnO), a wide direct band gap semiconductor, has attracted extensive attention for its potential optoelectronic applications, such as coherent ultraviolet light emitters. Pure one-dimensional ZnO structures such as nanorods and nanowires, etc. inevitably have some crystal defects, which makes them to emit not only in the ultraviolet region but also in the visible range. Photoluminescent ZnO-carbon nanocomposites are an emerging class of nanomaterials that has spurred a lot of interests due to its attractive optical properties. It has been shown that these composite structures yield an enhanced ultraviolet to visible emission ratio due to improved surface plasmon emission and a new defect emission mechanism. Hence, a novel one-dimensional structure of ZnO and carbon nanofibers composite material has been designed and prepared. The scaly ZnO is completely coated with carbon nanofibers. This new composite structure has strong ultraviolet emission photoluminescence characteristics in combination with low visible emission.

1. Introduction

Zinc oxide (ZnO) is a wide direct band gap semiconductor (\(E_g = 3.37\) eV), featuring a large exciton binding energy (60 meV), and a high electromechanical coupling constant [1]. In normal conditions of pressure and temperature, it crystallizes to the wurtzite hexagonal structure with space group (\(P6_3\)mc) [2]. ZnO has been applied for gas sensors, ultraviolet (UV) light emitters, UV laser source, luminescent screens, etc. [3]. Several techniques, such as magnetron sputtering, sol-gel, pulsed laser deposition (PLD), molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) are used for the fabrication of ZnO films [4–6]. Among the abovementioned methods, magnetron sputtering is a more effective and safe method. The photoluminescence (PL) performances of ZnO nanostructures have been exploited successfully by the luminescent device industry. ZnO exhibits two types of emission: UV and visible emission due to band-to-band emission (BBE) and deep level defects (DLE), respectively. In general, ZnO has six kinds of defects, such as O vacancy (\(V_{\text{O}}\)), O interstitials (\(O_i\)), O antisite (\(\text{O}_{\text{Zn}}\)), Zn vacancy (\(V_{\text{Zn}}\)), Zn interstitials (\(\text{Zn}_i\)), Zn antisite (\(\text{O}_{\text{Zn}}\)). In addition, PL performances of ZnO are strongly influenced by surface effects in low-dimensional nanostructures due to their large surface-to-volume ratio. C. Chen et al. have studied the surface passivation effect on the PL properties of ZnO nanorods [7]. Y. Lv et al. have studied the PL properties of ZnO nanowire arrays [8].

Growing ZnO films by sputtering method has some advantages when compared to other methods, as it allows accuracy control of the deposition parameters such as deposition rate, substrate temperature (\(T_s\)), working pressure. This technique is the relative simplicity and low cost when compared to sophisticated techniques such as PLD, MBE and MOCVD [9]. Photoluminescent ZnO-carbon nanocomposites are an emerging class of nanomaterials that has evoked numerous interests due to their distinctive optical properties [10]. It has been shown that these composite structures harvest an enhanced UV-to-visible emission ratio owing to improved surface-plasmon-mediated emission and a new defect emission mechanism. For instance, J. Zhang et al. have investigated the influence of ZnO nanowires on the interfacial micro-mechanical behavior of carbon fiber: carbon fibers were modified by adding ZnO nanowires to the surface [11]. B. Pant et al. have reported an electrochemical investigation of carbon nanofibers (CNFs) wrapped with ZnO nano-flakes for use in supercapacitors [12]. In most studies on
ZnO and CNFs composites, the electrospinning method is used to prepare CNFs: e.g. H. Ning et al. have studied the electrospinning ZnO/CNFs as anode for Li-ion batteries [13]; J. Mu et al. have studied the high photocatalytic activity of ZnO-CNFs composites prepared by electrospinning method [14]. Based on similar studies [15–18], it was found that ZnO clusters or particles adhere to the surface of CNFs, which prepared by electrospinning method.

For the ZnO@CNFs samples prepared in this study, the chemical vapor deposition (CVD) process was utilized to grow high-graphitization CNFs with a diameter of less than 100 nm. The ZnO completely coated the surface of CNFs by heating and rotating the substrate during radio frequency (RF) magnetron sputtering, and the ZnO on CNFs was distributed in the form of scales with fewer defects and higher crystallinity after natural cooling. To the best of our knowledge, no study has yet been reported on the synthesis of CNFs coated with scale-like ZnO and the investigation of the PL properties of this novel composite nanostructure. Due to excellent coverage of scaly ZnO on the surface of CNFs, we can consider it as a 1D ZnO structure. The preparation and characterization of scaly ZnO@CNFs will be reported. Through testing and comparison, it has found that this novel nanostructure has a strong UV luminescence characteristics and low visible emission.

Fig. 1. (a) The XRD spectrum and SEM images of Cu/SiO\(_2\) substrate, (b) CNFs, (c) ZnO@CNFs.
2. Experimental work

2.1. Preparation of CNFs

The CNFs were prepared by CVD and the catalyst is a layer of Cu atoms deposited by RF magnetron sputtering on the surface of a SiO2/Si substrate. A Cu target (99.99%) was used and the sputtering parameters of the Cu layer were as follows: RF power 150 W, sputtering time 120 min, TS 400 °C and sputtering pressure 1 Pa, respectively. A background pressure of about $10^{-4}$ Pa was used before the sputtering process. The CNFs are synthesized on the Cu layer by CVD. The TS was increased to 1000 °C in an Ar atmosphere with the gas flow set at 600 sccm. The Ar flow was adjusted to 1000 sccm when the TS was kept stable at 1000 °C. The deposition time was 10 min and the gas flow of CH4 and H2 was 10 sccm and 100 sccm, respectively.

2.2. Preparation of scaly ZnO@CNFs

Scaly ZnO was deposited on the surface of CNFs by RF magnetron sputtering. A 99.999% ZnO target with a 60 mm diameter was used. The distance between target and substrate was 80 mm. Deposition was carried out at a working pressure of 0.5 Pa after pre-sputtering with Ar during 10 min. RF power and TS were maintained at 200 W and 400 °C, respectively during the sputtering. The gas flow rate of Ar and O2 was 35 and 5 sccm, respectively. Substrate rotation was set to two revolutions per minute during the sputtering process and the whole process of sputtering deposition lasted 75 min. Natural cooling was adopted and the Ar and O2 were always connected in the cooling process.

2.3. Characterisation

Material phase analyses of samples were characterized by X-ray diffraction (XRD, Shimadzu 6100). Laser Raman spectrometer was used to characterize the graphitization of CNFs (Renishaw inVia, 514 nm, green laser). A high resolution (HR) scanning electron microscope (HRSEM, ZEISS SIGMA 300) was used to observe the HR morphology images. In addition, we have used a SEM and an energy dispersive spectrophotometry (SEM-EDS, Phenom ProX) to observe the morphology and atomic percentage (Eat%) of CNFs and ZnO@CNFs. A fluorescence spectrophotometer (HORIBA Fluoro Max-4p) was utilized to test and analyze the PL properties of all samples. Since the crystal quality, defect and surface roughness of ZnO crystal can affect the PL spectrum, the structure of the composite material can be studied from the emission spectrum of samples. An X-ray photoelectron spectroscopy (XPS) was used to test the surface analysis of ZnO@CNFs samples and surface atomic percentage (Xat%).

3. Result and discussion

3.1. Quantitative analysis of scaly ZnO@CNFs structure

The XRD spectrum and SEM images of the Cu layer on the SiO2/Si substrate is shown in Fig. 1a. The position of diffraction peaks of Cu in XRD curve are at 43.3°, 50.43° and 74.13° respectively, whereas the diffraction peak of Si atoms is located at 44.83°. The surface state of Cu layer is an island structure and the distribution of islands was relatively uniform. As shown in Fig. 1b, the CNFs were deposited on the Cu layer by CVD. The TS was increased to 1000 °C in an Ar atmosphere with the gas flow set at 600 sccm. The Ar flow was adjusted to 1000 sccm when the TS was kept stable at 1000 °C. The deposition time was 10 min and the gas flow of CH4 and H2 was 10 sccm and 100 sccm, respectively.

Fig. 2. (a)–(c) The HRSEM images of CNFs on the SiO2/Si substrate. (d) The Raman spectrum of CNFs.
and O\textsubscript{2} remained essential to enable ZnO to cover the surface of CNFs uniformly. The Ar covered with ZnO. Heating and rotating the substrate is vitally important on the sample surface are shown in Fig. 3b.

The element mapping of Si, Cu, C and O on the surface of sample was 0.2%, less than 100 nm. Fig. 3a shows the EDS spectra and Eat% of Cu, C and O on the surface of sample. It can be seen from the HRSEM image that the average diameter of CNFs is less than 100 nm. Fig. 3a shows the EDS spectra and Eat% of CNFs sample. The Eat% of Cu, C and O on the surface of sample was 0.2%, 30.6% and 65.7% respectively. The element mapping of Si, Cu, C and O on the sample surface are shown in Fig. 3b-e.

It can be seen from Fig. 4 that the surface of CNFs is excellently covered with ZnO. Heating and rotating the substrate is vitally important in the ZnO sputtering process. Through systematic experiments, we found that the rotation of substrate during sputtering process is essential to enable ZnO to cover the surface of CNFs uniformly. The Ar and O\textsubscript{2} remained flowing after the sputtering was completed until the T\textsubscript{S} dropped from 400 °C to 50 °C. The cooling process is equivalent to an annealing process, which has a huge impact on the crystallization of ZnO. This process can effectively reduce the defects of ZnO on the surface of CNFs. Meanwhile, the RF power, air pressure and the flow ratio of Ar and O\textsubscript{2} was set at 35 sccm and 5 sccm, respectively. The Eat% in Fig. 7b shows that the Eat% of O and Zn are 44.6% and 46.4%, respectively. In general, Zn atoms are more likely to be sputtered than O atoms. Therefore, during the pure Ar atmosphere sputtering process, deposition of ZnO is prone to the generation of O vacancies and other defects. In the next section, we will analyze the methods that control the ratio of Zn to O atoms.

XPS was used for further analysis of scale-like ZnO on the surface of CNFs. According to literature, XPS allows a qualitative, quantitative as well as surface analysis [23]. Fig. 6 shows the XPS characterization of ZnO@CNFs sample. Fig. 6a shows the Full spectrum of ZnO@CNFs, it can first determine that the surface contains C, O, Zn from the peak of binding energy of Cls, O1s and Zn2p. Fig. 6b displays the Zn2p spectrum, showing the binding energy peaks of Zn 2p 3/2 and Zn 2p 1/2 at 1021.37 and 1044.46 eV, respectively. Fig. 6c shows the binding energy spectrum of O1s. Two peaks are achieved by Gaussian fitting in this part of the spectrum. The peaks are located at 529.8 and 537.1 eV, respectively, and can be attributed to the Zn–O bond inside the ZnO crystal and O\textsubscript{2} or oxygen impurities absorbed on the sample surface, respectively. Fig. 6d shows the binding energy spectrum of Cls. Four peaks are achieved by Gaussian fitting. The peaks are located at 283.3, 284.7, 285.5 and 288.4 eV, respectively and can be ascribed to the existence of C−Zn, C−C, C−O and C=O bonds. Among them, the C−Zn bond links to the interface between CNFs and ZnO, the C−C bond comes from the CNFs crystal, the C−O and C=O bond are associated to the interface between CNFs and ZnO and surface absorption of ZnO@CNFs. Meanwhile, Fig. 6a shows the Xat% of ZnO@CNFs sample. In the next section, we will make a specific analysis combining the EDS result in Fig. 5 with the PL results.

3.2. Result analysis and photoluminescence properties of scaly ZnO@CNFs

For comparison, ZnO was deposited on the surface of SiO\textsubscript{2}/Si substrate and CNFs by means of the same sputtering process. Fig. 7a-b shows the XRD curve and SEM-EDS image with Eat% of ZnO film, which is directly sputtered on the SiO\textsubscript{2} surface. By comparing the XRD curves in Figs. 7a and 1c. There is multiple of diffusion peaks in Fig. 1c, which clearly indicates that the surface state of ZnO on CNFs is polycrystalline. To improve the crystal quality of ZnO in the growth process, O\textsubscript{2} was injected into the sputtering chamber. Through systematic experiments, we found that when the flow ratio of O\textsubscript{2} is small, there are not enough O atoms to combine with the Zn atoms during the sputtering stage, which results in more O vacancies and poor crystal quality. Conversely, when the O\textsubscript{2} content is too high during sputtering, the O\textsubscript{2} density in the chamber will increase, thus hindering the migration of Zn and O atoms emitted by sputtering, so that the sputtered atoms don’t have enough energy to arrive to their lattice positions. Meanwhile, the O\textsuperscript{2−} ions in the plasma have a strong bombardment effect on ZnO crystals, which induces a reduced crystal quality of ZnO. Through systematic experiments, the flow of Ar and O\textsubscript{2} was set at 35 sccm and 5 sccm, respectively. The Eat% on the SiO\textsubscript{2} substrate should be about 3.8%. Therefore, the Eat% of O in ZnO film is about 36.8%.
the ZnO/SiO$_2$ sample and ZnO@CNFs sample in the wavelength range of 300–800 nm are shown in Fig. 8a–b.

Photoluminescence (PL) is a technique, which can provide insights into the defect levels, and the ratio $I_{UV}/I_{DL}$ is a measure of defect states in ZnO material [24]. As mentioned above, ZnO exhibits two type of emission: UV emission and visible emission. ZnO usually has six kind of defects, such as VO, O$_i$, Zn$_{O}$, V$_{Zn}$, Zn$_i$, O$_{Zn}$ [25]. It is widely accepted that UV emissions in the 370–385 nm range are attributed to the recombination of free excitons in ZnO [26]. The visible emission spectrum mainly includes blue and green emission, but also includes red and yellow emission. X.Q. Wei et al. [27] reported that the mechanism of blue emission (420–460 nm) should dominantly drive from Zn$_i$. Most researchers think that the green emission (490–530 nm) can be attributed to the transition related with single ionized VO [28]. The yellow emission is caused by double ionized VO$_i$ [29], and the red emission from O$_i$ defects [30]. The PL spectrum of sample in Fig. 8a was measured with an excitation wavelength of 325 nm, which displays the UV emission peak at 367 nm, the broad blue emissions at 416 nm and the broad green emissions at 468 nm, respectively. As shown in Fig. 7b, the Eat% of Zn on the surface of ZnO/SiO$_2$ sample is 57.5%, and that of O is 36.8% after calculation. Hence, the content of O atoms in ZnO film is smaller than that of Zn atoms on the surface of this sample. Hence, the probability of the occurrence of VO, Zn$_{O}$ and Zn$_i$ defects in the ZnO thin film is higher than that of other defects, leading to an emission in the visible region as shown in Fig. 8a. These defects also inhibit UV emission.

We cannot directly calculate the Eat% of Zn and O of ZnO, which coated the surface of CNFs from Fig. 5a as a fraction of the ZnO was directly deposited on the surface of the SiO$_2$ substrate. The intensity of UV luminescence peak of ZnO@CNFs sample in Fig. 8b is significantly higher than that of the ZnO/SiO$_2$ sample in Fig. 8a. Through systematic experimental analysis, the UV emission of ZnO@CNFs could be
maximized under the process conditions described in this paper. As noted above, the ratio IUV/IDL is a measure of the number of defect states in the ZnO material. The IUV/IDL in Fig. 8a is 2.23 whereas in Fig. 8b is 12.53. This result shows that the ZnO growth on the surface of CNFs sample features a higher crystallinity than that of ZnO directly grown on the SiO2 surface under the same sputtering conditions.

For this comparison, we are not attempting to prove that the crystallization quality of ZnO grown on the surface of CNFs by magnetron...
sputtering is higher than that on the surface of SiO$_2$. It has been found from previous studies that a high-quality ZnO film can be grown on the surface of a SiO$_2$ under a normal temperature process. We inferred that in this experiment, the adsorption of O atoms on the SiO$_2$ surface may be affected by factors such as excessive substrate rotation, resulting in a large amount of Zn atoms on the surface of the substrate cannot being combined with O atoms. The PL results in Fig. 8a are only used as comparative examples. According to literature, there are extensive suspended bonds existing on the surface of CNFs grown in the gas phase which leads to interfacial polarization. Moreover, CNFs have a high specific surface area and can cause multiple scattering, which makes CNFs have microwave absorption properties. These dangling bonds on CNFs surface makes it easier to capture sputtered Zn atoms, O atoms and ZnO molecules. Therefore, the probability of the occurrence of defects in ZnO@CNFs is relatively smaller than in ZnO/SiO$_2$. As mentioned above, Zn atoms are more likely to be sputtered than O atoms. In the pure Ar atmosphere sputtering process, defects of ZnO are prone to V$_0$ and other defects. The result of Eaat% in Fig. 7b and the PL result in Fig. 8a also demonstrate this. As shown in Fig. 6a, the Xat% of O1s, C1s and Zn2p is 17.25%, 76.62% and 6.12%, respectively. XPS can accurately analyze the material surface, including composition and valence state analysis. Similar to CNFs, when ZnO@CNFs are in contact with air, the surface will inevitably absorb oxygen impurities. The binding energy spectrum of O1s in Fig. 6c can effectively prove this. Hence, the Xat% of O1s is larger than Xat% of Zn2p.

However, the result in Fig. 5a shows the Eaat% of Si, O and Zn is 9%, 44.6%, 46.4%. Because XPS and EDS have different testing mechanisms, the result of Xat% and Eaat% obtained by testing the same sample are also different. As is well-known, XPS analysis yields composition information by irradiating the sample surface with X-rays and measuring the energy of surface excited electrons, and the detection depth is only several atomic layers. EDS works by irradiating the sample surface with an electron beam and detecting the excited X-ray characteristics to obtain the composition information. Unlike XPS, EDS characterization is a bulk analysis method with a detection depth of several microns. The results of the Eaat% in Fig. 5a can also fully prove that the test depth of EDS has reached the surface of Si substrate. Although the Eaat% of O and Zn in Fig. 5a are very close, we cannot directly estimate the components of Zn and O growing on the surface of CNFs. The surface of the ZnO@CNFs sample is not as smooth as that of the thin film material, and the dense interlacing of the fibers results in anisotropy of the XPS test results. The result of Xat% shows that the surface of this fiber structure has a unique adsorption effect on gas molecules, and the surface of CNFs can effectively absorb O atoms to bond with Zn atoms during sputtering. As mentioned above, the surface of CNFs prepared by CVD method is not smooth, and the high surface roughness of the CNFs is conducive to bond with other matrix materials. This is also why the scale-like ZnO has a good coverage and crystal quality. The UV band of PL spectrum in Fig. 8b can strongly support this inference. In the meantime, lattice matching plays a decisive role in the crystallization quality of composites. The results show that carbon fiber as a carrier is beneficial to improve the crystal quality of ZnO. Although, we can still find the weak visible emission in the PL spectral line of CNF@ZnO sample in Fig. 8b. Through the above analysis, it can be concluded that ZnO@CNFs samples feature an excellent UV emission.

### 4. Conclusions

The basic structural unit of CNFs is a graphite microcrystal, exhibiting a conductivity level comparable to that of graphite. Electrons, photo-generated in the wide band gap ZnO will be introduced into CNFs when ZnO is combined with CNFs. CNFs do not only feature high conductivity and large specific surface area, but also have a large number of dangling bonds when prepared by the vapor growth method, which triggers the ZnO growth on the surface of CNFs and form scales. It can be concluded from the analysis: the ZnO can cover the surface of CNFs comprehensively and uniformly; this novel one-dimensional structure of ZnO and CNFs composite material has a very excellent UV photoluminescence property. The manufacturing technology is stable and easy to realize and this novel composite materials can be used to develop future UV laser sources, UV emission lamps, etc.

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