Research Article

Prepared and Characteristics of ZnO:YAG/Silicon Nanostructure Diodes Prepared by Ultrasonic Spraying

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This work presents a novel white light source. An yttrium aluminum garnet (YAG) phosphor incorporated zinc oxide (ZnO) (ZnO:YAG) film is deposited on a silicon substrate by ultrasonic spray pyrolysis to form a nanostructure diode. A nanoflower consisting of a hexagonal nanopetal is formed on the surfaces of the silicon substrate. A white broad band at the room temperature photoluminescence ranging from 420 to 650 nm for the ZnO:YAG/silicon nanostructure diode was observed. The white broad band consists of the emissions of defect level transition of the ZnO film and the 5D_4 level to the 7F_6 and 7F_5 level transitions of Ce^{3+} ions.

1. Introduction

Solid state lighting is the next generation light source, owing to its potential luminescence efficiency. The white light source of the solid state lighting consists of multiple emissions in visible. For example, GaN-based white light-emitting diode (LED) is the most widely used solid state light source, which included a blue LED chip and a yellow phosphor coating. The advantages of the GaN-based LED white light source are long lifetime, high energy efficiency, small size, ability to produce color light directly without filtering, and integration with other semiconductor electronic elements [1–6]. However, the disadvantages of the GaN-based LED white light source are high manufacturing cost and low yield rate due to the expensive growth technology and source materials of metal-organic chemical vapor deposition and the Ga-N bonding mechanism, respectively.

Therefore, it is imperative to develop a novel and low-cost white light device for light source. ZnO is commonly used as a material for optical device applications in the UV range owing to its wide direct band gap (3.37 eV) [7–10]. Several articles about n-ZnO/p-GaN heterostructure LED were reported [11–13]. However, that is a UV range structure, and no optical characteristics were demonstrated.

In this work, an yttrium aluminum garnet (YAG) phosphor incorporated ZnO film is deposited on silicon substrate by ultrasonic spray pyrolysis to form a ZnO:YAG/silicon nanostructure diode. Additionally, the crystallinity of YAG phosphor incorporated into ZnO films is studied using X-ray diffraction (XRD) analysis. The optoelectronic characteristics of the ZnO:YAG/Si nanostructure diode are also studied.

2. Experimental Details

ZnO incorporated yttrium aluminum garnet (YAG) phosphor film was deposited by ultrasonic spray pyrolysis on p-type silicon substrates at atmospheric pressure in nitrogen (N_2) gas, at a flow rate of 100 sccm for 20–60 min. The ZnO incorporated YAG phosphor film (YAG phosphor at 0, 1, 5, and 10 at wt%) (phosphor: NYAG4156, INTEMATIX, US) was produced by spraying aqueous solutions. Zinc acetate, ammonium acetate, and YAG phosphor were mixed in D.I. water to prepare the precursor solution. The solutions were stirred at room temperature for 1 h and then moved into a commercial ultrasonic nebulizer which makes the solutions be aerosol which contains TAG phosphor. The aerosol was transported to the substrate by high purity nitrogen gas and the substrate was kept at 500°C. The YAG phosphor

FIGURE 1: FESEM micrographs of the ZnO:YAG films (YAG phosphor at 5 wt%) with various deposition times: (a) 20 min, (b) 40 min, and (c) 60 min.

was incorporated in the film when the deposition of ZnO occurs. Single crystalline boron-doped p-type silicon with resistivity of $10 \Omega\text{-cm}$ was used as the substrate, which was etched with HCl for 5 min before deposition. An aerosol of the precursor solution was then generated using a commercial ultrasonic nebulizer. Ag/Ni electrodes were formed by evaporation onto both the surfaces of the ZnO:YAG layer and the silicon substrate, to complete the nanostructure diodes. Next, the morphology of film was studied by field emission scanning electron microscope (FESEM). The crystallinity was investigated by X-ray diffraction (XRD) using a rotating anode Rigaku X-ray diffractometer with $\text{Cu-K}\alpha_1$ radiation at a wavelength of $1.54 \text{ \AA}$, where the radiation was generated at 45 kV and 40 mA. Additionally, photoluminescence (PL) was measured at room temperature (RT). The excitation source for photoluminescence was a frequency-quadrupled Nd:YAG laser, which emitted 266 nm, 6 ns pulses at a 5 Hz repetition rate. The current-voltage (I - V) characteristics were measured using a Keithley 2420 programmable SourceMeter. Hall measurement was employed to study the electrical properties of the ZnO films with different concentrations of incorporated YAG which were deposited on glass substrate.

3. Results and Discussion

Figure 1 shows the FESEM micrographs of the ZnO:YAG (YAG phosphor at 5 wt%) films with various deposition times. The micrographs indicate that nanoflower consists of hexagonal nanopetal on the surface of the films, as shown in Figure 1. The nanoflower sizes were approximately 400 nm and the size of nanoflower almost has no changes with deposition time increasing. The average deposition rate is about 20 nm/min. The origin of the hexagonal nanoflower may contribute to decomposition and random nucleation of solution precursor leading to the formation of three-dimensional ZnO nuclei [7, 14, 15]. As the growth proceeds, the growth direction is longitudinal. However, as the growth process is terminated, the three-dimensional growth becomes two-dimensional growth owing to the reduction of the source and the aggregation of the residue precursor, subsequently leading to formation of the hexagonal nanopetal on the surface of the substrate [14, 15].

FIGURE 2: X-ray diffraction patterns of the ZnO:YAG films with various deposition times.

Figure 2 shows a typical X-ray diffraction (XRD) pattern of ZnO film incorporated YAG phosphor deposited on a sapphire substrate prepared by the ultrasonic spraying pyrolysis method. Three dominant diffraction peaks, that is, ZnO (100) ($2\theta = 31.79^\circ$), ZnO (002) ($2\theta = 34.37^\circ$), and ZnO (101) ($2\theta = 36.21^\circ$), are observed in the range from 30 to 45° . The film demonstrates a polycrystalline structure. The sample deposited for 20 min has the maximum ZnO (101) diffraction peak height. As the deposition time increase exceeds 40 min, the intensity in ZnO (002) diffraction peaks becomes higher than the intensity in ZnO (101) diffraction peaks. This may contribute to the fact that the grain with orientation of (002) is dominant. In order to attain the detailed structure information, the grain size G along with the c -axis was calculated according to Scherrer's equation [16]:

$$G = \frac{0.9\lambda}{\beta \cos \theta}, \quad (1)$$

where G , λ , β , and θ denote the grain size, the X-ray wavelength, the full width at half maximum (FWHM) in radians, and the Bragg angle of (002) or (101) peak, respectively. The grain sizes for the samples deposited with 20, 30, 40,

FIGURE 3: (a) Transmittance spectra of the ZnO:YAG films deposited for various times. (b) Relationship between the square of the absorbance and photon energy for the ZnO:YAG films.

50, and 60 min are 25.97, 32.14, 36.13, 39.78, and 46.18 nm, respectively. Therefore, the crystallinity of the samples with longer deposition time is better.

Figure 3(a) plots the transmittance spectra of the YAG incorporated ZnO films deposited for various times, and Figure 3(b) shows the results of the absorption measurements for the YAG incorporated ZnO films. It can be seen from Figures 3(a) and 3(b) that, as the deposition time increases, the transmittance decreases due to the thickness of the YAG incorporated ZnO increasing, and the absorbance edge keep almost in 3.15 eV. Typically, the band gap of ZnO film is around 3.37 eV corresponding to the absorption edge at 370 nm [14]. The red shift may be attributed to the defects in the YAG incorporated ZnO film [8, 17].

Figure 4 presents the room temperature (RT) PL spectra of the ZnO:YAG (YAG phosphor at 5 wt%) deposited for 60 min. The inset shows the photoexcited luminescent photographs. According to Figure 4, the RT PL spectrum of the YAG incorporated ZnO reveals one peak, denoted as peak A, that is, at ~3.27 eV (382 nm), and a broad band included four weak peaks, denoted as peaks B, C, and D at 2.71 eV (456 nm), 2.56 eV (484 nm), and 2.28 eV (544 nm), respectively. Peak A has the shortest wavelength and, therefore, is interpreted as being associated with free-exciton (FE) or band-to-band (B-B) recombination in the ZnO. Additionally, its position is reasonably close to that of the band gap of ZnO at RT, which is ~3.285 eV (377.5 nm) [8–10, 15, 17, 18]. Peak B may be attributed to the band-to-deep level transition in the ZnO film. Peaks C and D may correspond to the ⁵D₄ level to the ⁷F₆ and ⁷F₅ level transitions of Ce³⁺ ions, respectively [19–21]. The color of photoluminescence is nearly white, as shown in Figure 5. The white light may contribute to the wide emission band ranging from 420 to 650 nm. Figure 5 shows

FIGURE 4: RT PL spectra of ZnO:YAG phosphor (YAG phosphor at 5 wt%) on silicon substrate. The inset shows the photoexcited luminescent photographs.

the PL spectra of the ZnO:YAG thin films with different incorporated concentration at the RT. The intensity of all the peaks increases when the incorporated concentration increases. The chromaticity coordinates of the ZnO:YAG films at 1, 5, and 10 wt% on Si substrate are presented in the CIE chromaticity diagram, as shown in Figure 6. With the increasing incorporated concentration of YAG, the chromaticity coordinates move in white light area from $x = 0.2786$, $y = 0.3417$ (CCT = 7958) for the sample at 1 wt% to $x = 0.2476$, $y = 0.3665$ (CCT = 9328) for the sample at 10 wt%. Therefore, the ZnO:YAG film on Si substrate is suitable for solid state lighting because it has a stable white

FIGURE 5: PL spectra of the ZnO thin films with different concentrations of incorporated YAG at room temperature.

FIGURE 6: Chromaticity coordinates of the ZnO:YAG films at 1, 5, and 10 wt% on Si substrate.

light color when the incorporated concentration is in the range of 1–5 wt%.

Figure 7 shows the resistivity and the mobility as a function of the different concentrations for phosphor doped ZnO. In undoped ZnO thin films, the resistivity and the mobility were $33 \Omega\text{-cm}$ and $1.7 \text{ cm}^2/\text{V}\cdot\text{s}$, respectively. When phosphor doped ZnO at 1 wt %, the resistivity increases, phosphor doped concentration up to 5 and 10 wt %, and then it increases again. On the contrary, the mobility decreases with increasing the doped concentration. The changes in

FIGURE 7: Resistivity and mobility of the ZnO thin films with different concentrations of incorporated YAG deposited on glass substrate.

electrical properties of ZnO film for the defects increase caused by the doping of the phosphor.

Figure 8(a) plots typical I - V characteristics of the YAG phosphor incorporated ZnO/silicon heterostructure diodes at room temperature. The inset presents the cross-section of the completed structure. Figure 8(b) plots the current-voltage (I - V) of the Ni/Ag/ZnO:YAG and Ni/Ag/p-Si pad-to-pad structures, to check for ohmic characteristics and to optimize the performance of the devices. The diode has a turn-on forward bias of ~ 5 V. The forward bias is high because the ohmic contact condition is not optimized yet. Diode I - V characteristics can be expressed by the Shockley equation:

$$I = I_0 \left[\exp \left(\frac{qV}{nKT} \right) - 1 \right], \quad (2)$$

where I_0 is the saturation current density and n is the ideality factor. Equation (2) gives an ideality factor n and saturation current I_0 of 1.56 and 1.89 nA, respectively, indicating that when a diffusion current flows in the reverse direction, the reverse leakage current prior to breakdown is around 10^{-5} A. The breakdown voltage is soft and as high as around ~ 5 V.

4. Conclusions

In summary, an yttrium aluminum garnet (YAG) phosphor incorporated zinc oxide (ZnO) (ZnO:YAG) film has deposited on a silicon substrate by ultrasonic spray pyrolysis. A nanoflower consisting of a hexagonal nanopetal is formed on the surfaces of the silicon substrate, and the sizes of the nanoflower are approximately 400 nm. The ZnO:YAG/silicon nanostructure diode has a turn-on forward bias of ~ 5 V. The reverse leakage current prior to breakdown is around 10^{-5} A. The breakdown voltage is soft and as high as around ~ 5 V. A white broad band at room temperature photoluminescence ranging from 420 to 650 nm was observed. The white broad band consists of the emissions of defect level transition of the ZnO film and the $^5\text{D}_4$ level to the $^7\text{F}_6$ and $^7\text{F}_5$ level transitions of Ce^{3+} ions.

FIGURE 8: (a) Typical current-voltage characteristics of ZnO:YAG/silicon nanostructure diode. The inset shows the cross-section of the completed structure of the ZnO:YAG/silicon nanostructure diode. (b) The current-voltage (I - V) characteristics of Ni/Ag/ZnO:YAG and Ni/Ag/p-Si junctions, respectively.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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