Development of phosphor thin films on SiN substrate for electron beam excitation assisted optical microscope

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Abstract

We prepared ZnO thin films on SiN substrate as a phosphor thin film of EXA microscope. ZnO films were crystallized with high c-axis orientation and crystallinity of films was improved as annealing temperature increased. UV and visible emissions were observed in the annealed ZnO films. Blue-green emission was enhanced by annealing in H$_2$ atmosphere and suppressed by annealing in O$_2$ atmosphere.

1. Introduction

The electron beam excitation assisted optical (EXA) microscope [1] is originally designed for dynamic observations of living biological specimens with ultra-high resolution. This microscope system combines optical microscopy and scanning electron microscopy. Cathodoluminescence (CL) is used as the light source of this system. Focused electron beam excites the luminescent film and nanometric light source is prepared. The luminescent film is also employed as a separator of air and vacuum. The specimen is put on the air side surface of the film and an image is produced by scanning the specimen with nanometric light source.

In our previous work, the SiN thin film was used as the luminescent films [1, 2]. We reported the 50 nm diameter latex spheres could be clearly observed with EXA microscope. However, CL intensity of SiN film is not so high compare with phosphor materials. High CL intensity is required to obtain a high signal to noise ratio and high frame rate. Therefore, we propose to use phosphor thin films deposited on SiN film as the luminescent film.

In this system, acceleration voltage of electron beam is limited from 2.5 to 10 kV. In order to obtain nanometric light source, a very thin phosphor film of less than 200 nm and high CL efficiency under low voltage electron excitation are required.

ZnO is a candidate of the phosphor film. ZnO is well known as the low-voltage cathodoluminescent phosphor and is used for various applications such as vacuum fluorescent displays (VFD’s). When excited with either electron beams or UV light, ZnO has been known to emit ultraviolet (UV) and visible light. UV emission has been well understood to be due to the excitonic recombination. The blue-green emission, which is most commonly emission in visible region, has been attributed to the oxygen vacancies. Both emission bands can be used as light source of EXA microscope. Moreover, ZnO has some advantages such as stable against electron irradiation, chemically stable in air, non-toxic and good electron conductivity. Thus ZnO is suitable for applications in biomedical and biological fields.

In this work, we prepared ZnO thin films on SiN by rf magnetron sputtering and we investigated structural and luminescent properties of these films.

2. Experimental conditions

ZnO films were deposited by rf magnetron sputtering using ZnO target (99.99 % purity) in a reactive plasma (oxygen and argon mixed). An amorphous-like SiN film (50 nm) deposited on Si substrate was used as a substrate. The base pressure was less than $2 \times 10^{-4} $ Pa. The working pressure, Ar / O$_2$ ratio and rf power were 0.8 Pa, 5 / 1 and 100 W, respectively. The substrate temperature was 200 °C. The deposition was continued for 30 min and the thickness of ZnO films was about 100 nm. After deposition, ZnO films have been annealed at various temperatures between 500 and 800 °C for 1 hour in N$_2$ (pure N$_2$), O$_2$ (pure O$_2$ / pure N$_2$ = 1 / 4) and 1 % H$_2$ in Ar.

The structural properties of the films were investigated by x-ray diffraction (XRD, RINT-Ultima III, Rigaku, using Cu Kα radiation). The luminescence properties of the films were characterized by measuring CL under the electron beam excitation (current density 60 μA/cm$^2$, anode voltage 5 kV) at room temperature.

3. Results and discussions

3.1 Structural properties

The XRD spectra of as-grown ZnO film and films annealed in N$_2$ at 600 °C and 800 °C are shown in figure 1. The diffraction peak around 34 ° corresponding to the diffraction from the (002) plane of wurtzite ZnO is observed in each film while the other small peaks are attributed to the diffraction from substrates. These results indicate that all films are highly c-axis oriented ZnO films. Intensity of
ZnO (002) peak increases after annealing and by increasing the annealing temperature indicating the improvement of crystallinity of ZnO films.

For the as-grown film, peak position in the (002) diffraction is 34.3° and after annealing, this peak is shifted towards the higher angle (34.6°). This angle is higher than that of powder ZnO (34.34°) therefore, annealed ZnO films have tensile strain along (002) direction. This peak shift is caused by the difference in thermal expansion coefficient between the ZnO film and the SiN substrate (ZnO = 3.2×10⁻⁶ / °C and SiN = 2.6×10⁻⁶ / °C).

![Fig. 1 XRD spectra of ZnO films; (a) as-depo, (b) annealed at 600 °C in N₂ and (c) annealed at 800 °C in N₂.](image)

3.2 Luminescence properties

We investigated annealing temperature and atmosphere dependence of CL spectra of ZnO films deposited on SiN substrate. Figure 2 shows CL spectra of ZnO films annealed at different temperatures in N₂. No CL emission could be detected in the as-grown film and SiN films which is conventional luminescence film of EXA microscope. After annealing, UV emission and visible emission could be observed in all ZnO films. It indicates that annealed ZnO films achieved higher CL intensity than conventional luminescent film. The intensity of UV emission improved by increasing the annealing temperature. Blue-green emission was found in the films annealed above 600 °C and clearly observed in the film annealed at 800 °C. Increasing of intensity of UV emission can be attributed to improvement of crystallinity of the films by annealing (as proven by XRD spectra shown in Fig. 1). High temperature annealing reduces the non-radiation recombination centers in the films and increases oxygen vacancies. The origin of red emission is not understood in detail at present.

Figure 3 shows CL spectra of the ZnO films annealed at several temperatures and in different atmospheres. UV emission was observed in each film. Blue-green emission was showed clearly in annealed films in H₂ and N₂ and especially the annealed film in H₂ had strong emission. This result shows that reducing gas such as H₂ increases the oxygen vacancies in the film. On the contrary, oxidation gas such as O₂ compensates the oxygen vacancies. Therefore, the blue-green emission can be controlled by annealing atmosphere.

![Fig. 2 CL spectra of ZnO films annealed at different temperatures in N₂.](image)

![Fig. 3 CL spectra of ZnO films annealed at of 800 °C in O₂ or N₂ for 1 hour and ZnO film annealed at 700 °C in H₂ for 10 minutes.](image)

3. Conclusions

We investigated the structural and luminescence properties of ZnO thin films deposited on SiN substrate by rf magnetron sputtering. All ZnO films growth with c-axis orientation and crystallinity of films was improved with increasing annealing temperature. For ZnO films annealed above 600 °C in N₂, UV and blue green emissions were observed. The intensity of blue-green emission was sensitive to the annealing atmosphere. This emission was enhanced in H₂ and suppressed in O₂.

The emission intensity of annealed ZnO films was higher than conventional luminescence film of EXA microscope. Therefore, ZnO films can provide nanometric light source with high emission intensity and it promises to provide high resolution imaging with low signal to noise ratio and high frame rate.

References