Electrical characterization of In-N codoped p-type ZnO films grown by chemical methods

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Abstract. Preliminary results of the studies of electrical properties of ZnO films, codoped with donor and acceptor pair In-N are reported. The films were grown on Si substrates by chemical route procedures involving a sol-gel followed by hydrothermal treatment at 500°C. For electrical characterization, current-voltage and capacitance-voltage measurements were conducted on MIS structures with embedded ZnO(In,N) films. The estimated doping concentration in the studied films is higher than 1x10^{16} cm^{-3} corresponding to a semiconductor with good conductivity. However, the obtained large values of the differential specific resistivity (\rho = 3.2x10^5\ \Omega cm) suggest that the nitrogen acceptors in these films are compensated by some kind of donor-type defects.

1. Introduction
Zinc oxide is a transition metal oxide semiconductor with wide band gap (3.37 eV) and large exciton binding energy (~60 mV), good transparency, high electron mobility and strong room-temperature luminescence [1-3]. These properties determine its feasibility in emerging applications for transparent electrodes in liquid crystal displays, in energy-saving or heat-protecting windows, and in electronics as thin-film transistors and light-emitting diodes [3-5].

Zinc oxide can be obtained in a large variety of morphologies, function of the deposition method and technological conditions [6]. Among these, we count vapor-phase deposition [7], pulsed laser deposition [8], or metallic-organic chemical vapor deposition [9]. However, physical deposition techniques have a series of disadvantages such as complex equipment and process, as well as involving higher temperatures. Chemical methods for obtaining thin films such as chemical bath deposition [10-12] or sol-gel method [13] are more accessible, economical and can be more easily upscaled to industry [14]. The use of a ZnO seed layer, especially when promoting 1D formations, is well documented in the literature [15, 16] and promotes the nucleation and subsequent growth of continuous, homogenous ZnO films [17].

While ZnO as a material has been widely investigated, the current trend is the obtaining of p-type conduction through different doping mechanisms [18,19]. This may prove difficult due to the self
compensating effect, deep acceptor level and low solubility of acceptor dopant ions [4]. Codoping with a donor-acceptor pair (group III - group IV metal ions) has been reported to lead to p-type conduction in ZnO, with improved electrical properties as compared to monodoping [20].

In this work we report preliminary results of the studies of electrical properties of ZnO films, codoped with donor and acceptor pair In-N, further denoted as ZnO(In,N) films, grown by chemical route procedures involving a sol-gel and a hydrothermal chemical procedure. For electrical characterization, MIS structures with embedded ZnO(In,N) films were prepared and from their current-voltage (I-V) and capacitance-voltage (C-V) characteristics electrical parameters such as conductivity, mobility, carrier and doping concentrations were estimated and compared with Hall measurement data.

2. Experimental details
The studied ZnO(In,N) films were deposited on single-crystal p-type Si substrates (with specific resistivity of 19-29 Ω·cm), by applying a chemical method in two steps.

The first stage is aimed at obtaining an undoped ZnO seed player through dipping the substrates in a 0.5 M solution of zinc acetate dihydrate [Zn(CH₃COO)₂·2H₂O] in ethanol, to which triethanolamine was added as chelating agent. The seed layer was thermally treated at 400°C for 1 hour.

The second stage consisted of the hydrothermal deposition of the codoped layer. For this purpose, an aqueous solution (0.05 M) of zinc nitrate tetrahydrate [Zn(NO₃)₂·4H₂O] and hexamethylene-tetramine [(CH₂)₆N₄] with a ratio of 2:1 was prepared. In order to obtain 1 at. % indium concentration in the film, indium nitrate [In(NO₃)₃] was added to this solution. The resulted solution was treated at 90°C for 2 hours in a teflon autoclave. Finally, the codoped ZnO films were cleaned with hot water, dried at room temperature and subjected to heat treatment at 500°C for 1 hour in air. After the final technological step the film thickness was approximately 150 nm, as determined from ellipsometry.

For the electrical measurements, MIS structures with the ZnO(In,N) films were formed by vacuum evaporation of Al contacts, as on the film surface Al dots (contact area S=2.8x10⁻³ cm²) were deposited through a metal mask while continuous Al film was deposited on the Si wafer backside. The room temperature current-voltage (I-V) characteristics were measured with a cycle sequence beginning from 0 V toward negative or positive voltages applied to the Al-dot contact on the film surface followed by a voltage reversal toward zero applied voltage. The room temperature 1 MHz capacitance-voltage (C-V) measurements were carried out by a digital LCR meter E7-12.

Room temperature Hall effect measurements were done using the van der Pauw method, on a HMS-5000 equipment from Ecopia.

Spectroscopic ellipsometry (SE) measurements were performed by VASE-Woollam equipment at an angle of incidence of 70°, with 5 nm step, in the UV-VIS-NIR spectral range at room temperature.

3. Results and discussion
Typical I-V characteristics of a MIS structure with ZnO(In,N) film is shown in figure 1. When negative voltage is applied to Al-dot contact on the film surface the current is several times higher than that measured when positive voltage is applied.

At high negative voltages the current density is 50-60 times higher than that for positive voltages with the same magnitude. As the Si substrate is p-type, such current behavior is a direct evidence of the appearance of p⁺ - p junction at the ZnO(In,N) - Si interface. At negative voltages a hysteresis is observed because the current at given negative voltages is predominantly higher during voltage sweep toward the zero voltage in comparison with the current during the voltage sweep from zero to negative voltages. Furthermore, when the applied voltage describes a sweep from zero to highest voltage and back to zero, a residual current continues to flow with different time-constants and diminishing amplitude for several hours. These observations show that during the current flow some of holes are captured at deep levels in the ZnO(In,N) film and their release interferes with the current in the subsequent voltage sweep.
The specific resistivity $\rho$ of $3.2\times 10^5\ \Omega \text{cm}$ for ZnO(In,N) film is calculated from the I-V characteristics (figure 1) at negative voltages corresponding to an electric field of $10^6\ \text{V/cm}$.

The charge density can be estimated from the capacitance values in the depletion region (from -5 to 0 V) of the C-V characteristics. By measuring several MIS structures using Al-dot contacts at different places on the film surface a non-homogenous charge distribution in the film bulk was observed, resulted in different shape and capacitance values. This is illustrated in the inset in figure 2.

Replotting the C-V curves from figure 2 as $S^2/C^2$ versus applied voltage in the depletion region (not shown here), the density of acceptor charge $N_A$ can be calculated from the slope $B$ of the linear part.
of this dependence:

\[ B = \frac{2}{(qN_A \varepsilon_{ZnO})} \]  

(1)

where \( q \) is the electric charge (\( q = 1.6021 \times 10^{-19} \) C) and \( \varepsilon_{ZnO} \) is the dielectric permittivity of the film.

The density of acceptor charge obtained in depletion region close to 0 V in “+down” sweep direction is in the range of \( 10^{14} – 10^{15} \) cm\(^{-3} \) as it can be expected for Si substrates with specific resistivity in the 19-29 Ωcm range. For the depletion region near -5 V in “-down” sweep direction, the charge density value is above \( 10^{16} \) cm\(^{-3} \). As this value is determined by the charge of diffused holes from the film, i.e. from the p\(^+\) side of the p\(^+\) - p (ZnO-Si) junction, its value can be used for an estimation of net acceptor concentration, \( N_A \), in the ZnO(In,N) film. Therefore, the p-type doping level in the ZnO(In,N) film is in the order of \( 10^{16} – 10^{17} \) cm\(^{-3} \). Taking into account this net acceptor concentration (~ \( 2 \times 10^{16} \) cm\(^{-3} \)), the effective hole mobility in these ZnO films is estimated to be 9.83x10\(^{-4} \) cm\(^2\)V\(^{-1}\)s\(^{-1}\). Such low mobility values are a consequence of some kind of hopping conductivity via deep levels in semiconductor materials. Moreover, since the I-V characteristics revealed a high resistivity ZnO(In,N) film (\( \rho = 3.2 \times 10^5 \) Ωcm), it suggests that the nitrogen acceptors in the film are compensated by some kind of donor defects. As it has been shown, the use of a combined sol-gel and hydrothermal deposition method leads to the formation of randomly oriented ZnO nanorods [21, 22]. This could contribute to the low mobility most likely due to interface scattering between 1D structures.

From figure 2 it is seen that there is a hysteresis making a whole voltage sweep cycle and thus, the zero voltage capacitance values are different for negative and positive sweep directions. This effect is caused by carriers being captured at deep traps in the film. While remaining at zero voltage position, the return of the capacitance value to its initial level requires prolonged time, which is an indication of large time constants of these traps. Because of that, several hours are needed for complete discharging of the traps. This is partly illustrated in figure 3, where discharge of the deep levels with time after removing the applied voltage is given. From this plot it is evident that the release of captured charges in the ZnO film takes place with different time-constants in the order of minutes.

![Figure 3. Discharging of deep levels in time, at zero voltage.](image-url)

For a comprehensive electrical study of the codoped films, Hall effect measurement was also attempted. In order to avoid the influence of silicon substrate on the results, we have deposited a ZnO(In,N) film on glass substrate using the same chemical procedure parameters. The film thickness obtained was approximately 290 nm.
The Hall effect measurement has confirmed good semiconducting properties of the ZnO film, while also exhibiting p-type conduction. The p-type characteristic of the ZnO(In,N) film was proved by the positive sign of the Hall coefficient ($R_H = +29.7 \text{ cm}^3\text{C}^{-1}$). A high carrier concentration of $2.1 \times 10^{17} \text{cm}^{-3}$ was determined, which is well correlated with the value of $10^{16} - 10^{17} \text{cm}^{-3}$ obtained through C-V analysis. The resistivity was determined to be $1.8 \times 10^2 \Omega\text{cm}$ which is comparable to values reported in the literature for Hall effect measurement [23]. From this, a mobility of $0.2 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ is obtained. In contrary to that, the analysis of the I-V and C-V characteristics revealed hole mobility values in ZnO(In,N) films with approximately two orders of magnitude lower and resistivity values with three orders of magnitude higher than those from the Hall effect measurements. These differences could be attributed to the different method principles: during the Hall measurement the current flows parallel to the film surface between 4 contact points, while at the I-V and C-V measurements the current is perpendicular to the Al-dot area, as it flows through the p-type ZnO/p-type Si structure. Since non-homogenous charge distribution in the film bulk is registered (figure 2), this may lead also to different values for the same parameter as determined through the different techniques. Furthermore, as was discussed above, during I-V measurements holes are trapped in ZnO(In,N) film creating an internal electric field which decreases the external electric field of the applied voltage and, thus decreases the effective mobility. The establishment of real causes of the observed discrepancy needs further investigations.

4. Conclusions
It has been established that codoping with In and N of ZnO films and using the combined sol-gel and hydrothermal deposition method for film deposition yields a comparatively high net acceptor concentration of the order of $10^{16}-10^{17} \text{cm}^{-3}$. By I-V and C-V measurements, deep levels are registered in the investigated ZnO(In,N) films. Because of these deep levels the effective mobility of holes in these films is low and it is in the order of $10^{-3} \text{cm}^2\text{V}^{-1}\text{s}^{-1}$. Hall effect measurements have confirmed the p-type conduction of the film. While carrier concentration values were similar, resistivity and mobility determined through the two methods differed, due to the method principle of measurement. Thus, a non-homogeneous carrier distribution in the film was evidenced.

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