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Influence of pulsed laser deposition (PLD) parameters on the H_2 sensing properties of zinc oxide thin films

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Abstract

Thin films of n-type ZnO were produced by a novel two-target, two-pulsed laser deposition technique. This method allows on-line control of the film properties by just changing the laser parameters. A number of deposition parameters, as well as the dopants (Al, Au) and the substrate type (Si, SiO_2, glass), were changed. The sensing properties of the films were tested upon exposure to a H_2 flow in air ambient at working temperatures between 150 and 210 °C. Undoped ZnO thin films, deposited on SiO_2 substrates at 200 °C, in ambient O_2 at 20 Pa and with a laser fluence of 9.6 J/cm^3, exhibited a maximum sensitivity ($\Delta R/R_0$) higher than 97% and a response time lower than 3 min at the working temperature 180 °C. Decrease of the working temperature to 150 °C was achieved by means of surface sensitization of films after deposition of Au nanoclusters on the surface of the above-mentioned ZnO thin films.

1. Introduction

ZnO thin films have, among other applications, long been used as gas sensing materials [1–3]. An important application is the use of the above films to detect reducing or inflammable gases such as H_2 and CO [4,5].

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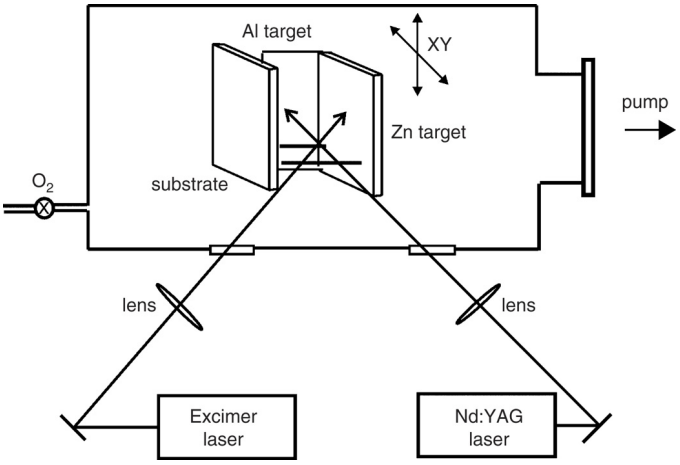

Fig. 1. Experimental set-up for the growth of ZnO thin films by the PLD technique.

The gas sensing mechanism is based on the reversible change of the surface film resistance due to the surface adsorption of gas species [2]. ZnO sensing films exhibit several advantages such as good stability, quick response, high sensitivity and compatibility with Si technology. The sensing properties of ZnO can be improved by means of dopants [6], surface catalysts [7] and mixed oxides [1,4]. Decrease of the working temperature is desirable in order to minimize the power consumption and to allow use of the sensor in explosive environments. The film growth processes [8–10] used mostly thus far (rf sputtering, CVD etc.) are either time-consuming for target preparation or do not allow doping at all.

In this study, ZnO sensing thin films were produced by a novel two-target, two-pulsed laser deposition device. Starting with two metallic targets, the method allows on-line control of the film doping or surface sensitization by catalysts. The optimization of the deposition parameters, as well as the type of substrate, has been performed in combination with the dynamic response measurements.

2. Experimental procedure

2.1. Growth

In the present work, various kinds on ZnO-based thin films have been investigated regarding their functionality as H_2 sensors. The samples have been grown by a novel two-target, two-pulsed laser deposition technique inside a stainless steel high vacuum chamber. Prior to each irradiation, the chamber was evacuated, down to a residual pressure of 7×10^{-4} Pa. Two pure metallic targets, Zn for the host ZnO film and the dopant (Al, Au, etc.), have been irradiated in ambient (O_2) reactive gas by the two different laser systems employed.

The experimental set-up used is depicted schematically in Fig. 1. The UV laser pulses of a Lumonics TE-861T ArF laser ($\lambda = 193$ nm, $\tau_{FWHM} \sim 12$ ns) were use to ablate

the Zn foil, for the host ZnO film. For the ablation of the dopants, the pulses of a Quantel YG851 laser ($\lambda = 355$ nm (THG), $\tau_{\mathrm{FWHM}} \sim 10$ ns) were used. The two lasers were synchronized and operated at 10 Hz pulse repetition rate. The laser beams were focused by quartz lenses outside the vacuum chamber and impinged on the targets with an incidence angle of about 30° relative to the normal to the target surface. To avoid fast drilling, both targets were placed on a vacuum-compatible and computer-controlled XY table. A total surface of 10×10 mm^2 was uniformly scanned. The substrates were mounted on a home-made stainless steel oven, positioned at 40 mm from the targets, in the place where the two ablation plasmas intersect with each other. Various kinds of substrates were used (Si, SiO_2, glass) to investigate their influence on the sensing characteristics of the films.

The ZnO film growth was performed for oxygen pressures (in flow) between 10 and 20 Pa, measured by a Baratron gauge. The substrate temperature was varied in the range 200–400 °C. Almost 43 000 laser pulses were used for the ZnO film growth and the ArF fluence on the Zn target was measured at 4.8 and 9.6 J/cm^2 while the Nd:YAG laser fluence for the Al dopants was measured to be 1.8 J/cm^2. This resulted in a film thickness of the order of 220–250 nm (measured by a Tencor profilometer). For the Au dopants, the target irradiation was performed after the ZnO film deposition. The Au targets were irradiated by 3600 laser pulses with a fluence value of 2.4 J/cm^2. This resulted in a smooth coverage of the ZnO surface with Au nanoclusters, thus increasing the effective film surface and working as promoters for a more efficient gas sensing. Therefore, the methods employed above allowed the on-line control of the degree of the film doping or film surface coverage by just changing the laser parameters.

2.2. Electrical measurements

The sensing properties were tested using a set-up comprising a stainless steel tube of approximately 1 litre with an inlet and outlet for the gases tested, in order to measure the gas sensing response of the ZnO sensing films. After injecting the gas into the tube, the resistance versus time for the samples was measured by changing the samples' temperature. The sample was placed on an appropriate holder with a copper heater resistance, capable of reaching temperatures up to 400 °C and controlled with an accuracy of ±1 °C. A platinum resistor as a temperature sensor and four mechanical point contacts for the measurements of the thin film resistance were used. Tests were made under H_2 mixed with air or N_2 (carrier gas) before reaching the tube inlet. The gas flows were controlled with two calibrated flowmeters and fed into an injection point located below the sample holder. The electronic circuit for resistance determination consisted of a current source (Keithley Model 225) and a digital multimeter (Agilent 34401A). For the control of the samples' temperature an ITC-502 (Oxford Instruments) controller was used. The sensitivity (relative response) of the sensing films is determined from the formula

$$S = \frac{R_O - R_g}{R_O}$$

where R_O is the film resistance at ambient temperature and R_g is the film resistance in the gas atmosphere. The R_{Hall} coefficients were measured under a magnetic field of 0.4 T.

Table 1
Measured parameters of the thin films

Sample code number	130104	110104	310104	300104	290104	190504-2	130504	190504-1
Dopants	Al	Al	–	–	–	–	–	–
Substrate type	Si	Si	Si	Si	Si	Si	SiO_2	glass
Laser fluence (J/cm^2)	4.8	4.8	4.8	4.8	4.8	9.6	9.6	9.6
Deposition temperature (°C)	400	300	300	300	200	200	200	200
Pressure of O_2 (Pa)	20	20	10	20	20	20	20	20
Working temperature (°C)	180	180	180	180	180	180	180	180
Relative response (max) S_{max} (%)	2	28	1	11	22	45	97	98.5
Response time t_{rs} (min)	11	12.8	11.3	10.7	13	10.4	3.1	2.2
Recovery time t_{rc} (min)	3.7	8.2	2.5	2.7	11	4.9	3	7.2

3. Results and discussion

The goal of our paper was first reached through the optimization of the deposition parameters such as laser fluence, O_2 pressure and substrate temperature.

The first step was the study of resistance dynamic response of the n-ZnO undoped sensing films deposited at $T = 300\,°C$ for various laser fluences under H_2 (3%) in air ambience. The above-mentioned results are summarized in Table 1. The best result was obtained for 9.6 J/cm^2 and this value has been utilized for all the other depositions. The same cycle: depositions and dynamic response measurements, was repeated using the above laser fluence value for various O_2 pressures. The best response results were obtained for O_2 pressure of 20 Pa. The third step was the choice of the deposition temperature keeping the above two parameters constant. In this case the optimal sensitivity properties were obtained for the sample deposited at 200 °C.

Fig. 2 shows the XRD patterns of ZnO sensing films deposited on (100) Si at temperatures between 200 and 400 °C. The preferred orientation to the *c*-axis (002) is observed for all temperatures as a basic characteristic of ZnO structure [11]. Increasing the deposition temperature from 200 to 400 °C, the peak intensity increases corresponding to the increase of the crystalline size. This means that the ZnO thin films deposited at 200 °C exhibit the lowest crystallinity. From the full width at the peak's half-maximum of the XRD spectra the average crystallite sizes *D* were obtained using the Scherrer formula [12]. The effect of the grain size reduction with the decrease of the temperature results in a high porosity of the sensing ZnO thin films. This means that the diffusion of H_2 and the reaction inside the ZnO thin films are strongly assisted by the high active area per unit volume of the porous thin films. This explanation is confirmed by the optimum sensing properties of the films deposited at 200 °C (Table 1).

Further experiments were carried out to investigate the influence of the substrate type and dopants on the sensing properties of the optimized ZnO films. The H_2 sensing characteristics of the ZnO thin films can be improved drastically by using non-crystalline substrates such as SiO_2 and glass instead of single-crystal Si. As is shown in Table 1 the maximum sensitivity of undoped ZnO thin films, deposited on SiO_2 and glass substrates at 200 °C, is about 97% at a working temperature of 180 °C, with response and recovery times of about 3 min. A comparison of the dynamic response characteristics for ZnO thin

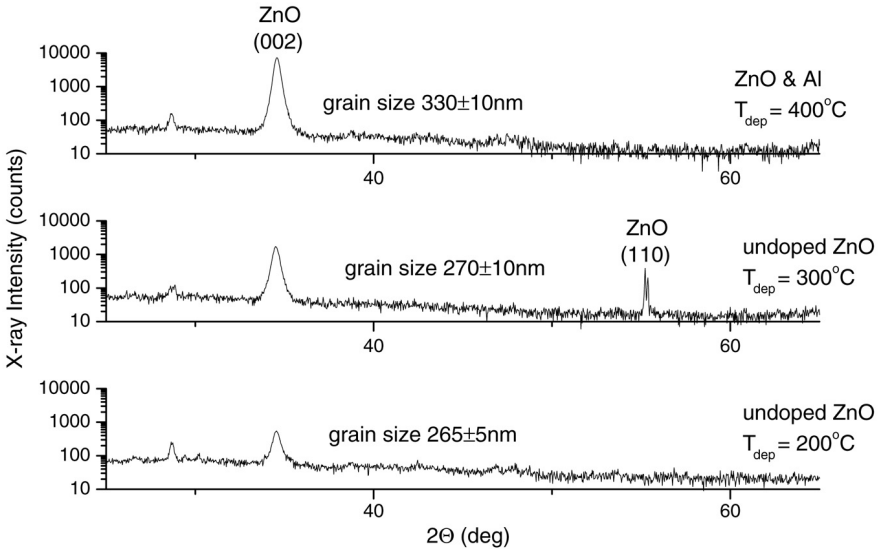

Fig. 2. XRD patterns of ZnO thin films on Si substrates for various deposition temperatures.

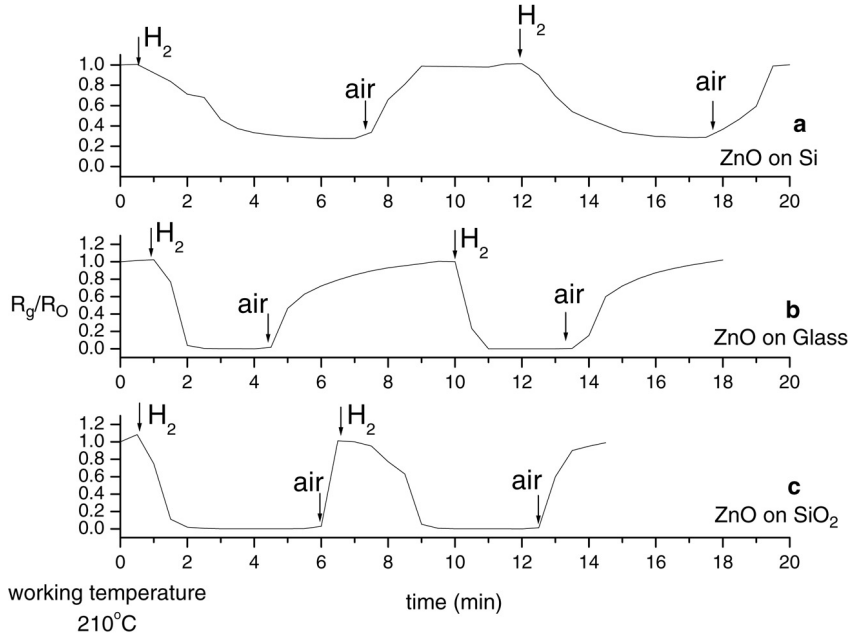

Fig. 3. Comparison of dynamic response characteristics for ZnO thin films deposited on various substrates at 210 °C.

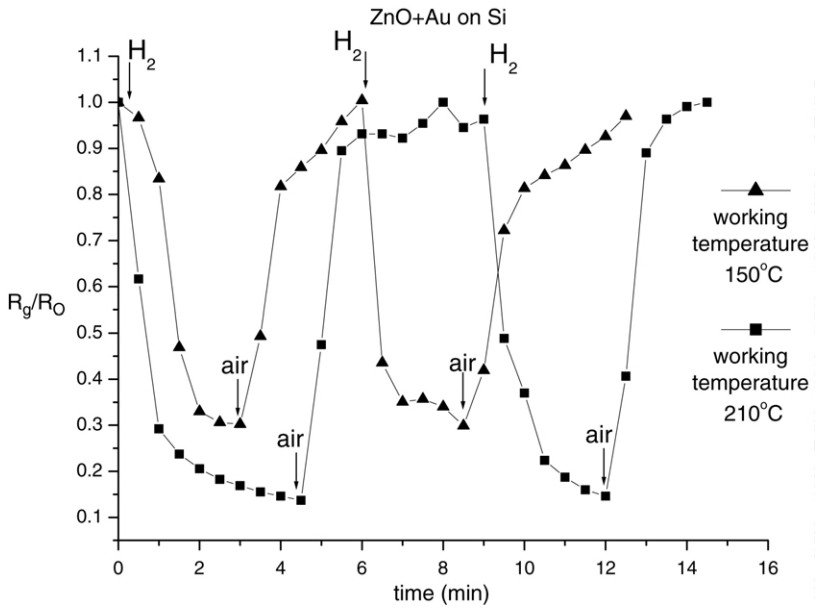

Fig. 4a. Comparison of dynamic responses of Au sensitized ZnO thin films on Si substrates at working temperatures of 210 and 150 °C.

films deposited on the three substrates at 210 °C is shown in Fig. 3. It is noticeable that the sensing parameters of the ZnO thin films on SiO_2 exhibit a very good stability and reproducibility in the temperature range of 150–210 °C, while the films deposited on glass sustain a sufficient stability at working temperatures 210 °C (Fig. 3). The low crystallinity of ZnO thin films caused by the influence of the amorphous or non-crystalline substrates, having high surface area per unit volume, is probably responsible for the improvement of the sensing properties of these films in comparison with the properties of the films deposited on single-crystal Si.

A high sensitization of ZnO thin films in H_2 mixture air was realized by deposition of Au nanoclusters on the surface of the films. The sensitivity (S_{max}) of the ZnO thin films deposited on SiO_2 was increased from 48% for unsensitized ZnO to about 99% for Au sensitized ZnO at the working temperature 150 °C (Fig. 4b). A large improvement is also observed in the response and recovery times. The response time decreases from 12.5 to 0.8 min and the recovery time from 9.5 to 4 min for unsensitized and sensitized films respectively. Sensitized ZnO films deposited on single-crystal Si substrate also exhibited enhanced sensing properties in comparison to the unsensitized ones at higher optimum working temperature (Fig. 4a). The enhanced sensing properties exhibited by the Au sensitized ZnO films could be explained by the action of Au as a catalyst in the mechanism of sensing H_2 at 150 °C [2]. This mechanism is probably assisted by the formation of reactive species consisting of atomic H and Au.

From the electrical resistivity results for the ZnO films it follows that the high resistivity values are consistent with good H_2 sensing properties, while the low resistivity results are

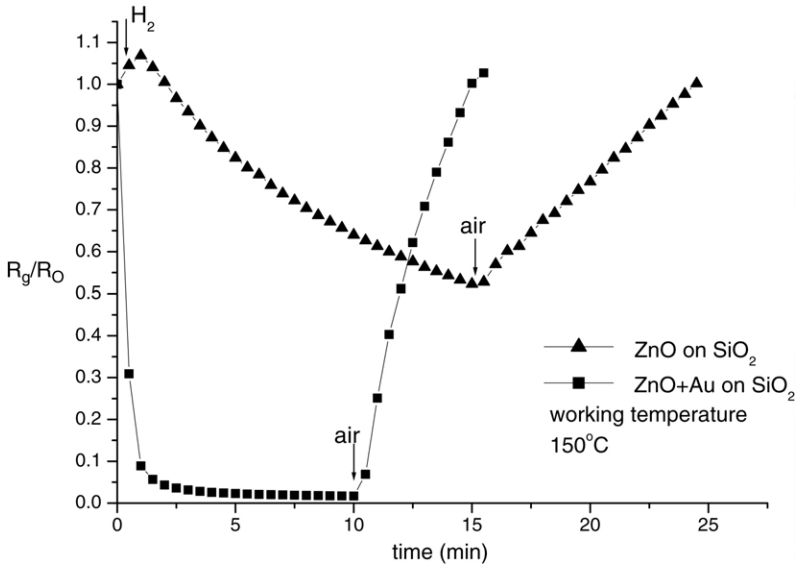

Fig. 4b. Dynamic response characteristics of Au sensitized and unsensitized ZnO thin films on SiO_2 at the working temperature 150 °C.

consistent with very poor sensing properties of the films. For example, ZnO films on SiO_2, with $\rho = 12$ Ωcm, exhibit a sensitivity of 97% at 210 °C while Al doped ZnO films, with $\rho = 0.002$ Ωcm, present very poor sensing properties. This behaviour can be explained by the grain size effect on the electrical properties of the films described before.

4. Conclusion

A PLD technique using two targets and two lasers allows on-line control of deposition parameters and is a suitable method for growth of ZnO thin films exhibiting optimal H_2 sensing properties. From the dynamic response measurements it follows that undoped n-ZnO thin films, deposited on a cheap and Si compatible substrate such as SiO_2, exhibit optimal sensing properties at 180 °C. This working temperature decreases to 150 °C after surface sensitization of the above films with Au nanoclusters.

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