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Growth of cubic $Mg_xZn_{1-x}O$ alloy films by electron beam evaporation

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Abstract

We report the growth of cubic $Mg_xZn_{1-x}O$ alloy thin films on quartz by electron beam evaporation. It can be found that all the samples have sharp absorption edges by the absorption measurements. X-ray diffraction measurements indicate the $Mg_xZn_{1-x}O$ films are cubic phase with preferred orientation along the (1 1 1) direction. Energy dispersive spectrometry (EDS) demonstrates that the Mg concentration in $Mg_xZn_{1-x}O$ films is much higher than the ceramic target used, and the composition can be tuned in a small scope by varying the substrate temperature and the beam electric current. The reasons of this phenomenon are also discussed.

Keywords: Electron beam evaporation; $Mg_xZn_{1-x}O$ thin film; Beam electric current

1. Introduction

$Mg_xZn_{1-x}O$, realized by alloying MgO with ZnO, exhibits excellent optical properties, which is a promising candidate for blue and UV photon emitters and detectors [1–4]. The band gap of $Mg_xZn_{1-x}O$ material can be changed from 3.3 to 7.8 eV by varying the Mg concentration, extending the cut-off wavelength from UV-A (320–400 nm) to UV-B (280–320 nm) and UV-C (200–280 nm) regions [5–7]. Such a wide range of sensing spectra enables $Mg_xZn_{1-x}O$ UV detectors to have many applications, such as solar UV radiation monitoring, ultra-high temperature flame detection, and airborne missile warning systems [8]. Moreover, $Mg_xZn_{1-x}O$ with high Mg mole fraction is expected to have an important application in the detection of UV light in the range from 157 to 230 nm. It is predicted that $Mg_xZn_{1-x}O$ will have higher photoresponsivity than AlGaN, SiC or diamond [11].

There have been some reports on $Mg_xZn_{1-x}O$ films grown by pulsed laser deposition (PLD) [10,11], radio frequency magnetron sputtering [9] and molecular beam epitaxy (MBE) [12]. Compared with the above-mentioned methods, electron beam evaporation (EBE) is relatively simple and cheap. The growth mechanism of EBE can be understood as follows: in high vacuum environment, high energy electric beam emitted from electron gun was focused on the target inside of the crucible; the surface radicals of the target would be evaporated under the bombing of the high-energy electrons and the evaporated radicals will form thin films on the substrates. In this letter, cubic $Mg_xZn_{1-x}O$ films were synthesized on quartz by EBE at different substrate temperature and beam electric current, and the characterizations of $Mg_xZn_{1-x}O$ films were discussed.

2. Experiments

$Mg_xZn_{1-x}O$ films were grown by electron beam evaporation system on quartz substrates. The sintered ceramic $(MgO)_{0.50}(ZnO)_{0.50}$ target was used as the evaporation source. It was prepared as follows: polycrystalline MgO (the purity of $\geq$98%) and ZnO (the purity of 99%) powder were blended in the mole ratio of 1:1, then the mixture was compressed and finally sintered at 1000 °C in oxygen atmosphere to form the ceramic target. The quartz substrate was ultrasonically degreased in acetone, ethanol and rinsed in de-ionized water for 5 min in each step, then blown dry with high purity nitrogen.

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Table 1
Growth parameters of $Mg_xZn_{1-x}O$ thin film

Sample	A	B	C	D	E
Substrate temperature (°C)	240	320	370	240	240
Beam electric current (mA)	35	35	35	25	45

The background vacuum in the reaction chamber is 2.5×10^{-3} Pa in the deposition process. Five samples were prepared, the detailed experimental conditions of which were listed in Table 1.

The structural properties of the films were characterized by a Ringaku O/max-RA X-ray diffractometer with Cu Kα radiation (λ = 0.154 nm). The compositions were determined by energy dispersive spectroscopy (EDS). The optical properties were analyzed by absorption spectra and transmittance spectra in the range from 190 to 600 nm by UV-3101 spectrometer at room temperature.

3. Results and discussion

One of the major requirements for the candidate materials of photodetector is that they should have sharp absorption edge in the demand wavelength region. So we examined absorption spectra of the $Mg_xZn_{1-x}O$ samples at room temperature when substrates contribution was excluded. They are shown in Fig. 1. All the films show sharp absorption edges, which indicate the films have high quality. In addition, the absorption edges show a red shift by decreasing the substrate temperature (a) or increasing the beam electric current (b). By varying the growth conditions, the absorption edges can be tuned at a certain wavelength range from 200 to 230 nm.

XRD spectroscopy is used to characterize the crystal structure of the films, and the results are shown in Fig. 2. It can

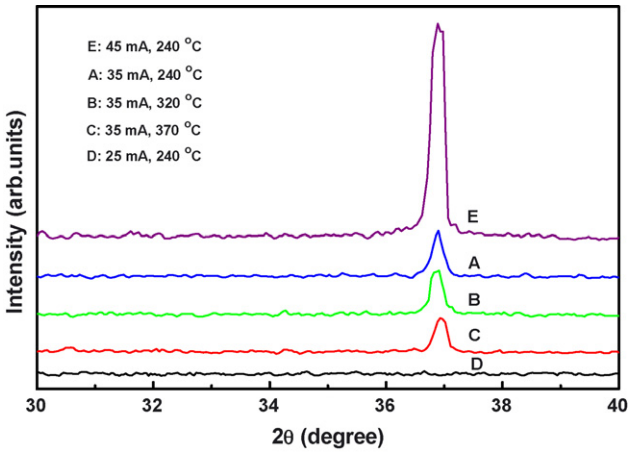

Fig. 2. X-ray diffraction patterns of $Mg_xZn_{1-x}O$ samples grown at different beam electric current and substrate temperature.

be noticed that only one peak corresponding to the diffraction from (1 1 1) face of cubic $Mg_xZn_{1-x}O$ can be observed for samples A, B, C, and E. The absence of characteristic peaks of wurtzite phase (such as (1 0 1), (0 0 2) peak) indicates that the four $Mg_xZn_{1-x}O$ samples possess only cubic phase, and have preferred (1 1 1) orientation. Furthermore, the full width at half maximum (FWHM) values for these samples corresponds to be about 0.2°, which are almost the same for all samples. The peak values of 2θ for samples A, B, C and E are 36.90, 36.91, 36.93 and 36.88°, respectively. The positions of diffraction peaks shifting to large angle can be attributed to spacing of the plane narrows as the Mg mole fraction increase in samples (the ion radii of Zn and Mg are 0.74 and 0.71 Å, respectively). Fig. 3 shows the peak position of $Mg_xZn_{1-x}O$ (1 1 1) as a function of Mg mole fraction (E, A, B, C are 0.66, 0.69, 0.73 and 0.75, respectively).

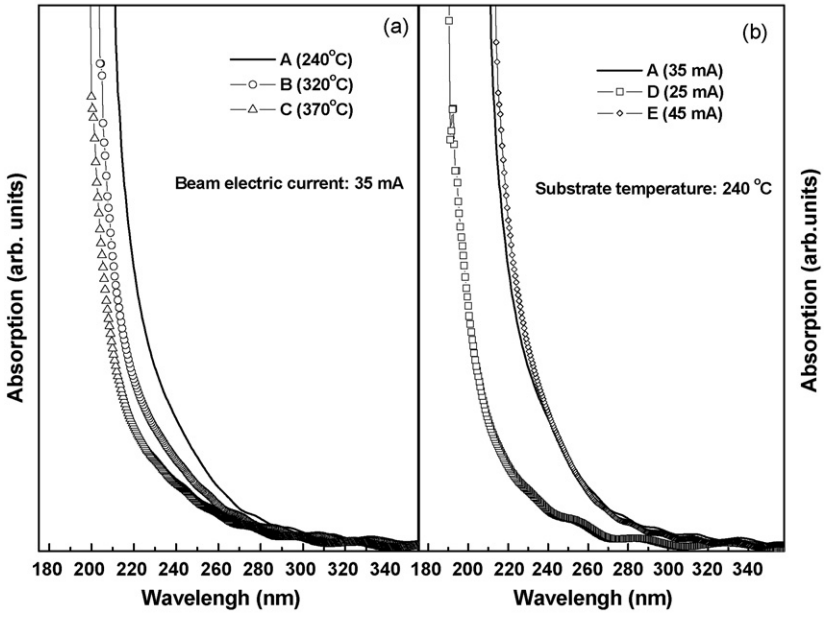

Fig. 1. Room temperature UV–vis absorption spectrum of $Mg_xZn_{1-x}O$ samples grown on quartz substrate at different substrate temperature (a) and at different beam electric current (b).

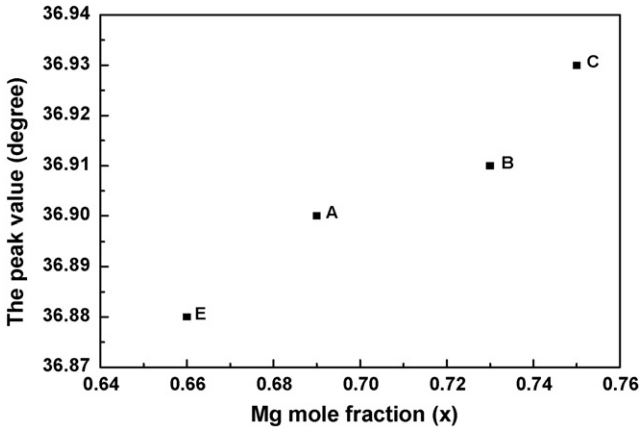

Fig. 3. The diffraction peak positions of $Mg_xZn_{1-x}O$ (1 1 1) as a function of Mg molefraction of the samples A, B, C and E.

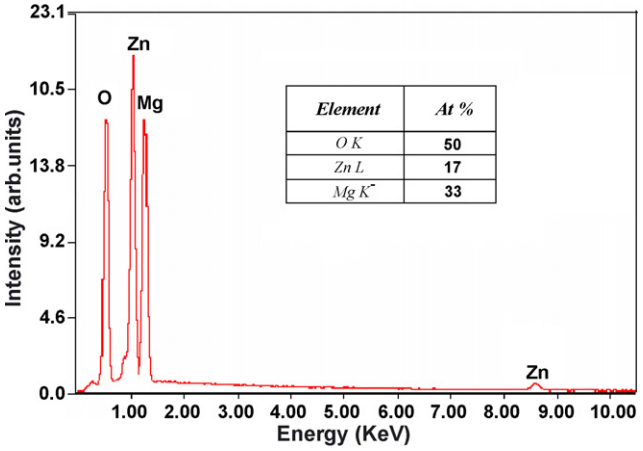

Fig. 4. A typical EDS spectrum of sample E.

The composition of $Mg_xZn_{1-x}O$ films and the atomic percentage of Mg in the samples were measured using EDS. From the results, it can be observed that the O:(Mg + Zn) ratio is nearly 1:1 for all the samples. Fig. 4 shows a typical EDS spectrum of sample E. The Mg composition is found to be 0.66 and the Mg:Zn ratio is the smallest among the five samples (see in Fig. 5). No other impurity elements in films can be observed within the detection limit of EDS (1%), revealing the high purity of the films. Fig. 5(a) and (b) show the dependence of the Mg mole fraction in $Mg_xZn_{1-x}O$ films on the substrate temperature and beam electric current, respectively. It can be found that the Mg concentration increases with increasing the substrate temperature or decreasing the beam electric current. Furthermore, the atomic percentages of Mg for the five $Mg_xZn_{1-x}O$ samples are much higher than that of evaporative target, Mg:Zn ratio is nearly up to 2:1 even in sample E.

The reason of the high Mg:Zn ratio in the samples is attributed to the higher vapor pressure of Zn than that of Mg [5]. As a result, Mg atoms are easier to be absorbed on the substrate while Zn atoms are prone to desorb from the surface of substrate. It is thought that the growth process of the $Mg_xZn_{1-x}O$ thin films using electron beam evaporation is as follows: the vapor composed of Zn, Mg and O with the same composition to the target was produced by the electron beam evaporation. However, when the vapor arrives at the substrate, Zn element is more difficult to deposit on substrate than Mg for its higher vapor pressure. Therefore, the formed structure at initial stage should be a cubic MgO-like one, then the following growth of the film takes the cubic phase structure as the foundation, Mg sites in the lattice were occupied by Zn partly. Thus, the cubic $Mg_xZn_{1-x}O$ films were formed with higher Mg mole fraction than target.

Lower Mg mole fraction films have been obtained at lower substrate temperature or higher beam electric current. The reason for this phenomenon lies in that, the desorption of Zn is reduced at low temperature. While at higher beam electric current, much more gaseous materials from the ceramic target raised up to substrate and growth rate of the film increases, result in more Zn atoms that were covered by the materials that followed, meanwhile restraining the desorption rate of Zn atoms on the substrate. Therefore, by varying the substrate

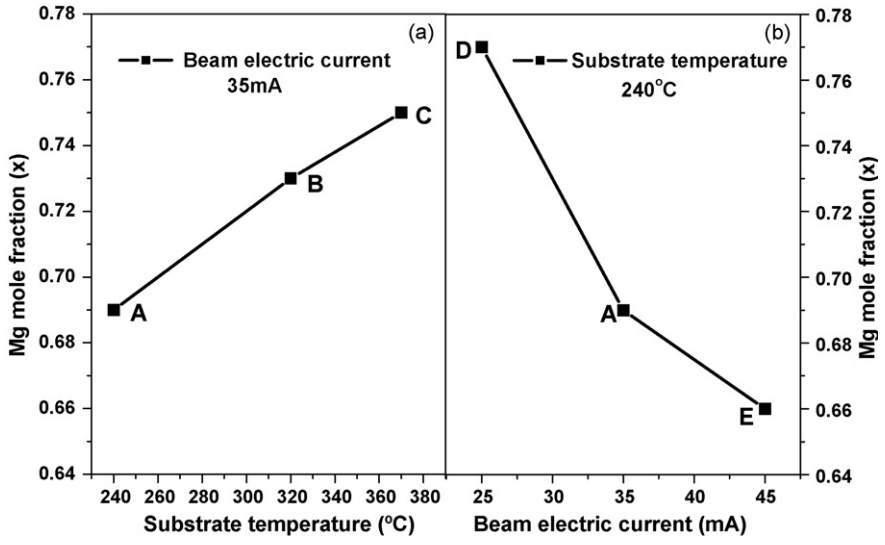

Fig. 5. The Mg mole fraction as a function of the substrate temperature (a) and the beam electric current (b).

temperature and the beam electric current, the Zn:Mg ratio of the depositions can be adjusted at a certain range for samples grown by electron beam evaporation.

4. Conclusions

In summary, cubic $Mg_xZn_{1-x}O$ samples were prepared on quartz wafers by using electron beam evaporation. XRD results indicated that the $Mg_xZn_{1-x}O$ films are cubic phase with preferred orientation along the (1 1 1) direction. EDS measurement demonstrated that the Mg mole fraction in the film is larger than that in the evaporation source, and it increases with increasing the substrate temperature or decreasing the beam electric current. This phenomenon can be well understood considering that the vapor pressure of Zn is higher than that of Mg. For EBE method, low substrate temperature is suitable for Zn atoms deposited on substrate, high beam electric current can increase the film growth rate and restrain the desorption rate of Zn on the substrate. Therefore, by changing the growth conditions, $Mg_xZn_{1-x}O$ films with multiple compositions can be obtained by the simple and cheap electron beam evaporation method.

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