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# Thermal post-processing of spray-pyrolysis deposited ZnO thin films

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Spray-pyrolysis deposited ZnO thin films, subjected to non-isothermal annealing and excimer laser modification, are studied. X-ray diffraction, optical spectrophotometry and scanning electron microscopy are applied for identifying, analysing and imaging the phase composition, optical properties and surface morphology respectively. The electrical conductivity of the ZnO films is estimated on the basis of DC resistance measurements. Comparison of the physical properties of samples subjected to conventional and laser stimulated thermal post-processing is performed. The advantages of laser modification for obtaining good quality crystalline ZnO coatings having a wurtzit structure are demonstrated.

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*Keywords*: Zinc oxide, Thin films, Thermal treatment, Physical properties

## 1. Introduction

Zinc oxide thin films are modern functional materials with a wealth of applications in contemporary micro- [1] and opto-electronics [2,3], catalysis [4,5], sensor techniques [6] etc. A great variety of physical [3,7] and chemical [2,8,9] coating techniques are applied for their preparation. Spray-pyrolysis is a low-cost large scale chemical deposition method. However, the microstructure and properties of thin films obtained on its basis are known to be very sensitively to the substrate temperature.

Amorphous and polycrystalline phases are usually found to co-exist in as-deposited spray-pyrolysis ZnO films on quartz or glass substrates. This phase composition is commonly improved via post-deposition annealing, since the crystalline phase determines to a great extent the properties that are important for the technological films. Effective thermal processing usually requires temperatures exceeding that of the substrate during spray pyrolysis. However, the melting ($T_m$) or softening ($T_g$) temperature, or those of the substrate restrict the annealing conditions to a narrow temperature range and long processing times - i.e. conditions that are not suitable for the applied technologies. An attractive alternative approach could be that of applying pulsed laser irradiation as a tool for the post-deposition annealing of spray pyrolysis ZnO. In this case, the optical absorption of the irradiated areas of the films is accompanied by a significant transient heat release, with a minor change in the substrate temperature.

Recently, this approach was successively applied to improve the structure and corresponding properties of $ZrO_2$ [10], $TiO_2$ [11] and $Al_2O_3$ [12] ceramic thin films, for variety of applications. In the present work, an attempt to expand the scope of laser processed solid state matter is made. It aims to compare the efficiency of laser stimulated and thermal annealing for modifying the structure, as well as the physical properties, of spray-pyrolysis ZnO thin films, for sensor applications.

## 2. Experimental

The experiments were carried out with 200 - 500 nm thick ZnO films, deposited on soda-lime glass plates in specially constructed automated equipment. 0.1M $Zn(NO_3)_2.6H_2O$ or $Zn(CH_3COO)_2.2H_2O$ ethanol solutions were multiple sprayed on glass substrates held at a temperature of 350 °C. At higher temperatures, glass plate fracture was observed due to local overheating during the spraying procedure. We shall further denote for simplicity the abbreviations ac-ZnO and ni-ZnO for spray-pyrolysis thin films prepared on the basis of $Zn(CH_3COO)_2.2H_2O$ or $Zn(NO_3)_2.6H_2O$ precursors, respectively.

Some of ZnO thin coatings thus obtained were isothermally annealed for 14 hours in an inert atmosphere of pure dry nitrogen at 590 °C, that is very close to $T_g$. In parallel, samples coated under the same conditions were exposed in air by means of an excimer Kr*F pulsed laser ($\lambda$=248 nm, $\tau$=40 ns, Lambda Physics, Germany) in the presence of a beam homogenizer. The laser energy density at the sample surface $E_d$ was varied in the range 150 - 500 mJ/cm$^2$. The changes in the film thickness after the laser exposure were identified using a Taylor Hobson Talistep stylus profilometer.

A vibrating capacitor electrometer (RFT Vacutronik VA-J-51 (Germany)) was used for DC-conductivity measurements. The resistance of the ZnO films was measured parallel to the substrate plane, with an accuracy of ±2%, using 0.5 mm narrow strip gold electrodes, vacuum deposited on the film surface. A specially designed vacuum thermostat allowed us to maintain the sample temperature between 20° and 150 °C, with an accuracy of ±0.5 °C. All measurements were carried out in dry pure $N_2$ at atmospheric pressure. More details of this experimental set-up are described elsewhere [11].

The virgin, as well as thermally and laser treated ZnO films, were further analysed using optical photometry, by means of a Carry 5 UV-VIS-NIR spectrophotometer. The surface morphology of the samples was visualized under scanning electron microscope Philips SEM 515, and their phase composition was studied via WAXRD with a Philips PW 1050 diffractometer.

## 3. Results

Fig. 1 presents scanning electron micrographs of as-deposited spray-pyroysis ac-ZnO (a) and ni-ZnO (b) films. It is clearly seen that both films are characterised by a nanosized grain-like morphology, with minor differences in the mean grain size and surface roughness. Also, these structural peculiarities are slightly affected by the applied isothermal annealing at 590 °C.

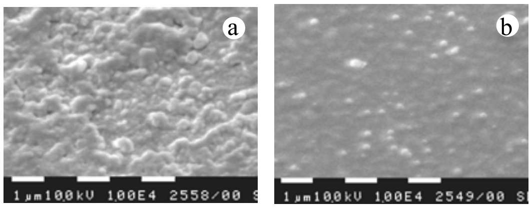

*Fig. 1. Morphology of virgin ZnO films spray coated from: (a) ac-ZnO, (b) ni-ZnO.*

Furthermore, excimer single shot laser irradiation conditions at different pulse energy densities were found leading to a considerable smoothing of the initial grain-like surface. This is shown by the scanning electron micrographs in Figs. 2 (a, b) for laser processed ZnO films. Simultaneously, a film thickness reduction of the order of 25% for both types of coating was established by stylus profilometer measurements.

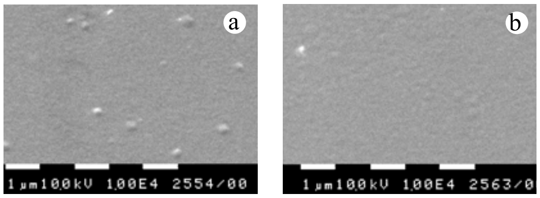

*Fig. 2. Surface morphology of single shot laser irradiated: (a) ac-ZnO films at $E_d = 380$ mJ/cm$^2$, (b) ni-ZnO films at $E_d=540$ mJ/cm$^2$.*

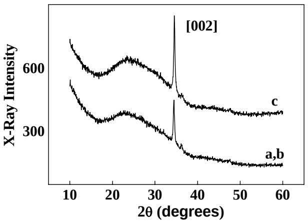

*Fig. 3. X-ray diffraction spectra of ac-ZnO films: (a) virgin, (b) thermally annealed, (c) laser irradiated with a single pulse at $E_d=380$ mJ/cm$^2$.*

This laser induced effect could be reasonably explained by the occurrence of laser induced ZnO recrystallisation, as evidenced by the XRD spectra in Fig. 3 for ac-ZnO and in Fig. 4 for ni-ZnO films. For comparison, the X-ray diffraction spectra of thermally annealed films are also included in these figures.

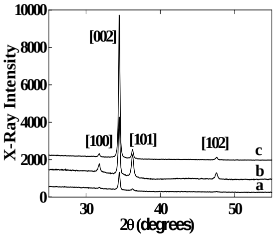

*Fig. 4. X-ray diffraction spectra of ni-ZnO films: (a) virgin, (b) thermally annealed, (c) laser irradiated with a single pulse at $E_d=540$ mJ/cm$^2$.*

The temperature dependence of the dark DC conductivity, σ, measured in virgin as well as in the thermally modified samples, is shown in Fig. 5. It is clearly seen that, depending post-processing applied to the spray pyrolysis ZnO films - either thermal annealing or laser irradiation, the dark conductivity of the modified films is orders of magnitude higher or lower than that of the virgin samples.

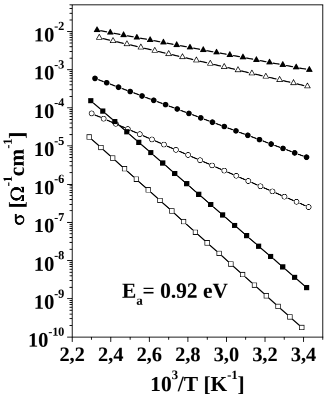

*Fig. 5. Dark DC conductivity of (a) ac-ZnO (filled), (b) ni-ZnO (unfilled symbols) films - virgin (o), thermally annealed (Δ) and excimer laser irradiated (□) under the conditions of Fig. 2.*

Furthermore, it was established that the differences in the optical transmittance and reflectance spectra of as-deposited and thermally annealed ZnO films were close to the sensitivity limit of that analytical method, and on this basis could be neglected. In contrast, a significant change of the same optical parameters was found for ZnO samples after excimer laser processing, as compared to those of nonirradiated samples. This is evidenced by the recorded transmittance (T) spectra for ac-ZnO (Fig. 6) and ni-ZnO (Fig. 7). It is clearly seen that T changes strongly depends on either the laser energy density, $E_d$, (Fig. 6) or pulse number (Fig. 7). The results from optical reflectance measurements showed that the virgin spray pyrolysis ZnO films are characterized by low R values, typically less than 15% in the wavelength interval studied. Also, these R values undergo minor variations upon excimer laser exposure. For this reason, the recorded R spectra of virgin and laser processed films are not included in the paper.

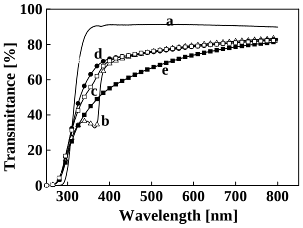

*Fig. 6. Optical transmittance vs. wavelength of a glass substrate (a), virgin ac-ZnO films (b) and those single shot irradiated at $E_d$ 330 mJ/cm$^2$ (c), 380 mJ/cm$^2$ (d) and 480 mJ/cm$^2$ (e).*

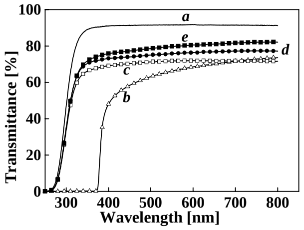

*Fig. 7. Optical transmittance vs. wavelength of a glass substrate (a), virgin ni-ZnO films (b) and those irradiated at $E_d$ 540 mJ/cm$^2$ with a single pulse (c), 10 pulses (d) and 100 pulses (e).*

## 4. Discussion

The results from applying electron imaging and analytical techniques unambiguously showed that as a rule, the microstructure and optical properties of sprayed ZnO thin films are slightly affected by prolonged conventional isothermal annealing near the glass softening temperature, except for a small improvement in the degree of crystallinity of ni-ZnO samples. In contrast, it was found that for both acetate and nitrate based ZnO samples, the DC conductivity substantially increases after the same thermal treatment. It should be noted here that special precautions were taken in order to avoid the influence of oxygen adsorption on the conductivity of the ZnO films studied. All conductivity measurements were performed after careful sample heating for one hour in a nitrogen atmosphere followed by thermostat pumping out and final re-filling with dry pure nitrogen. However, one could not exclude the presence of incomplete spray pyrolysis products. In our opinion, they are responsible for the orders of magnitude lower resistance of the thermally annealed, as compared to the virgin, ZnO films. Unlike conventional isothermal annealing, it was found that excimer laser post-processing strongly influences the structure and properties of sprayed ZnO films. The observed surface smoothing of the samples was accompanied by a substantial rise in the $2\theta=34.5°$ XRD peak, typical for ZnO with a wurzite structure (Figs. 3 and 4). Simultaneously, the measured thickness reduction of laser modified ac-ZnO and ni-ZnO films is evidence for an increased crystallinity and a more compact structure, compared to as-deposited films.

It was further shown that the described structural changes of laser post-processed samples are accompanied by a strong decrease in the DC conductivity. At room temperature, this reaches a value of $\sigma=5.10^{-9}\Omega^{-1}cm^{-1}$ for ac-ZnO and $\sigma=6.10^{-10}\ \Omega^{-1}cm^{-1}$ for ni-ZnO; their values for as-deposited films being $8.10^{-6}\Omega^{-1}cm^{-1}$ and $5.10^{-7}\Omega^{-1}cm^{-1}$ respectively. Additionally, the conductivity of both the spray pyrolysed ac-ZnO and the ni-ZnO laser irradiated films is characterized by the same activation energy, $E_a$ = 0,92 eV. This value is lower than the characteristic $E_a$ = 1,6 eV for intrinsic sputtered ZnO films, but is typical of the conductivity controlled by chemisorbed oxygen [13]. Obviously, the heating procedure before $\sigma$ measurements has an effect only on the oxygen physisorbed on the ZnO surface.

Finally, it was demonstrated that laser post-processing also substantially changes the optical properties of the sprayed ZnO films studied. High laser fluences are found to result in a higher optical transmittance, its maximal value of 80% being reached under optimal exposure conditions (Figs. 6 and 7). An increase in the laser energy density $E_d$ above the optimum value is accompanied by a photodarkening effect (Fig. 6e), as also observed in ceramic thin films [10, 11].

## 5. Conclusions

Experimental post-processing conditions for the efficient modification of spray pyrolysis ZnO thin films are found, clearly demonstrating some advantages of excimer laser modification with respect to conventional isothermal heating. On this basis, the opportunity is revealed for the application of laser annealing in the large area production of good quality ZnO thin films, spray-deposited on substrates having low melting points or softening temperatures.

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