

Transparent, high mobility InGaZnO thin films deposited by PLD

Arun Suresh, Praveen Gollakota, Patrick Wellenius, Anuj Dhawan, John F. Muth*

Department of Electrical and Computer Engineering, North Carolina State University Raleigh, NC 27606, USA

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Abstract

Transparent oxide semiconductor, InGaZnO, thin films were prepared by pulsed laser deposition at room temperature. The carrier concentration was found to vary by several orders of magnitude from insulating to 10^{19} carriers/cm³ depending on the oxygen partial pressure during deposition. Hall mobilities as high as 16 cm²/V s were observed. This is approximately an order of magnitude higher than the mobility of amorphous silicon and indicates that InGaO₃(ZnO)_x with $x \leq 5$ may be suitable for transparent, thin film transistor applications. Post-deposition annealing was found to strongly influence the carrier concentration while annealing effects on the electron mobility was less influential.

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1. Introduction

High performance electronic devices such as microprocessors and power transistors rely on crystalline materials because of their superior electronic properties. However, there are numerous niche applications where the speed or power performance of the transistor is not the key parameter. In applications such as liquid crystal displays, uniform deposition of materials over large areas using scalable technologies such as sputtering is necessary. For displays to be integrated into the windshields of automobiles or airplanes it would be advantageous for the materials to be transparent. In flexible electronic applications, such as displays that can be rolled up or folded, the durability of the material and its ability to accommodate large strains are the key parameters. In flexible electronics it is also usually important to develop low-temperature processes to be compatible with the polymer substrate.

While there have been significant advances in flexible polymer electronics that show promise, the workhorse material for thin film transistors for these types of applications has been amorphous silicon. However, both the polymer-based materials such as pentacene [1] and amorphous silicon [2] have low

mobilities of less than 1 cm²/V s which limit the transistor's performance. In general, low mobilities are typical of amorphous materials because the conduction occurs via an electron hopping mechanism. Recently, advances in amorphous oxide semiconductors (AOS) by Takagi et al. and Nomura et al. [3,4] have shown that significantly higher mobilities on the order of ~ 10 cm²/V s can be obtained; furthermore, these materials can be transparent throughout the visible spectrum.

The origin of high mobilities of AOS semiconductors is believed to be the result of the overlap of spherical *s*-orbitals of the heavy metal cations with $(n-1)d^{10}ns^0$ ($n \geq 4$) electronic configurations [5–7]. Various transparent semiconductors using the above scheme have been reported, including AgSbO₃ [8], Cd₂GeO₄, [9], Cd₂PbO₄ [10,11], indium tin oxide [12], indium oxide [13], zinc indium oxide [14,15], zinc tin oxide [16,17], and zinc rhodium oxide [18,19].

AOS films based on ternary–quaternary oxides in the In₂O₃–Ga₂O₃–ZnO system have several advantages over other AOS materials including low toxicity, and higher observed electron mobilities. The use of a multi-component system helps ensure that the films remain amorphous under conventional processing conditions [5,17]. In this study, InGaO₃(ZnO)_x-based, highly transparent and *n*-type electrically conductive films were deposited at room temperature, using pulsed laser deposition (PLD). The oxygen ambient in the chamber was used to control

* Corresponding author.

E-mail address: muth@ncsu.edu (J.F. Muth).

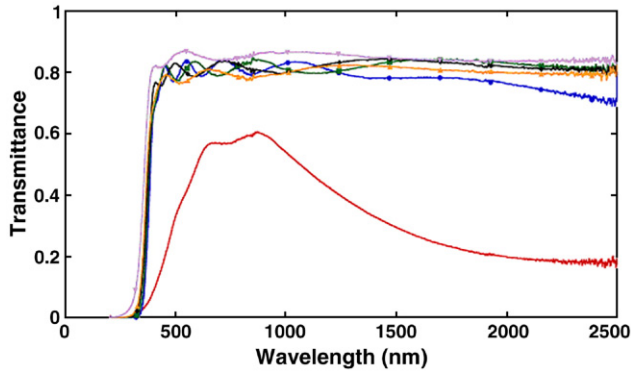


Fig. 1. Optical transmission spectrum of the IGZO films deposited at various oxygen partial pressures. Note that the optical absorption edge blue shifts with increasing oxygen partial pressure and that the transmission decreases with decreasing oxygen partial pressure as the conductivity increases. Pressures were (–) 5.8×10^{-4} mTorr, (●) 5 mTorr, (■) 10 mTorr, (◆) 20 mTorr, (▲) 40 mTorr and (▼) 80 mTorr.

the conductivity over several orders of magnitude. Post-deposition annealing studies showed that conductivity can also be controlled by oxygen diffusion into the film.

2. Experimental

The $\text{InGaO}_3(\text{ZnO})_5$ ablation targets were prepared by mixing In_2O_3 , Ga_2O_3 and ZnO powders in a 1:1:10 molar ratio and then compressed under 5000 psi at room temperature to form a disc. The compressed disc was then sintered for 9 h at 1250 °C to increase its hardness.

Pulsed laser deposition (PLD) was used to deposit uniform IGZO films at room temperature in an oxygen ambient by ablating material from the prepared target. The oxygen partial pressure was varied between vacuum and 80 mTorr. Oxygen gas flow is regulated by a mass flow controller while a variable-position gate valve maintains the desired chamber pressure. A KrF excimer laser, operating at 248 nm, 10 Hz and with a power of up to 4 J/cm^2 per pulse, was used for target ablation.

The structure of the films was studied by θ – 2θ and glancing angle X-ray diffraction. The film composition was studied using

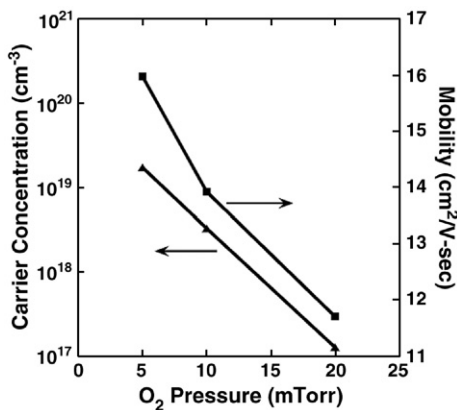


Fig. 2. Carrier concentration and Hall mobility measurements as a function of oxygen partial pressure during film growth.

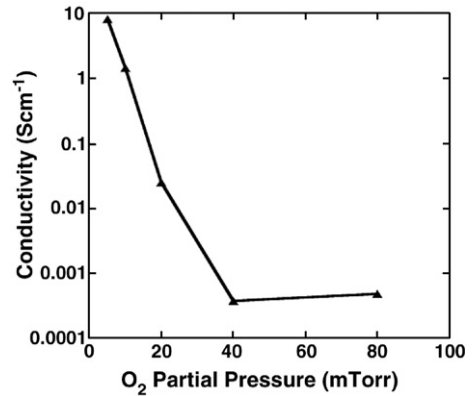


Fig. 3. Conductivity of IGZO films as a function of oxygen partial pressure during film growth.

the XPS technique. Hall mobility and carrier concentration were measured at room temperature using the Van der Pauw configuration at magnetic fields of 0.5 T. Conductivity measurements were carried out using a four-point probe stand, equipped with rounded osmium tips, spaced 1 mm apart. Post-deposition annealing studies were carried out by annealing the samples in air on a temperature-controlled hot plate.

3. Results

The room temperature deposited $\text{InGaO}_3(\text{ZnO})_5$ films when studied using the θ – 2θ X-ray showed only the peaks corresponding to the (0006) and (00012) crystal planes from the sapphire substrate. Glancing angle X-ray using a Phillips Xpert MRD triple axis diffractometer with a high intensity X-ray source option and Ge [220] crystal in a double bounce configuration was performed to remove the influence of the substrate and used to investigate the possibility of nanocrystallites. Initially no secondary peaks were observed, but when the instrument configuration was altered to remove Ge [220] crystal to obtain an open detector geometry relatively low intensity crystalline peaks appeared. The broad width of these

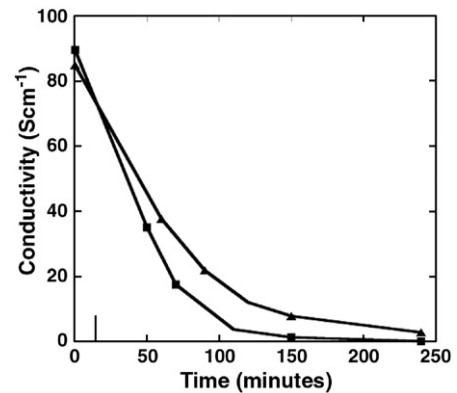


Fig. 4. Effect of post-deposition annealing in air on electrical conductivity as a function of time for two different temperatures, (▲) 175 °C and (■) 200 °C.

peaks indicated the possible presence of nanocrystallites in the 5- to 10-nm diameter range. Further X-ray and TEM studies are planned to investigate the structural properties of the films.

One potential complication of the pulsed laser deposition in the reactive oxygen atmosphere is that the fluctuations in the composition of the films can be influenced by the oxygen partial pressure. A set of XPS studies on the films deposited at various oxygen partial pressures showed that in the films, indium to gallium ratio was closer to 1:1.5 than to 1:1 and the indium to gallium ratio decreased slightly with increased oxygen partial pressure. Due to the low melting point of indium the target preparation process likely produced an indium-deficient target. However, the stoichiometric relationship of deposited films as a function of oxygen partial pressure appears to be complicated and dependent on deposition conditions.

The optical quality of the films was high, with optical transmission for films deposited on double side polished sapphire substrates greater than 80% through out the visible spectrum. As shown in the transmission spectra presented in Fig. 1, distinct interference fringes were also observed indicating smooth films with little scatter and a relatively sharp optical absorption edge near 345 nm for the film grown at 20 mTorr. The positions of the optical edges of all of the films grown were blue shifted with respect to the optical edge of single crystal ZnO. The optical quality and conductivity of the films correlate with the oxygen partial pressure of deposition, with more conductive films having more near infrared absorption. The optical band edge or Tauc gap of the films also shifted to the red with films deposited at lower oxygen partial pressures. However, it is interesting to note that with the exception of the film deposited in vacuum, the optical band edge remains relatively sharp. The increase of the absorption edge energy with increasing oxygen partial pressure may partially be due to the decreasing indium to gallium ratio that was observed by XPS. However, the filling of absorptive defect states with oxygen under increased oxygen partial pressure may also have an influence.

The carrier concentration of the films, shown in Fig. 2, was found to vary strongly with the oxygen partial pressure during deposition and was found to be *n*-type in agreement with Takagi et al. [3]. The film grown in vacuum was found to be metallic in nature with a carrier concentration of $\sim 10^{20}$ but with lower mobilities ($3\text{--}4\text{ cm}^2/\text{V s}$) than films grown in an oxygen partial pressure. For semiconducting films grown between 5 and 80 mTorr the conductivity decreased consistently with increasing partial pressure of oxygen as shown in Fig. 3. The Hall mobility and carrier concentration of films deposited at pressures greater than 20 mTorr were hard to measure accurately due to the limitations of our Hall measurement system with respect to high resistivity materials. By extrapolation, it is assumed that the carrier concentration for the insulating films was in the $10^{14}\text{--}10^{15}$ carriers/cm³ range. The Hall mobility was found to be highest for films deposited at 5 mTorr with a value of $16\text{ cm}^2/\text{V s}$ and decreased to $11\text{ cm}^2/\text{V s}$ for films deposited at 20 mTorr. For the 40 mTorr and 80 mTorr films the high resistivity of the films prevented the Hall mobility to be measured with suitable precision.

A preliminary post-deposition annealing study was carried out using films deposited at 5 mTorr to study the effect of oxygen diffusion on the conductivity and mobility of the films. It was found at relatively low temperatures that the conductivity could be decreased by about 4 orders of magnitude as shown in Fig. 4. While the conductivity of the films changes dramatically with annealing, the Hall mobility does not change considerably.

Preliminary cathodoluminescence and photoconductivity studies were also carried out. When exposed to visible light, no photoconductive response was readily observed in the conductive films. Similarly, these transparent conductive films did not luminesce under electron beam excitation.

4. Conclusion

High optical quality, high mobility, transparent InGaO₃(ZnO)₅ films have been deposited by PLD at room temperature. The electronic properties of the films were found to be controllable by varying the partial pressure of oxygen in the deposition chamber. The mobility demonstrated by these experiments compares favorably with amorphous oxide semiconductors and is over an order of magnitude higher than that of amorphous silicon. The conductivity of the films was also controllable by post-deposition annealing. Optically, the deposited films were all highly transparent throughout the visible region and into the near-infrared. Films also demonstrated minimal optical response. These films have demonstrated excellent electronic and optical qualities, making InGaO₃(ZnO)_x a very interesting material for the fabrication of assorted, transparent electronics.

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