Effect of Pico Second Laser on Structural and Photoluminescence Properties of Aluminum Doped Zno Film Prepared by Sol Gel Method

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Abstract: Aluminum (Al) doped zinc oxide (Al-doped ZnO) thin films with different Al concentrations were prepared using the sol-gel method and the spin coating technique. The films were irradiated by high power pico-second pulsed laser source of 355 nm with different energy. The laser irradiated Al-doped ZnO films were then characterized by X-ray diffraction, scanning microscopy, UV–Vis absorption and photoluminescence techniques. The diffraction pattern indicates increase in crystallinity of ZnO thin films due to the influence of Al doping and laser irradiation. The change in surface morphology of ZnO and Al-doped ZnO films are confirmed by SEM. The absorption spectra of the films show that slightly change in band gap of pure and Al-doped ZnO after the laser treatment. No significant change in band gap with different Al doping percent under laser treatment. Significant influence in photoluminescence (PL) and spontaneous properties of the pure ZnO and Al-doped ZnO thin films by laser energy was observed. The PL and spontaneous intensity of Al-doped ZnO films decreases upon increasing the laser energy which is attributed to effect of nanostructured of the film.

Keywords: ZnO films, Aluminum, SEM, Absorption, Emission, Laser source
تأثير ليزر بيكو الثاني على الخصائص الإنشائية والتلألؤ الضوئي لفيلم أكسيد الزنك المخدر بالألمنيوم المحضر بطريقة المحلول الهلامي

الملخص: تم تحضير أغشية رقيقة من الألومنيوم (Al) ومخدر أكسيد الزنك (Al-doped ZnO) بتركيزات مختلفة من الألومنيوم باستخدام طريقة المحلول الهلامي وتكنولوجيا الطلاء الدوراني. تم تشعيع الأغشية بمصدر ليزر نبضي عالي الطاقة يبلغ 355 نانومتر مع طاقة مختلفة. تم بعد ذلك تمييز أفلام مخدر من أكسيد الزنك المشعة بالليزر بتقنيات حيود الأشعة السينية والمستوحاة وتقنيات امتصاص UV-Vis والتلألؤ الضوئي. يشير نمط الحبوب إلى زيادة في تبلور UV-Vis النطاق التدريجي لأشعة المعدن. أغشية أكسيد الزنك الرقيقة نتيجة لتأثير المنشطات Al وتشعيع الليزر، تتأثر التغير في nivel السطحي لإفلاس Al و تخدر أكسيد الزنك بواسطة. SEM تظهر أطياف الامتصاص للأغشية تغيرًا طفيفًا في جوهر النطاق من أكسيد الزنك النقية والمخدرين الدوراني بعد العلاج بالليزر. لا يوجد تغيير كبير في نمط النطاق مع نسبة المنشطات المختلفة تحت العلاج بالليزر. تؤثر تأثير كبير في النتائج الضوئي (PL) والخصائص الإنشائية لغشاء أكسيد الزنك النقية ومخدرين أكسيد الزنك بواسطة طاقة الليزر. تنخفض كثافة PL والشدة الإشعاعية لأغشية مخدر أكسيد الزنك عند زيادة طاقة الليزر التي تُعزى إلى تأثير البنية النانوية للفيلم.
1. Introduction

Zinc oxide (ZnO) based nanostructured materials have been considered as a self-structured growth into different such as nanorods, nanowire etc., which are a promising material for different optoelectronic devices, in particular light emitting diodes (LEDs) and laser diodes (LDs) [1-4]. Moreover, ZnO has a wide band gap with energy of 3.37eV and a large exciton binding energy of 60 meV at room temperature, commonly considered as an efficient UV emitter [5]. During the past years, the different properties of Zinc Oxide (ZnO) based transparent conducting oxide (TCO) have been studied and proposed to be favorable materials for applications of LEDs, optical waveguides, piezoelectric transducers, gas sensors and transparent conductive electrodes in solar cells [6-8].

On the other hand, the metals-doped ZnO were extensively interested for their enhancement of properties due to native defects existent in its structure. It can reduce the high electrical resistivity of ZnO by doping metals such as aluminum (Al), boron (B), gallium (Ga), or indium (In) [9-12]. Aluminum (Al) is considered as one of the suitable dopant among the metals due to its smaller ionic radius and lower cost. Addition of Al in zinc oxide materials can be improved in their electrical conductivity by replacing the Al ions. Several researches were endeavored to improve in electrical and optical property of Al-doped ZnO thin films and powder using different methods such as spray pyrolysis [13], sol–gel method [14], precipitation [15] and hydrothermal processes [16]. Traditional post-annealing in a furnace at high temperatures in excess of 700 °C has undesirable effects on device fabrication, which give rise to the high cost of the device fabrication [17]. In view of these, our group studied on the properties of nanocrystals Al-doped ZnO that noticed a blue shift in energy band gap and UV emission due to the carrier concentration and degree of crystalline order induced by Al-donor [18].

In addition, researches are extensively interested to engineer and improve in the different properties of the TCOs material for various applications especially in optoelectronic devices. For this, laser irradiation technique has shown as a powerful tool for surface transformation and physical properties of certain functional materials [19-20]. Because the laser irradiation technique offers some advantages over the traditional annealing method in terms of less in thermal exposure, local-heating, reduced effect on the substrate temperature, and easy manageable [21]. Further, laser annealing technique can yield the high quality Al-doped Zinc oxide (AZO) films at low temperature for the fabrication of solar cell and liquid crystal display (LCD) [22]. Some reports of laser irradiation effect on the optical band gaps [23-24] and
photoluminescence (PL) [25-28] of non-doping ZnO nanostructured films were appeared in literature. Many more works to develop the high quality ZnO for the improvement in electrical conductivity using laser irradiation technique have been reported [29-30]. Further, the electrical, surface morphology, optical transmission and gas sensing properties including resistivity and optical band-gap of Al-doped ZnO films were investigated [31-33].

Though the laser irradiation studies on the electrical properties of Al-doped ZnO thin films were reported, there is still limited works on the optical, infrared (IR), structural and photoluminescence (PL) properties of nanostructured Al-doped ZnO thin films. Recently, we have reported the effect on optical properties of pure ZnO films by laser irradiation [34]. In continuation of previous work, studied on the irradiation effect of Al-doped ZnO thin films using different energy of a high power pico second laser (355nm). The main interest of 355 nm laser is UV source that can impact on the surface of thin film. The influence of laser energy on the different properties of the Al-doped ZnO thin films were investigated.

2. Materials and Method

2.1. Preparation

The ZnO solution was prepared by dissolving the zinc acetate dehydrate [ZnAc:2(Zn(CH3COO)2 2H2O)] in 2-propanol and diethanolamine (DEA, C4H11NO2). In the beginning, ZnAc was dissolved in 2-propanol and then added DEA to increase the solubility. The corresponding molar ratio of DEA/ZnAc to solution was taken as 1 with 0.5 M concentration. In addition, dopant agent was taken as aluminium acetate basic hydrate [(CH3CO2) AlOHH2O] for Al-doped ZnO precursor solution. Al-doped ZnO thin films were prepared using different concentration of Al. The molar ratios of Al/Zn were taken as Al3+/Zn2+ = 0.5 % and 1.0 %, by mixing the aluminium acetate basic hydrate into the precursor solution used for ZnO. The final solution was stirred at 700 °C for 2 hr to produce homogenous solution. The size of glass substrates was 10 x 10 mm² and cut and cleaned with ethanol for 10 min before used. Cleaning of substrate was performed in an ultrasonic cleaner and finally cleaned with deionized water and dried. The gel solution was dropped onto cleaned glass substrate at 3000 rpm for 30 s using a spin coater (Laurell EDC-650-23B). After the deposition by spin coating, the films were preheated at 2500 °C for 10 min on hot plate to evaporate the solvent and remove organic residuals. Finally, the films were annealed 4000 °C for 2 hr.

2.2. Characterizations

All prepared thin films were irradiated using 355 nm laser source from a mode-locked and Q-switched Nd: YAG Pico Second Tunable Laser System (LS-2151, LOTTIS II, Belarus). The
355 nm wavelength was generated with third harmonic generation from fundamental wavelength 1064 nm. Pulse duration of the fundamental beam was 70-80 ps. The pulsed repetition rate of the laser was 15 Hz. The maximum output pulse energy at 355 nm with 15Hz is 21 mJ. In the experiment, the very short laser pulse of energy fluence at 10 mJ/cm², 15 mJ/cm² and 20 mJ/cm². The laser exposure time for all samples was about 3 min at 6 mJ, 9 mJ and 12 mJ energy of 355 nm laser source was used under the below threshold ablation and varied the peak power of laser.

The sample was positioned without focus the beam and keeping all other parameters constant except the laser energy. The exposure area of the sample with the laser beam are fixed during the laser irradiation. The laser energy is increased to see the laser influence on surface of the films. The diameter of laser beam was 6 mm and exposed on the sample area since the position of all samples was fixed.

The optical absorption, emission and Infrared spectra (IR) of the films before and after laser irradiation were measured in UV-Visible-NIR spectrophotometer (670, JASCO), Lumina Fluorescence spectrophotometer (Thermo Scientific,) and Fourier Transform Infrared Spectroscopy (FTIR) (Perkin Elmer) respectively. XRD images of the ZnO and Al-doped ZnO films was investigated using X-ray diffraction (XRD, PANalytical X’Pert) with Cu Kα radiation (λ=0.154 nm) operated at 45 kV and 40 mA. The surface morphology of Al-doped ZnO films before and after laser irradiation was studied by a Field Emission Electron Microscope (FESEM).

3. Results and Discussion

3.1. Structural analysis: The influences of laser energy on the structural property of pure ZnO and Al-doped ZnO films were investigated. The characterization of crystals and molecular structures of the ZnO and Al-doped ZnO films were conducted by X-ray diffraction and FTIR techniques. The XRD feature of pure ZnO and Al-doped thin films before and after the laser treatment at different energy is shown in Figure 1. The observed diffraction peaks including the prominent (101), (002) and (101) of ZnO correspond to a hexagonal wurtzite crystal structure. These observed peaks are in accordance with the pristine and the irradiated films which is confirmed from (JCPDS card No. 36-1451). There are no additional peaks observed which correspond to other crystalline phases or aluminum. The observed peaks are generally broadening which indicate the smaller sizes of the particle. There is slightly deteriorated in intensities of the pure ZnO film after laser irradiation with time. As clearly seen in Figure 1 that pattern of ZnO is slightly broaden when Al is contained within ZnO. The reason of
broadening the peaks with Al containing ZnO may attribute to the effect on size of the particles. Intensities of Al-doped ZnO after laser exposure is influenced over the irradiation time but the rate of decrease in their intensities are different from the pure ZnO film. It means that induce of laser energy power on the structure of Al-doped films are less influenced as compared to pure ZnO due to Al involvement. The diffraction pattern indicates that increase in crystallinity of ZnO thin films due to the influence of Al doping and laser irradiation. The reason may possible and attribute to the addition of Al and absorption of heat radiation from laser source promote grain growth of the films [19].

The infrared spectra of the ZnO and Al-doped ZnO films was investigated by IR over 500-4000 cm\(^{-1}\) region. The IR peak positions of ZnO film in the 2000-4000 cm\(^{-1}\) region are slightly shifted as compared to the relative peaks of Al-doped ZnO films. When the laser irradiated on ZnO and Al-doped ZnO films, the relative intensities of IR features are decreased with increasing the laser energy as shown in Figure 2 (i, ii, iii). Doping of Al in ZnO induces to the relative intensity. When the Al doping percentage increases, the relative intensity of ZnO is slightly decreased. For instance, the absorption intensity of features around at 3570 cm\(^{-1}\), 2916 cm\(^{-1}\), 2852 cm\(^{-1}\) and 2107 cm\(^{-1}\) (shoulder) are slightly reduced due to laser irradiation with increasing the time. For instance, the two bands of ZnO at round 2852 cm\(^{-1}\) and 2916 cm\(^{-1}\) are noticeably decrease in their relative intensities with respect to irradiation time. These two peaks of very weak intensities at 2852 and 2916, cm\(^{-1}\) are due to C–H stretching vibrations of alkane groups [35]. There is small influenced of Al to the peaks of ZnO. The observed peaks correlate well with the observed frequencies of the C–H\(_2\) symmetric stretch (2855 cm\(^{-1}\)), C–H\(_2\) asymmetric stretch (2926 cm\(^{-1}\)), and C–H\(_3\) asymmetric stretch (2962 + 10 cm\(^{-1}\)) of saturated hydrocarbons, respectively as reported in [36].
Figure 1: XRD spectra of (i) pure ZnO and (ii and iii) Al-doped ZnO after irradiation at different laser energy.

Overall the change in relative intensities of Al-doped ZnO films after laser irradiation may attribute to the influence on structure of Al-doped ZnO due to laser energy.
The existence of ZnO nanorods in the surface of film is seen in the image of surface morphology of ZnO film is displayed in Figure 3 (i). The SEM images of Al-doped ZnO films before and after laser irradiation is shown in Figure 3 (ii-iii). The presence of ZnO nano rods with Al materials in film is confirmed by the EDX spectrum as shown in Figure 3 (iv). The surface of Al-doped ZnO film before laser treatment shows ZnO nano rods exist inside Al surface layer. After the laser treatment on the surface, dispersal of ZnO nanorods in the Al layer is detected with a condense surface. It means that after the laser exposure on the surface, the distribution of ZnO nano rods in the Al containing surface is remarkably changed with their location i.e., majority of nano rods becomes agglomerate and overlap. It seems to be loosely binding with Al. It suggests that when the laser beam fall on surface, energy could penetrate and deform the uniformity of Al-doped ZnO surface that lead to aggregate the nano rods as
shown in Figure 3 (iii). The agglomeration of nano-rods may effect that when laser light interacts with the surface of Al-doped ZnO, laser energy could induce to defect to Al and ZnO nano rods. Therefore, it may lead to cause the length of ZnO rod become shorten. The morphological particle size of Al-doped ZnO was clearly seen in figure 3 that the average sizes was significant decreased after laser irradiation. Similar result was reported the effect on sizes of Al-doped ZnO as the laser energy exposed [37].

Figure 3. FESEM images of (i) ZnO [34]. (ii-iii) Al-doped ZnO film before and after laser irradiation, (iv) EDX spectrum
3.2. Absorption property

The absorption property of pure ZnO and Al-doped ZnO films was studied after the laser treatment at different laser energy. The laser irradiation influence in the absorbance of the samples were recorded. The band gap energies of the films were also determined using the absorption spectra. The typical absorption spectra for pure ZnO and Al-doped ZnO films after the laser irradiation are shown in Figure 4 (i-iii). The absorption edge for pure ZnO and Al-doped ZnO films shows slightly sharp after irradiation the films. The peaks are blue shifted from the corresponding bulk value (340 nm) as listed in table 1.

![Absorption spectra of (i) pure ZnO and (ii and iii) Al-doped ZnO after irradiation at different laser energy](image)

Figure 4: Absorption spectra of (i) pure ZnO and (ii and iii) Al-doped ZnO after irradiation at different laser energy
The absorbance of the ZnO film was affected as the pump energy increase from 6 mJ to 9 mJ and 12 mJ as shown in Figure 4 (i). There is similar pattern shown in the absorbance of Al-doped ZnO at different laser energy. The rate of decay in peaks of Al-doped film with respect to different laser energy is more inclined. As clearly seen in Figure 4 (ii-iii), absorption spectra of Al-doped ZnO with Al (0.5 %) and (1%) is observed different from the absorption spectra of pure ZnO under the laser treatment. In general, absorption peaks of ZnO is influenced when the Al included. The reason of influence is not discussed in detail since the interest of present work was focused on laser energy effects on the ZnO and Al doped materials. But, the reason of Aluminum influence in ZnO were attributed to the increase in band-gap energy, decrease in particle sizes and surface roughness when Al included as detailed in [18, 38-39].

<table>
<thead>
<tr>
<th>Pump energy</th>
<th>Peak positions of Pure ZnO</th>
<th>Peak positions of Al-doped ZnO Al (0.5%)</th>
<th>Peak positions Al-doped ZnO Al (1%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 mJ</td>
<td>359 nm</td>
<td>360 nm</td>
<td>352 nm</td>
</tr>
<tr>
<td>9 mJ</td>
<td>361 nm</td>
<td>362 nm</td>
<td>352 nm</td>
</tr>
<tr>
<td>12 mJ</td>
<td>361 nm</td>
<td>362 nm</td>
<td>352 nm</td>
</tr>
</tbody>
</table>

The absorption coefficient $\alpha$ associated with the optical band gap for a direct band gap can be determined by Tauc plots:

$$ahv = A(hv - E_g)^{1/2}$$

Where $hv$ is photon energy, $A$ is the transition probability of the parameter and the optical band gap represents as $E_g$. The $E_g$ value is determined from an intercept on energy axis of $hv$ vs $(ahv)^2$ plot as shown in Figure 5 (i-iii) and given in table 2. It is seen from table 2, there is slightly effect in band gap of ZnO and Al-doped ZnO films under laser treatment. The energy gap values increase with the increasing of the energy fluences. No doubt, effects in band gap are observed when the Al doped into ZnO nanostructures as listed in table 2, the reason of effect may attribute to the introduction of defect levels within the band gap. As clearly seen in table 2, there is slightly changed in energy band-gap with the variation of irradiation laser energy which may attribute to little effects in crystallite size with the thickness of the films as a result of confinement effect [35] and heat on samples etc.
<table>
<thead>
<tr>
<th>Pump energy</th>
<th>Pure ZnO (Eg)</th>
<th>Al-doped ZnO Al (0.5%) (Eg)</th>
<th>Al-doped ZnO Al (1%) (Eg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 mJ</td>
<td>3.04 eV</td>
<td>3.07 eV</td>
<td>3.09 eV</td>
</tr>
<tr>
<td>9 mJ</td>
<td>3.05 eV</td>
<td>3.07 eV</td>
<td>3.08 eV</td>
</tr>
<tr>
<td>12 mJ</td>
<td>3.09 eV</td>
<td>3.07 eV</td>
<td>3.08 eV</td>
</tr>
</tbody>
</table>

There is no much significant effect on band gap of ZnO and Al-doped ZnO by laser energy but the stability of band gap is slightly higher with ZnO than the Al-doped ZnO as seen in listed table 2.

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3.3. Photoluminescence spectra

The room-temperature photoluminescence spectra of pure and Al-doped ZnO thin films irradiated at different energy of Pico second laser source is shown in Figure 6 (i-iii). The emission spectra observed from the samples were excited at 325 nm as excitation wavelength under same environment. The ZnO sample exhibits similar UV emission band centred at 385 nm, which is attributed to band-to-band transitions, excitonic emissions [40-41], and donor-acceptor pair transitions.

![Photoluminescence spectra](image)

Figure 6. Photoluminescence spectra of (i) pure ZnO and (ii and iii) Al-doped ZnO after irradiation at different laser energy.

The observed emission peak corresponds closely to calculated bandgap wavelength. The band edges remain sharp of the pure ZnO and Al-doped ZnO which correspond to emission, indicating well integrated the Al dopants into the ZnO lattice. But the effect in emission intensity of ZnO and Al-doped ZnO films are significant after the laser irradiation as shown in
Figure 6 (i-iii). The rate of decay on emission peaks of ZnO and Al-doped ZnO films is followed by the different laser energies. For instance, emission peak with band-shape of ZnO film is slightly stable as compared to Al-doped ZnO after laser exposure. Even the higher percent (Al-1%) of Al-doped ZnO film is more affected in intensity due to laser energy but remain stable in peak positions as shown in Figure 6 (ii-iii). It means that no significant effect on emission peaks of ZnO and Al-doped ZnO film due to laser energies except the intensity and band shape as seen in listed table 3. It is worth to mention that different laser energies make influence on the surface of both type of samples but there is more influenced on Al-doped ZnO. It may contribute to the integration of Al in ZnO films that laser energy more penetrate in layer of film.

In order to confirm, the emission property of both films i.e., pure ZnO and Al-doped ZnO films, spontaneous emission spectra were recorded during the laser exposure at same environment. The spontaneous emission spectra of ZnO and Al-doped ZnO films are displayed as in Figure 7 (i-iii).

Table 3: Peak positions of emission and spontaneous spectra of Pure ZnO and Al-doped ZnO after irradiation at different laser energy

<table>
<thead>
<tr>
<th>Samples</th>
<th>Emission peaks</th>
<th>Spontaneous peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6 mJ</td>
<td>9 mJ</td>
</tr>
<tr>
<td>Pure ZnO</td>
<td>385 nm</td>
<td>387 nm</td>
</tr>
<tr>
<td>Al-doped ZnO Al (0.5 %)</td>
<td>384 nm</td>
<td>383 nm</td>
</tr>
<tr>
<td>Al-doped ZnO Al (1 %)</td>
<td>381 nm</td>
<td>383 nm</td>
</tr>
</tbody>
</table>

As clearly seen in the figure and table 3, the spontaneous peaks, intensities and band shape are differently observed. Though emission peaks of both type samples do not shift significant under laser irradiation but there is substantial different at peak position of spontaneous peak position from emission peak. For instance, the emission peaks of Al-doped ZnO (0.5 %) and (1 %) do not much shift upon the different pumped energy but the corresponding spontaneous peaks of the samples are significantly influenced by laser energy. The minor change in emission peaks of the pure ZnO and Al-doped ZnO films under different energy is attributed to site effects as well influence of laser energy.
In both observation, intensities are deteriorated with respect to laser energies. The rate of deterioration on intensifies for the samples is slightly higher at Al doped sample and also depend on the percent of dopant. It may a reason to the change in grain distribution and roughness of surface in films after laser irradiation that can lead to deteriorate the intensities of emission peaks.

4. Conclusion
In present work, pure ZnO and Al-doped (0.5 % and 1 %) ZnO thin films were prepared by the sol-gel method using spin-coating technique. Laser irradiation effects on structure, optical, energy band gap and emission spectra induced by Pico second laser source were investigated.
Results reveals that laser irradiation influences on the optical properties and structure. There is no significant caused at fundamental peaks of pure and Al-doped ZnO films but substantial changed in their intensities. It is found that the band gap narrowing with changed in films due to laser power which has been attributed to the increase in the localized tail states. The observed photoluminescence spectra of pure ZnO and Al-doped ZnO thin films exhibits near-band edge (NBE) emission peaks. In addition, the PL and spontaneous intensities of the Al-doped films decreases after the laser irradiation due to defect annihilation.

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