Effect of infrared laser irradiation on electrical conductivity and ethanol sensitivity of sol-gel ZnO thin films

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Abstract. Zinc oxide thin films are prepared by spin-coating sol-gel method. Warm air flow is used as a first step in the drying procedure during the preparation of a part of the films. Post-deposition irradiation of some films with infrared pulse laser is also applied. Spectroscopic ellipsometry, X-ray diffraction and conductivity measurements are used to get information about the influence of the laser irradiation and the usage of the warm air flow on the properties of the films. It is shown that all films are nanocrystalline and the treatment with warm air flow and laser beam irradiation improves films crystallinity and reduces their conductivity. The results are related to lower porosity and smaller amount of defects in treated films.

1. Introduction
Zinc oxide (ZnO) is II-VI wide band gap semiconductor material with properties that make it widely studied in physics, material science, chemistry, biochemistry, etc. ZnO is used in the rubber and ceramic industry, concrete manufacturing, sunblock creams, food etc. [1]. It is also promising material for thin film optoelectronics, piezoelectronics, transparent electronics, sensing, and solar energy conversion [2]. ZnO can be prepared in various forms by various methods as the preparation method is usually chosen taking into account its specific possibilities to grow films with desired properties. For fabrication of structures of ZnO with well controlled properties molecular beam epitaxy, metalorganic chemical vapor deposition, pulsed laser deposition, magnetron sputtering [3], or atomic layer deposition [4] are applied. However these well-established techniques are based on usage of specialized and usually costly and complicated equipment. Various chemical techniques for growing ZnO thin films are also used, such as spray pyrolysis, sol-gel, electrodeposition, inkjet printing [5] which are significantly easier and cost-effective as they do not require high vacuum equipments and ultrapure elements or gases. Among them sol-gel deposition [6, 7] is one of the most straightforward techniques for ZnO thin film preparation. A colloidal particle suspension is prepared by mixing selected precursors in a solvent with a stabilizer until a homogeneous sol forms. The suspension is coated on the substrate and then annealing or other post-deposition treatments are carried out, which play role in improving the crystalline quality and modifying film properties.

In recent decade, laser irradiation has emerged as a powerful method for modifying material structure and surfaces, in particular for processing of metal oxides [8]. Compared with the thermal annealing methods, laser irradiation possesses some advantages, such as fast crystallization at room temperature, rapid local-heating and possibility of local crystallization and low influence on the substrate. A comparison of the effect of post-treatment of ZnO films by an Ar+ laser (514 nm) for...
5 min and thermal annealing at 500°C for 1 h, has found [9] that the laser irradiation was more effective both for the relaxation of the residual compressive stress in the as-grown films and for the modification of the surface morphology. It has been shown [10] that the level of crystallinity is greater and average crystallite size is larger in ZnO thin films annealed by KrF laser than those of thermally annealed films. The effect of laser irradiation on the electrical properties of pure and Al-doped ZnO films have also been explored [11-13]. It has been obtained in Ref. [12] that after irradiation of ZnO films by pulse infrared laser the electrical properties of the films have been improved.

In this study ZnO thin films are deposited by spin-coating sol-gel method using the standard and a modified drying approaches. Some films are further thermally annealed at 400°C, others are irradiated by a nanosecond infrared pulse laser at constant laser beam fluence for various times. The effects of the modified drying procedure and laser irradiation on the films structure, dc electrical conductivity and ethanol sensitivity at room temperature are investigated and discussed.

2. Experimental details

Zinc oxide thin films were prepared by spin coating sol-gel method on crystalline silicon substrates covered with a 300 nm thick SiO2 film grown by thermal wet oxidation. Before the film deposition the substrates were cleaned with a H2O2 + NH4OH solution, then with C2H5OH (99.98 % purity) and finally ultrasonically treated for 20 min in ethanol (99.98 %). Zinc acetate dehydrate (Zn(CH3COO)2•7H2O, ≥ 99.5 % purity) was used as Zn precursor. The zinc compound was dissolved in a mixture of ethanol and monoethanolamine (C2H7NO, 99.6% purity) as complexing agent. The mixture was continuously stirred by a magnetic stirrer at 45°C for 45 min until a clear and homogeneous solution was obtained. Before the film preparation the solution was aged at ambient conditions for 24 hours. Films deposition was performed by dropping equal amount of solution on each substrate (2×3 cm2) and applying spin-coating (2800 turns/min) for 30 sec. Then four groups of samples were produced by using one or two drying steps and applying further annealing at 400°C. Following the standard approach, a part of the films was furnace dried by heating in static air at 140°C for 10 min immediately after film deposition and some films were further annealed at 400°C for 60 min. Another part of the films was first dried for 5 min with a hot air flow (90-95°C) with volume flow rate of 7.5 l/sec and then furnace dried at 140°C for 10 min; films from this group were annealed in static air at 400°C for 60 min. The preparation conditions are described in table 1. Samples from all groups were laser irradiated in several consecutive steps with duration of 60 sec or at a step of 20 sec at room temperature in air using Q-Switched Nd:YAG laser at 20 Hz, wavelength $\lambda = 1064$ nm and fluence $f = 90$ mJ/cm². The laser beam was focused on a nearly circle area of around 0.19 cm² on the surface of each sample and the rest of the sample was non-irradiated.

The thickness of the ZnO layers was determined by fitting the experimental ellipsometry Psi and Delta data obtained by an automatic M2000D spectroscopic ellipsometer in the transparent wavelength range (600 – 1000 nm) using a two layer model consisting of a silicon substrate covered with a 300 nm thick SiO2 as a first layer and a second (main, top) layer of ZnO. To estimate the ZnO thicknesses, the layers were represented by the Cauchy dispersion equation.

The effect of the warm air drying and laser irradiation on the films crystal structure was explored by X-ray diffraction (XRD) measurements performed by PANalytical Empyrean diffractometer using the CuKα line. The crystallite size was estimated according to Sherrer's equation.

Electrical conductivity measurements in darkness were carried out at room temperature before starting film irradiation and immediately after each step of laser irradiation. Temperature measurements in the 22-135°C range in darkness and under white light illumination (50 mW/cm²) were also performed at a heating rate of 0.1°C/sec on non-irradiated and laser irradiated films around 60 days after the laser irradiation for 200-240 sec. For the first group of measurements planar contacts (around 0.5 cm long and 0.2 mm spaced) on the top surface of the films were prepared by dc gold sputtering since they were not destroyed when laser beam occasionally hit the contact. Planar contacts from melted indium with similar geometry were also used in some dark and sensing measurements.
**Table 1.** Preparation steps, film thickness and crystallite diameter, $d$, of non-irradiated ZnO films.

| Sample type | Preparation procedure                                                                 | Film thickness (nm) | Diameter, $d$ (nm) |
|-------------|----------------------------------------------------------------------------------------|---------------------|-------------------|
| I-1         | Step 1 – warm air drying for 5 min                                                     | 380                 | 10                |
|             | Step 2 – drying at the thickness of film I-2 for 10 min                                |                     |                   |
| I-2         | Step 1 - warm air drying for 5 min                                                     | 260                 | 15                |
|             | Step 2 - drying at 140°C for 10 min                                                    |                     |                   |
|             | Step 3 - annealing at 400°C for 60 min                                                 |                     |                   |
| II-1        | Step 1 - drying at 140°C for 10 min                                                    | 450                 | 9                 |
| II-2        | Step 1 - drying at 140°C for 10 min                                                    | 255                 | 15                |
|             | Step 2 - annealing at 400°C for 60 min                                                 |                     |                   |

Resistive sensing measurements were carried out at room temperature in home-made equipment. The sample was fixed up under a closed non-transparent glass test chamber with a volume of 1500 cm$^3$, full of atmospheric air. Ethanol vapours were produced by evaporating 100-500 μl of liquid ethanol (99.7%). A propeller was used for distributing the vapours homogeneously inside the chamber. The layer’s response to ethanol vapours was registered as the change of the dc dark current through the layers. A current increase was observed upon film exposure to ethanol vapours as the maximum value $I_{\text{max}}$ was achieved 3 min after starting ethanol evaporation. The gas sensitivity, $S$, was calculated using the relation $S = \frac{(I_{\text{max}} - I_{\text{din}})}{I_{\text{din}}}$, where $I_{\text{din}}$ is the dark current measured before the film exposure to ethanol. The concentration dependences were taken by gradually increasing the ethanol concentration. The ethanol vapours were removed by exposing samples to atmospheric air.

3. Results and Discussion

The film thickness determined from the ellipsometry is in the range 250-450 nm (table 1). As seen from the table the thickness of the film I-2 - dried with warm air flow and annealed at 400°C- is about 30% lower than that of the corresponding film annealed only at 140°C (film I-1). For the samples prepared without warm air drying this percentage is ~40%. A comparison of the thickness of films I-1 and II-1 shows that the thickness of sample I-1 is smaller (of ~ 15%) than that of the II-1 sample. This difference indicates that the warm air drying for 5 min before the drying at 140°C was also caused a film thickness reduction though it is smaller than the reduction caused by the annealing at 400°C. The thickness decrease is most likely due to both a porosity decrease and effusion of the organic remains [14].

Figures 1 and 2 show X-ray diffraction patterns ($\Theta$ - diffraction angle) of two non-irradiated (a) and two laser irradiated for 200 sec (b) ZnO films prepared by applying the standard preparation approach (see table 1). The characteristic bands of wurtzite ZnO (JCPDS No 98-016-9463) are observed in all patterns which shows that all films possess crystalline structure. While a good crystallinity of the films annealed at 400°C is expected, the as-prepared films dried at temperatures less than 200°C are normally very disordered. Crystalline structure has been reported by other research groups and related to the usage of monoethanolamine [15]. The band intensities in figure 2(a) are higher than the intensities of the bands in figure 1(a) which indicates that the furnace annealing at 400°C improves crystallinity of the non-irradiated films. Besides, the full width at half maximum of the bands in the spectra of the non-irradiated film annealed at 400°C is smaller and the estimated crystallite size in these films is greater (as expected) than the grain size in the non-irradiated films only dried at 140°C (table 1). Similar results have been obtained for the films prepared by applying the modified drying procedure. A comparison of the patterns of non-irradiated and laser beam irradiated II-1 films (figure 1 (a) and (b)) indicates that the laser annealing also improves the film crystallinity which, according to the nanocrystallite size estimation, is accompanied by a size increase from 9 nm to 11 nm. In both group of films (group I and group II) no significant laser induced structural changes
have been observed in the films annealed at 400°C (figure 2); the estimated crystallite size is 15 nm and the band intensities in the XRD spectra of non-irradiated and laser beam irradiated films are comparable. These results indicate that the effect of laser irradiation applied (~200 sec) is similar to that of thermal annealing; it improves the crystallinity of the films with higher lattice disorder. The observed effect is weaker than that of the furnace annealing at 400°C for 60 min but usage of a higher fluence or longer irradiation time seems promising for the achievement of stronger structural changes.

**Figure 1.** XRD patterns of ZnO films from group II-1 (only dried at 140°C): (a) non-irradiated and (b) laser beam irradiated for 200 sec, $f = 90$ mJ/cm².

**Figure 2.** XRD patterns of ZnO films from group II-2 (dried at 140°C and then annealed at 400°C): (a) non-irradiated and (b) laser irradiated for 200 sec, $f = 90$ mJ/cm². The inset in (a) illustrates the spectrum deconvolution applied to estimate nanocrystallite size.

Metals with low work function (In, Al, etc.) form Ohmic contacts to n-ZnO while those with high work function (Au, Ag, Pd) are expected to form Schottky contacts as the barrier height and electrical behaviour are affected by the interface defect states [16], the contact preparation method [16, 17], etc. In most cases magnetron sputtered gold forms Schottky contacts to ZnO [17, 18] but Ohmic behaviour has also been observed [19]. Current-voltage ($I$-$V$) characteristics we measured have shown Ohmic behaviour of the contacts from melted In when applying dc electric fields in the range 5-150 V/cm. $I$-$V$ characteristics were measured on all samples with Au contacts and two $I$-$V$ characteristics are shown in figure 3 in log-log coordinates. All characteristics obtained in the range 5-150 V/cm were super linear with different slopes for the different samples resembling the characteristics observed in the case of space-charge-limited currents through a dielectric material in the presence of charge traps [20]. Therefore, conductivity measurements on all samples were performed at applied voltages of 2 V and 10 V. Very similar conclusions have been drawn from the results obtained at both voltages.

The results for the dark currents through the samples at room temperature measured immediately after each laser irradiation step are summarized in figure 4. The values at zero seconds represent the currents through the as-prepared samples. The first look at the figure shows that: (i) the dark conductivity of the non-irradiated samples prepared by applying warm air drying (group I) is much lower than that
II-2

$10^{-10}$ $10^{-8}$ $10^{-6}$ $10^{-4}$

$10^{-10}$ $10^{-8}$ $10^{-6}$ $10^{-4}$

Figure 3. Current-voltage characteristics measured on non-irradiated and laser irradiated II-2 samples annealed at 400°C provided with dc sputtered gold contacts.

Figure 4. Dark current through four samples denoted in the figure measured immediately after each step of laser irradiation. The arrows denote the opposite effect on the dark current values of the thermal annealing (left) and laser irradiation (right).

of the samples from group II; (ii) the furnace annealing at 400°C of as-deposited samples from group II results in a strong conductivity decrease while the conductivity of the samples from group I treated at 140°C and 400°C is quite similar.

It is well known that undoped ZnO with a wurtzite structure is an $n$-type semiconductor and this fact was related to the presence of intrinsic and extrinsic defects; the group of native defects includes interstitial Zn, oxygen vacancy, Zn-on-O antisite [21, 22]. However, subsequent works [23, 24] argued that oxygen vacancies are deep donors which cannot be responsible for the $n$-type conductivity, interstitial Zn is shallow donor but have large formation energies, oxygen and zinc antisites also have too large formation energy to exist in significant concentrations in the material. Hydrogen was found to be acting as a shallow donor at the interstitial position with 35 meV ionization energy [25] and it is regarded as one of the main, not intentionally incorporated impurity leading to the $n$-type conductivity. Based on these considerations one can think that during the preparation of the group I samples the warm air flow effectively reduces the incorporation of organic products that can be source of hydrogen. Probably for this reason hydrogen concentration is relative low even in the films only dried at 140°C. This assumption is supported by the fact that the thickness of the I-1 films is significantly smaller than that of the thickness of II-1 films (table 1). For the group II films the postdeposition annealing at 400°C causes effective effusion of the organic products and the film thickness decreases together with a strong conductivity reduction. Some reduction of the oxygen vacancies is also possible as result of the warm air flow and the annealing at 400°C.

Figure 4 also shows that the conductivity of all types of samples, measured immediately after each step of laser irradiation, increases and the increase reaches saturation after $\sim 200$ sec. In order to check whether the current increase is irreversible, we carried out temperature measurements in darkness and under white light illumination about 60 days after the laser irradiation experiments. Dark current temperature dependences of laser beam irradiated samples from all four groups measured 60 days after irradiation are shown in figure 5(a). The differences between the room temperature conductivity of the irradiated samples are similar to those seen in figure 4 for non-irradiated ones. However the current values seen in figure 5(a) are significantly smaller than the values measured immediately after the irradiation. They were also lower from the currents through the non-irradiated samples and this observation is illustrated in figure 5(b). Hence the laser-induced current increase seen in figure 4 is a reversible effect while the irreversible effect of the laser beam irradiation is a conductivity decrease. Based on the observed long time relaxation of the photocurrent through all samples after turning off
the light (figure 5(b), inset) one can assume that the current increase registered immediately the laser irradiation is due to slow recombination of the carriers generated by the laser beam due to the existence of deep traps. The irreversible conductivity decrease is most likely due to laser annealing effect similar to the thermal annealing effect discussed above.

Figure 5. (a) Dark current temperature dependences of samples from all four groups denoted in the figure obtained about 60 days after laser irradiation. (b) Dark current temperature dependences of an II-2 sample taken before and 60 days after irradiation. The Inset in figure 5 (b) shows photocurrent relaxation when the light is turned on and turned off.

Ethanol sensing experiments at room temperature were performed on all type of samples. No good sensitivity was detected for the samples annealed at 400 °C. Figure 6 displays the best results obtained for the films deposited by using drying with warm air flow as first step and thermal treatment at 140 °C as second step. They show strong response at room temperature of both non-irradiated and laser irradiated samples from group I-1 type, as the sensitivity increases after laser beam irradiation. Experiments on the films morphology and porosity are planned to understand and improve the obtained sensing results.

Figure 6. Room temperature ethanol sensitivity of non-irradiated and laser beam irradiated samples from group I-1.

4. Conclusions
The effect of application of warm air flow as a first step in the drying procedure during the sol-gel preparation of ZnO thin films, as well as the influence of post-deposition irradiation of the films with infrared pulse laser on their structure and conductivity have been investigated. It has been shown that the warm air usage results in film thickness reduction similar to that caused by a post-deposition furnace annealing at 400 °C. It has also been found that all types of films are crystalline with wurtzite structure as both the application of warm air flow during the preparation and laser irradiation of the films annealed at 140 °C improve films crystallinity. These results have been explained with reduction of the amount of organic inclusions and films porosity. Besides, the treatment with warm air flow caused a strong reduction of the electrical conductivity of the film which is similar to the effect of the
thermal annealing at 400°C. The laser irradiation also resulted in irreversible decrease of the electrical conductivity. It has been assumed that the conductivity decrease is due to smaller amount of defects in treated films (incorporated hydrogen, oxygen vacancies, etc.) than in the non-treated ones. Non-irradiated and laser irradiated films prepared by applying warm air flow and annealed at 140°C have shown good response to ethanol vapours at room temperature.

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