Structure and optical properties of La-doped ZnO thin films at room temperature

Iwan Sugihartono1,∗, Bambang Soegijono2, Erfan Handoko1, Tan Swee Tiam3, Akrajas Ali Umar4

1Program Studi Fisika, FMIPA, Universitas Negeri Jakarta, Jalan Rawamangun Muka no. 01, Jakarta Timur, 13220, Indonesia
2Departemen Geoscience, FMIPA, Universitas Indonesia, Kampus Baru UI Depok, 16424, Indonesia
3School of Energy and Chemical Engineering, Xiamen University Malaysia, Selangor Darul Ehsan 43900, Malaysia
4Institute of Microengineering and Nanoelectronics (IMEN), Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

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Abstract

La-doped ZnO (with 0, 1, 5 and 7 wt.% La) thin films were deposited on Si substrates by ultrasonic spray pyrolysis, using frequency of 1.7 MHz, and heated at 450 °C for 15 min. The effect of La addition on the structural and optical properties of ZnO thin films was analysed. X-ray diffraction patterns confirmed that all prepared thin films had a polycrystalline hexagonal wurtzite structure with highly preferred texture in the (002) plane in the case of the ZnO containing 7 wt.% La. Atomic force microscopy analyses confirmed that the surface morphology is affected by La addition and the root mean square (RMS) roughness tended to be higher by increasing La content. The optical band gap energies of the La-doped thin films are smaller than that of the undoped ZnO. The photoluminescence properties of the prepared thin films confirmed that there was a significant redshift of DLE to wavelength of 711 nm when 1 wt.% of La was incorporated in ZnO structure. It was proposed that the incorporation of La into the ZnO structure caused the oxygen atoms to have a strong bond with La.

Keywords: La-doped ZnO, thin films, ultrasonic spray pyrolysis, structure, photoluminescence

I. Introduction

ZnO belongs to II-VI semiconductors and has been intensively studied in the last three decades. This is due to the wide direct band gap energy of 3.34 eV and a strong exciton binding energy of 60 meV at the room temperature [1]. Therefore, it is believed that ZnO has high potential in optoelectronic applications. Furthermore, it is still a challenge to realize a homojunction with a p-type ZnO. Alternatively, ZnO has been deposited on various substrates such as Si [2], Al2O3 [3], indium tin oxide (ITO) glass [4] and GaAs [5]. As reported, many device-based ZnO heterostructures have been demonstrated, i.e. light-emitting diodes (LEDs) [6], solar cells [3], photocatalysts [7], field-effect transistors [8], etc.

Rare earth (RE) elements such as Er, Tm, Eu, Tb, La, Sm as dopants for II-VI semiconductors have received attention due to their capability to modify optical and electrical properties [9]. Among REs elements, La has excellent gas and photocatalytic sensitivity [9]. Some methods have been demonstrated to fabricate RE-doped ZnO thin films, such as ultrasonic spray pyrolysis (USP) [10], combustion method [11], chemical solution route [12], ion implantation [13], magnetron sputtering [14] and sol-gel [15].

La-doped ZnO thin films have been investigated and showed interesting behaviour. Lan et al. [14] observed that La-doped ZnO thin film has a strong and broad violet peak. Korake et al. [16] reported that the RE element
can be used as the electron trap. Hence, it can effectively reduce the recombination of the photo-generated electron-hole pairs. Zafar et al. [17] reported that the La-doped ZnO thin film as electron buffer layer enhanced the conductivity and carrier density of the inverted organic solar cells. Moreover, the large difference in the radii of La$^+\text{+}$ (0.106 nm) and Zn$^+$ (0.074 nm) ions may induce the stress in the ZnO lattice [9]. Maache et al. [18] investigated photoluminescence spectra of the La-doped ZnO nanoparticles and indicated on their potential for blue-green LED application [18].

In our work, undoped and La-doped ZnO thin films were deposited on Si substrates by ultrasonic spray pyrolysis at a frequency of 1.7 MHz. Compared to other methods, USP offers low cost, simplicity, high deposition rate and low growth temperature. Subsequently, the influence of lanthanum dopant on the structure and optical properties of ZnO thin films has been studied and reported.

II. Experimental

Undoped and La-doped ZnO thin films were deposited on Si substrates by ultrasonic spray pyrolysis (USP). Zinc acetate dihydrate (Zn(CH$_3$COO)$_2$·2H$_2$O, 99.99%, Sigma-Aldrich) and lanthanum(III) acetate hydrate (La(C$_3$H$_7$O$_3$)$_3$·xH$_2$O, 99.9%, Sigma-Aldrich) were chosen as host and dopant precursors, respectively. Zinc acetate (0.02 mol/ml) was mixed with lanthanum(III) acetate hydrate and then dissolved in deionized water. Four samples with different La content were prepared, i.e. ZnO, ZnO-L1, ZnO-L5 and ZnO-L7 containing 0, 1, 5 and 7 wt.% La, respectively. The aerosols of the precursor solutions generated by USP at frequency of 1.7 MHz were injected onto a Si substrate and heated at 450 °C for 15 min.

Crystal structure of the prepared thin films was analysed by X-ray diffraction (XRD, Shimadzu X-ray diffraction 7000 MAXima X) using CuKα radiation. Atomic force microscopy (AFM, Scanning Probe Microscope, Terra Universal) was used to examine the surface morphology, average size, size distribution and root mean square (RMS) roughness of the prepared thin films. All samples were scanned within a size of 0.8 × 0.8 μm and the RMS surface roughness was calculated from the height distribution of islands on the surface of the prepared films.

Reflectance data of the undoped and La-doped ZnO thin films in the wavelength range of 300–850 nm were measured at room temperature by UV-Vis Diffuse Reflectance U-3900H Spectrophotometer. The obtained data were used to determine optical band gap energy.

Photoluminescence (PL) properties at room temperature were determined using FLS920 Fluorescence Spectrometer (Edinburg Instruments) with the light source wavelength of 325 nm.

III. Results and discussion

3.1. Crystal structure

Figure 1 shows XRD patterns of the undoped and La-doped ZnO thin films. According to the inorganic crystal structure database (ICSD) number #98-005-7478, the prepared thin films have a polycrystalline hexagonal wurtzite structure. Moreover, the average ratio of unit cell axes lengths (c/a) of all the samples is ~1.60 and the change of lattice parameters with the increase of La content is not so large (Table 1). It confirms that the incorporation of La ions does not change the ZnO film structure considerably. We observed that there are seven peaks corresponding to (100), (002), (101), (102), (110), (103) and (112) planes with no other peaks belonging to any impurity phases, such as La$_2$O$_3$ etc.

Preferred growth orientation of the prepared thin films was also analysed and the texture coefficient (TC) was calculated using three diffraction peaks of (100), (002) and (101) planes [10]. Compared to the (100) and (101) planes, a more intense peak can be seen for (002) plane (Fig. 1). As it can be seen from Fig. 2, the TC value-

![Figure 1. XRD patterns of prepared ZnO thin films with different La content](attachment:image.png)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$2\theta$ [°]</th>
<th>$a = b$ [Å]</th>
<th>$c$ [Å]</th>
<th>$c/a$</th>
<th>FWHM</th>
<th>$D$ [nm]</th>
<th>Microstrain [%]</th>
</tr>
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<tbody>
<tr>
<td>ZnO</td>
<td>34.4027</td>
<td>3.2465</td>
<td>5.2015</td>
<td>1.6022</td>
<td>0.1851</td>
<td>22.1</td>
<td>0.589</td>
</tr>
<tr>
<td>ZnO-L1</td>
<td>34.4732</td>
<td>3.2475</td>
<td>5.2023</td>
<td>1.6019</td>
<td>0.2154</td>
<td>45.7</td>
<td>0.284</td>
</tr>
<tr>
<td>ZnO-L5</td>
<td>34.5299</td>
<td>3.2472</td>
<td>5.1958</td>
<td>1.6001</td>
<td>0.1947</td>
<td>26.9</td>
<td>0.482</td>
</tr>
<tr>
<td>ZnO-L7</td>
<td>34.5779</td>
<td>3.2477</td>
<td>5.1875</td>
<td>1.5973</td>
<td>0.2174</td>
<td>8.9</td>
<td>1.452</td>
</tr>
</tbody>
</table>
Figure 2. Texture coefficient (TC) of (100), (002) and (101) planes

values for the (002) plane of the ZnO, ZnO-L1, ZnO-L5 and ZnO-L7 films are 1.85, 0.72, 1.77 and 2.41, respectively. This indicates that the ZnO thin films with higher La concentrations have preferential growth in the c-axis. However, the ZnO thin film with 1 wt.% La has a TC value of 1.42 for the (101) plane indicating its preferred orientation in this direction. The preferred orientations of La-doped ZnO films along (002) and (101) planes were also reported in the literature [11–13].

Further analysis of XRD results indicates that there is a shift of the diffraction angle (2θ) of (002) peaks to higher angles (inset Fig. 1). As it can be seen in Table 1, 2θ values of the (002) peak for the samples ZnO, ZnO-L1, ZnO-L5 and ZnO-L7 are 34.40°, 34.47°, 34.53° and 34.58°, respectively. As reported by Manikandan et al. [14], the presence of La ions in the ZnO structure causes shift of the peak to higher diffraction angle. It is believed that the shifting is due to the substitution of Zn^{2+} by La^{3+} ions having higher ionic radii. Furthermore, it causes small lattice distortion and affects the internal micro-strain (Table 1). However, opposite behaviour can be found in the literature [15,16], i.e. shifting of the peak to lower angle when La is incorporated in ZnO thin film structure.

In addition, the full width at half maximum (FWHM) of the La-doped ZnO thin films have higher value compared to the undoped ZnO thin film (Table 1). The mean crystallite size $D$ was calculated by using the Scherrer equation [17]:

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos \theta}$$

where $\lambda$ is the X-ray wavelength, $\beta$ is the full width at half maximum peak height (FWHM), $\theta$ is the Bragg angle and $K$ is a constant (0.91). As compared to the undoped ZnO thin film, the crystallite sizes of the ZnO-L1 and ZnO-L5 films are higher. However, the crystallite size of the ZnO thin films with 7 wt.% La has much smaller than the undoped ZnO thin film. Bouznit et al. [11] reported that proper amount of La improves crystal growth of ZnO thin films.

3.2. Surface morphology

AFM images of the prepared films are shown in Fig. 3. It can be seen that all the films appear to be granular and composed of many small islands of various sizes. The average height of the islands for the ZnO, ZnO-L1, ZnO-L5 and ZnO-L7 films are 28, 27, 31 and 36 nm, respectively. Meanwhile, the RMS roughness was calculated from the height distribution of the islands. The calculated values of RMS roughness for the ZnO, ZnO-L1, ZnO-L5 and ZnO-L7 films are 8, 8, 10 and 14 nm, respectively. It means that by increasing La amount in ZnO films, the height of the islands and RMS roughness tend to increase (Table 1) even though the mean crystallite size of the ZnO thin films with the highest La content is the smallest. Similar results were published by Maache et al. [18].

3.3. Reflectance

Figure 4 shows the room temperature reflectance spectra of the prepared thin films in the wavelength range of 300–850 nm measured by UV-Vis. The reflectance of the undoped ZnO thin film is 0–5.5%, while the reflectance of the doped ZnO thin films decreases with the incorporation of La^{3+} ions in ZnO structure. Thus, the ZnO thin film with 1 wt.% of La has the lowest reflectance (0–1.44%). The characteristic peak in UV region (around 390 nm) can be seen in spectra of all prepared films and corresponds to the maximal reflectance in UV-Vis region (i.e. 5.5%, 1.44%, 3.37% and 5.26% for the samples ZnO, ZnO-L1, ZnO-L5 and ZnO-L7, respectively). Interestingly, in the range from visible up to near-infrared wavelength (450–800 nm), the undoped ZnO thin film has very broad reflectance peak. However, in the doped ZnO films peaks are sharper and their positions vary with La concentration. Thus, in the range of
Vis-NIR wavelength, the maximum reflectance of the ZnO thin films with 1 and 5 wt.% La are 1.20% and 1.89%, respectively, while the maximal reflectance of 3.88% for the ZnO film with 7 wt.% La is in wavelength range 450–600 nm (Fig. 4).

From the reflectance data the absorption coefficient of the prepared thin films can be determined by the Kubelka-Munk equation [19]:

\[ F(R) = \frac{(1 - R)^2}{2R} \]  

\( F(R) \) is equal to the absorption coefficient (\( \alpha \)) in the Tauc equation and \( R \) is reflectance [19]. The optical bandgap energy can be determined by extrapolating the linear plot of the Tauc equation [20]:

\[ (\alpha \cdot h \cdot \nu)^2 = A(h \cdot \nu - E_g) \]  

where \( h \) is Planck’s constant, \( \nu \) is frequency and \( E_g \) is optical bandgap energy. The obtained optical band gap energy values of the prepared thin films are shown in Fig. 5. The band gap energies of the doped ZnO thin films with 1, 5 and 7 wt.% La are 3.09, 3.19 and 3.20 eV, respectively. These band gaps are lower than the band gap energy of the undoped ZnO thin film (3.24 eV). Manikandan et al. [14] proposed that the energy level of the defects will be close to the lower edge of the conduction band when La occupies the Zn site, and the strong orbital coupling between La and O causes optical band gap energy narrowing. However, we believed that incorporation of La in ZnO lattice causes broadening of the optical bandgap energy of the prepared ZnO thin films.

3.4. Photoluminescence properties

To investigate the nature of the defects, photoluminescence (PL) properties at room temperature were analysed (Fig. 6). The room temperature PL spectra of the undoped and La-doped ZnO thin films show behaviour typical for ZnO. The spectra consist of near band edge (NBE) and deep-level emission (DLE) due to the free excitonic recombination and the intra-atomic transition which is feature of the native defects, respectively [21].

Regarding the NBE emission, shift to higher wavelengths can be seen for the doped ZnO films (Fig. 6). Thus, the NBE emission peaks of the samples ZnO, ZnO-L1, ZnO-L5 and ZnO-L7 are 375, 376, 380 and 379 nm, respectively. This can be explained with La incorporation in the ZnO structure and small distortion of ZnO lattice as indicated by the change in lattice parameter (Table 1). Thus, the redshift of NBE emission in the La-doped ZnO thin films could be due to the strain created in the ZnO structure as compensation for the incorporation of larger La\(^{3+}\) ions in ZnO lattice [14]. Moreover, due to the La incorporation into the ZnO structure electrons accumulate near the conduction band.

Regarding the DLE emission more complex behaviour is observed in the prepared thin films (Fig. 6). The DLE intensity decreases when La\(^{3+}\) ions are in-
corporated in the ZnO structure, and blueshift (502 nm) and redshift (528 nm) of DLE are related to the samples doped with 5 and 7 wt.% La, respectively. In addition, there is a significant redshift of DLE to 711 nm when La concentration is 1 wt.% The incorporation of La into the ZnO structure causes the stronger bonding between oxygen ions and La. As reported, the Zn(1.65)–O(3.5) bond has lower electronegativity than the La(1.2)–O(3.5) bond. Therefore, it is more difficult for the oxygen to detach from the La–O bond [15]. We believe that the sample with 1 wt% La has more delocalized La states which may cause overlap with the valence band [22].

IV. Conclusions

In conclusion, La-doped ZnO thin films were deposited using ultrasonic spray pyrolysis (USP) and their polycrystalline hexagonal wurtzite structures was confirmed by XRD analyses. The La incorporation into ZnO lattice was also confirmed, as well as highly preferred texture in the (002) plane and small lattice distortion. AFM measurements showed that with the increase of La content, the La-doped ZnO thin films become rougher than the undoped ZnO films.

The optical band gap energies of the doped ZnO films increase with the increase of La content, but are still lower than the band gap energy of the undoped sample. The room temperature PL spectra of the prepared films have two typical PL peaks, i.e. near band-edge (NBE) and deep-level emission (DLE). The observed large DLE redshift to the wavelength of 711 nm was observed for the ZnO films doped with 1 wt.% La and was due to the delocalization of the La state in the ZnO structure.

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