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*Dedicated to Professor Ioan-Iovitz Popescu's 80th Anniversary*

# DOPED ZINC OXIDE THIN FILMS AS TRANSPARENT CONDUCTIVE ELECTRODES

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*Abstract*. Sn doped ZnO thin films have been deposited on c-cut sapphire single crystal substrates at 200°C by pulsed electron beam deposition. The kinetic energies of the ions in the plasma plume–determined from ion probe measurements, present a relatively broad distribution of the energies from a few eV to one hundred eV. Sn doped ZnO films have a graded composition, with a slightly in-depth variation of Sn. The transmittance of the films was about 87% in the visible wavelength range. The resistivity was 0.4 Ωcm at room temperature and showed a classical semiconductor behavior with the temperature.

*Key words*: doped zinc oxide, thin films, pulsed electron beam deposition, channel-spark.

## 1. INTRODUCTION

The 2012 low-temperature plasma science and technology roadmap has shown that real-time control and monitoring of plasma deposition processes are becoming increasingly important to achieve precise control of deposited thin films [1]. Up to now, thin films have been fulfilled a simply main function as requested by applications. Future thin films should fulfill more specifications simultaneously and therefore they will be multi-functional, allowing fabrication of functional devices. A typical example is thin films of transparent conducting oxide (TCO) which have to present both high optical transparency and high electrical conductivity in view of numerous applications [2]. This new challenge will require the development of original approaches for materials processing simultaneously with the knowledge of fundamental physics mechanisms governing plasma deposition [3, 4].

Pulsed electron beam sources were developed in order to find a cheaper alternative to pulsed laser deposition [5–11]. In particular, the channel-spark discharge [8] was successfully used to grow thin films due to its specific features:

(i) the presence of a capillary tube in which the electron beam is produced and guided from the anode to the target and (ii) an energy per beam pulse enough for target ablation [8–11]. This method based on the channel-spark discharge was named "Pulsed electron beam deposition" (PED) [11].

PED presents some advantages [10] for the formation of polycationic oxide thin films and thus it has been used for the growth of TCOs films presenting the properties of the bulk materials needed for the development of the "transparent electronics". Pure or doped Sn or In oxide films were thus grown by PED [11–13], with potential interesting properties for applications.

The growth of zinc oxide films by PED was also studied and it was shown that PED allows the growth of amorphous, polycrystalline or epitaxial thin films by controlling the substrate temperature and deposition conditions [14–18]. Epitaxial ZnO thin films have been grown by PED on c-cut single crystal substrates even at low substrate temperature (300°C) [16], with the classical epitaxial relationships observed in PLD [17]. It has been demonstrated that in PED the physical properties of ZnO films could be tuned by controlling deposition conditions, *i.e.* by controlling the oxygen composition and crystalline quality of the films. Indeed, semiconducting films [18] can be obtained as well as films presenting a metallic-like conductivity at room temperature and a metal-semiconductor transition to lower temperatures [18].

These results are related to the specificities of the PED deposition method, in particular to the high energies (a few eV to tens of eV) of the plasma plume species, which allow growing oxide thin films with different functionalities. Moreover, doping an oxide with an element it is possible to change some properties or to induce a new one. With this aim, in this work we report on the growth of Sn doped ZnO thin films by PED using a sectorial target. The plasma plume was investigated using an ion probe to estimate the kinetic energies of the species arriving on the substrate. The oxide film composition and morphology were determined and the physical properties of these films were studied, in order to evaluate the potential of PED to form doped ZnO films presenting the expected characteristics for applications as transparent conductive electrodes.

## 2. EXPERIMENTAL SET-UP

In the PED method a pulsed electron beam is produced in a channel-spark discharge [10]. Briefly, an external capacitor (16 nF) charged at 15.5 kV is discharged between a hollow cathode and a grounded anode (the vacuum chamber), through a capillary tube of 6 mm diameter and 110 mm length. A pulsed electron beam is produced having about 100 ns FWHM and a fluence of about 2.5 J/cm$^2$, with a repetition rate of 1–2 Hz. The pulsed electron beam is polyenergetic with electron energies in the range 0–15.5 keV [10].

The thin film growth was performed under controlled Ar gas at a $1.4 \times 10^{-2}$ mbar pressure, and at 45° angle of incidence between the beam and the rotating target. A sectored target [19] was made from a ZnO target with a sector of 2 mm width of thin Sn plate placed radially on its surface. The target-substrate distance was 40 mm.

Sn doped ZnO thin films were grown on Si and c-cut sapphire single crystal substrates at substrate temperatures between room temperature and 200°C. The energy of the ablated species was measured with an ion probe in the position of substrate holder. The thickness and composition of the films were measured by Rutherford Backscattering Spectrometry (RBS) using the $^4He^+$ ion beam of the 2 MeV Van der Graaff accelerator (INSP, Université Paris 6). The thickness, composition and in depth distribution of elements were obtained by RUMP simulations [20]. The surface morphology of films was investigated by Scanning Electron Microscopy measurements. The electrical resistivity of thin films was performed by the four probe method, from room temperature to liquid helium [21].

## 3. RESULTS AND DISCUSSIONS

In the PED method the pulsed electron beam interaction with the target leads to the vaporisation of the target material and the formation of a plasma plume, which propagates in a direction normal to the target, forming a film on the substrate. Optical emission spectroscopy and fast imaging of the plasma plume [22] proved that the composition of the emissive species is similar with the one obtained with nanosecond pulsed laser deposition, but with the particularity that the electron beam ablation induces a higher ionization of the plume and background gas than in the case of PLD.

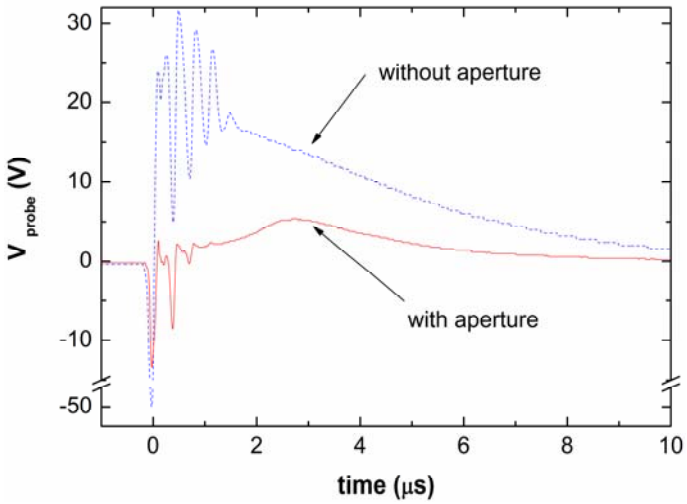


Fig. 1 – Ion probe signals recorded without aperture (dashed line) and with 1mm aperture (solid line).

In this work the ion energies in the plume were measured using a 4 mm planar Langmuir probe. The recorded signal is shown in Fig. 1 and corresponds to the contribution of the plasma plume and background plasma. When a 1 mm aperture connected to the ground was placed in front of the Langmuir probe, the contribution of the Ar plasma to the signal was eliminated, and ions from the ablation plasma moving perpendicularly to the probe were solely collected. As a result, a typical signal of the Zn and Sn ions ablated from the sectorial target for a probe bias to –24 V is shown in Fig. 2. The ion energies were calculated using the time of flight method. The time zero is given by the negative signal due to the high energy (a few keV) electrons scattered on the target which reach the probe in a very short time compared to the ion time of flight [23]. The ion signal has a maximum at 2.8 μs, corresponding to a velocity of the Zn and Sn ions of 1.32 cm/μs.

The Zn and Sn ions signals are separated in our measurements due to their different atomic mass values only when the target is not rotating. A signal was recorded when the beam interacted with the ZnO target (solid line in Fig. 2) and a second one for the beam interaction with the Sn sector of the target (dashed line Fig. 2).

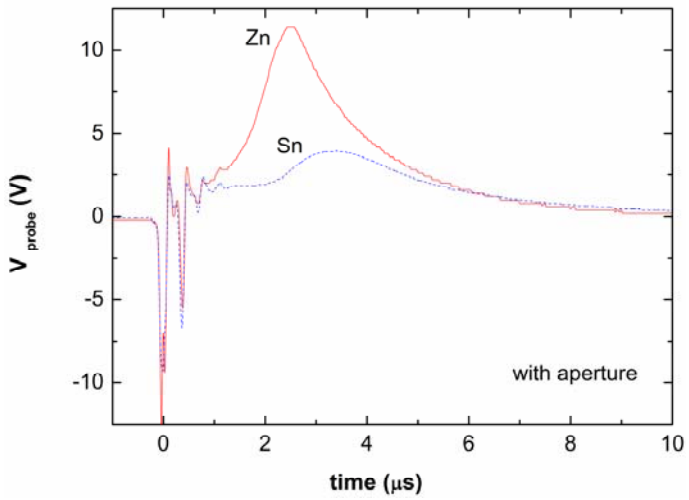


Fig. 2 – Ion probe signals for Zn ions (solid line) and Sn ions (dashed line).

The maximum of the Zn ion signal is at 2.5 μs, and that for Sn ions at 3.4 μs respectively, corresponding to a velocity of 1.48 cm/μs, and 1.09 cm/μs respectively. The kinetic energies of both Zn and Sn ions corresponding to the maximum signals of the ion probe are approximately equal to 75 eV.

The ion energies show a relatively broad distribution from a few eV to one hundred eV. This leads to the enhancement of the adatom mobility on the substrate surface, and thus to a rather smooth surface and a low temperature of

crystallization. The control of the kinetic energies of the species during PED is an important parameter for the growth of thin films with specific properties. In previous works the influence of the composition on the structural and physical properties of oxide films was demonstrated [24, 25], especially in the case of Sn based oxides [26].

The thickness and composition of thin films grown on Si and c-cut single crystal substrates at a temperature of 200 °C was performed by means of RBS. The Figure 3 shows the RBS spectra of a Sn doped ZnO thin film grown at 200 °C on a c-cut sapphire substrate.

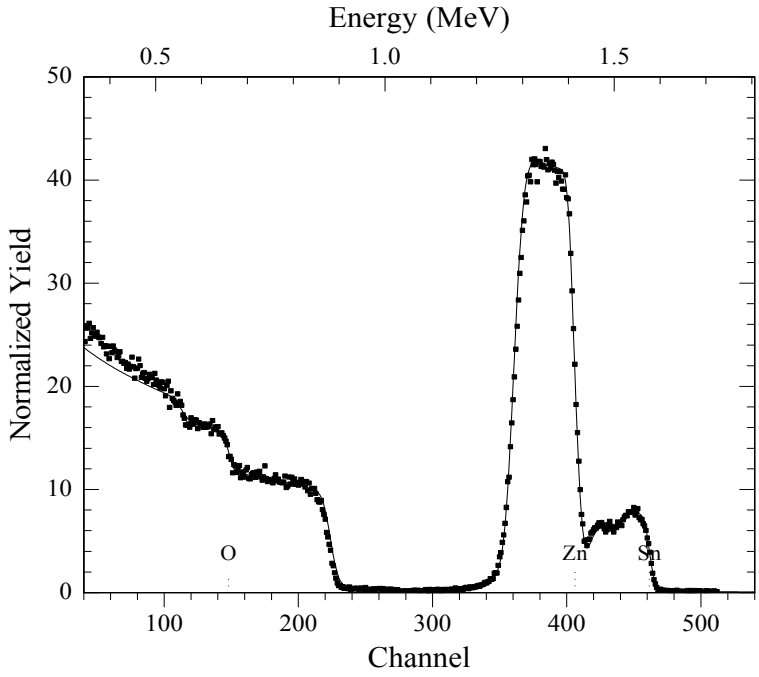


Fig. 3 – A typical RBS spectrum recorded for a Sn doped ZnO film grown by PED on c-cut sapphire substrate at 200°C.

The RBS spectrum shows that the presence of Sn leads to slight variations in the in-depth composition of thin films, leading to a composition graded thin film whatever the substrate used (Si or sapphire). This particularity could be explained by two reasons. The first one is related to the sectorial target used. As demonstrated in PLD, the beam interaction with a sectored target allows an additional control of the second phase material or dopant in respect with the typical deposition parameters, leading to an improvement of the properties of the growth thin films [19]. The second one is due to a specificity of Sn which is very sensitive to the oxygen pressure during deposition, and which typically leads to the variation in composition of oxide thin films [26].

The sharp front edge of the Al (from c-cut sapphire) contribution and rear edges of each element spectrum of the film, excludes any film-substrate interdiffusion during the film growth. A rather smooth surface of the film can be deduced for this RBS spectrum. This was checked by SEM analysis, as shown by the cross-section SEM image (with a slight tilt angle) of a doped ZnO film grown on a Si substrate at 200°C, presented in Fig. 4. This figure shows the presence of nanoparticles (may be related to a specificity of Sn ablation by PED), superimposed on a dense and smooth film presenting a columnar aspects. Such a columnar growth is typical of the pure or doped ZnO film formation [17] whatever the substrate is. This is related to the classical (002) texture of the ZnO film growth which has been checked on these films by complementary X-ray diffraction analyses.

It has to be noticed, that the kinetic energy of the species impinging the surface of the growing film plays a major role on the film morphology and microstructure. An increase of this kinetic energy is deleterious for the surface morphology and film orientation [10].

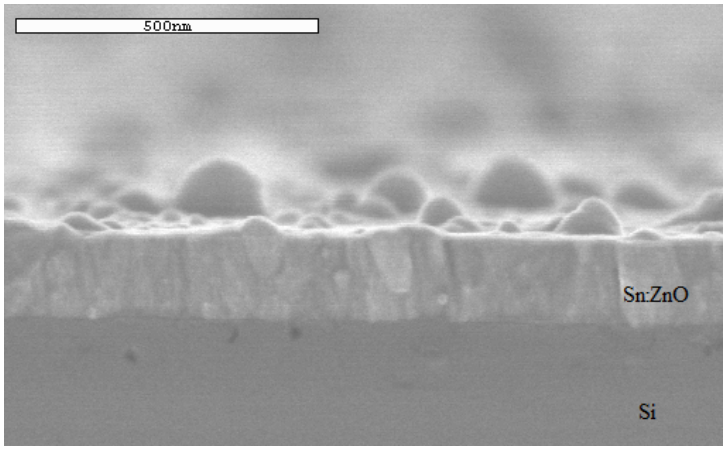


Fig. 4 – Cross-section SEM image of a Sn doped ZnO thin film grown by PED on Si substrate at 200°C.

Indeed, the kinetic energy of the ions can be very much higher than the characteristic bond energies of the elements of the oxide film, and therefore ions can create significant “damage” to the crystalline grains of the growing film. In addition to the structural disorder, oxygen vacancies can be created and as a result changes in the electrical conductivity of the films may occur. Thus, a careful optimization of the deposition conditions for each kind of oxide has to be carried out in order to reach the optimum structural and physical properties.

The physical properties of such composition graded oxide films were studied. Optical transmittance measurements of Sn doped ZnO thin films show that these films have a mean transmittance of about 87% in the 400–700 nm visible

wavelength range, *i.e.* a value similar to those measured on pure ZnO films obtained by PLD or PED.

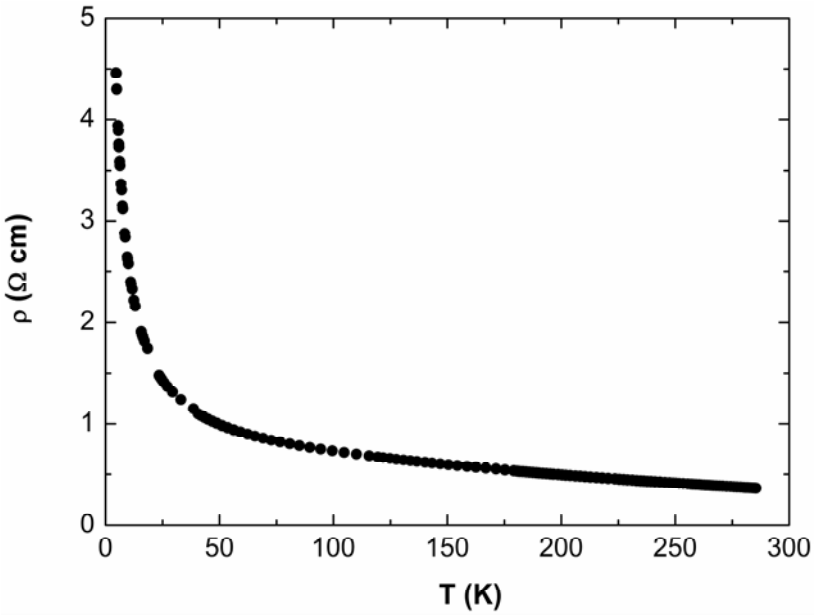


Fig. 5a – The resistivity as a function of temperature of Sn doped ZnO thin film grown by PED on c-cut sapphire substrate at 200°C.

The transport properties of the Sn doped ZnO films were measured through temperature dependence of resistivity, and a typical curve is shown in Fig. 5a. A classical semiconductor behaviour is observed on this curve, despite the graded composition of the film. The room resistivity of such Sn doped ZnO films was about 0.4 Ωcm, without any optimisation of the oxygen composition of the films which is known to play a major role on the conductivity of semiconducting oxides [21].

Figure 5b shows the Arrhenius plot of the resistivity of a Sn doped ZnO thin film grown on a c-cut sapphire substrate at 200°C in the limited range 285–215 K, the ln ρ following an Arrhenius law *versus* temperature. The activation energy estimated from the slope is equal to 19 meV, a value comparable to those obtained on pure ZnO films. At lower temperatures, the thermally activated carrier transport mechanism is no longer valid as a pronounced curvature is observed in Fig. 5b. Such a behaviour classically observed in oxide semiconductors [27] could be explained by the localisation phenomenon leading to variable range hopping (VRH) mechanism [28] frequently observed in such oxide materials.

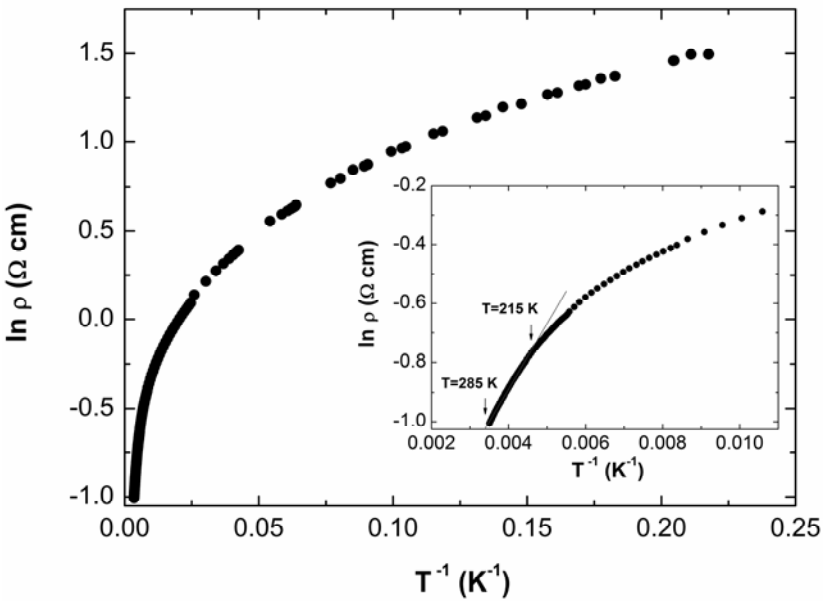


Fig. 5b – Arrhenius plot of the resistivity of a Sn doped ZnO thin film grown by PED on c-cut sapphire substrate at 200 °C. The inset shows the variation in the 285 to 215 K range on an expanded scale.

These results were obtained on Sn doped ZnO films for which the oxygen composition was not optimized in order to obtain the highest electrical conductivities [29]. In the same time, the films were obtained at a low substrate temperature (lower than 250°C), and thus their crystalline quality was not ideal for their transport properties. Despite these points, the physical properties of such films are promising in view of applications as transparent electrodes.

## 4. CONCLUSIONS

In this work we have grown Sn doped ZnO thin films on Si and c-cut sapphire single crystal substrates at 200°C by PED using a sectorial target. The kinetic energies of the species arriving on the substrate were estimated from ion probe measurements, a broad distribution from a few eV to one hundred eV being measured. A slightly in-depth variation of Sn in films was evidenced by RBS measurements, but the physical properties of the films are not affected. A value of the resistivity of 0.4 Ωcm was measured at room temperature. The resistivity dependence of the temperature shows the classical semiconductor behaviour, with the activation energy of 19 meV. The mean transmittance of the films was 87% in the 400–700 nm wavelength range. Thus, PED has the potential to form doped ZnO films presenting specific characteristics for applications as transparent electrodes.

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