Laser ablation of Co:ZnO films deposited from Zn and Co metal targets on (0001) Al$_2$O$_3$ substrates.

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Abstract

We report on the synthesis of high-quality Co-doped ZnO thin films using the pulsed laser deposition technique on (0001)-Al$_2$O$_3$ substrates performed in an oxidizing atmosphere, using Zn and Co metallic targets. We firstly optimized the growth of ZnO in order to obtain the less strained film. Highly crystallized Co:ZnO thin films are obtained by an alternative deposition from Zn and Co metal targets. This procedure allows an homogenous repartition of the Co in the ZnO wurzite structure which is confirmed by the linear dependance of the out-of-plane lattice parameter as a function of the Co dopant. In the case of 5% Co doped, the film exhibits ferromagnetism with a Curie temperature close to the room temperature.

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Diluted Magnetic Semiconductors (DMS) of III-V or II-VI types have been obtained by doping semiconductors with magnetic impurities (Mn for example)\textsuperscript{1,2}. These materials are very interesting due to their potential applications for spintronics\textsuperscript{3}. However, the low Curie temperature ($T_C$) has limited their interest\textsuperscript{4}. Based on the theoretical works of Dietl \textit{et al.}\textsuperscript{5}, several groups\textsuperscript{6} have studied the growth of Co-doped ZnO films\textsuperscript{7-10} which is a good candidate having a high $T_C$\textsuperscript{5}. Using pulsed laser depositions (PLD), Ueda \textit{et al.} reported ferromagnetism (FM) above room temperature\textsuperscript{7}, while Jin \textit{et al.} found no indication of FM by utilizing laser molecular beam epitaxy\textsuperscript{8}. This controversy between research teams may result from the growth method used and/or from the growth conditions (oxygen pressure, deposition temperature, etc...). In the particular case of the PLD technique, it may also arise from the targets preparation and this parameter has never been considered up to now. One of the reason is that the control of the dopant incorporation would be quite difficult to obtain using a pre-doped ceramic oxide target\textsuperscript{11}. This is a crucial point since the properties of the DMS are very sensitive to the percentage of dopant\textsuperscript{12}. The homogeneity of dopant incorporation as well as the precise control of the growth might be responsible for the changes in the physical properties of the films obtained by the different groups.

Therefore, the objective of this investigation is two fold: first to develop an accurate method to grow the Co:ZnO films with a precise doping and second to understand their properties. To achieve such a goal, Co-doped ZnO films were deposited from two pure metal targets of Zn and Co and our results are reported in this letter.

The Co:ZnO films were grown using the pulsed laser deposition technique. Zinc (99.995\%) and Cobalt (99.995\%) targets were used as purchased (NEYCO, France) without further preparations. The films are deposited using a KrF laser ($\lambda = 248nm$)\textsuperscript{13} on (0001) Al$_2$O$_3$ substrates. The substrates were kept at a constant temperature in the range 500°C-750°C during the deposition which was carried out a pressure around 0.1Torr of pure oxygen. After deposition, the samples were slowly cooled to room temperature at a pressure of 300mTorr of O$_2$. The deposition rate is $3Hz$ and the energy density is close to $2J/cm^2$. The composition of the film was checked and corresponds to the nominal one in the limit of
the accuracy.

The structural study was done by X-Ray diffraction (XRD) using a seifert XRD 3000P for the $\Theta - 2\Theta$ scans and an X’Pert Phillips for the in-plane measurements (Cu, $K\alpha_1$, $\lambda = 0.15406$ nm).

In order to grow Co:ZnO films, we firstly need to deposit high quality ZnO films. The resulting XRD pattern of ZnO is show in Fig.1. The two diffractions peaks observed around 34.48° and 72.66° are characteristic of the hexagonal ZnO wurzite, the $c$-axis being perpendicular to the substrate plan. The out-of-plane lattice parameter is calculated to be 0.52mm which corresponds to the theoretical bulk one. The sharp and intense peaks observed indicate that the films are highly crystallized which is confirmed by the low value of the full-width at half maximum (FWHM) of the rocking curve recorded around the 002 reflexion (see inset of Fig1). The epitaxial relationships between ZnO films and Al$_2$O$_3$ substrates are determined using asymmetrical XRD. Fig.2 displays the $\Phi$–scan of the ZnO films obtain from the (103) planes. The peaks are separated by 60°, indicating a six-fold symmetry with a rotation of 30° of the ZnO symmetry in the plane, with respect to the sapphire substrate. The averaged in-plane lattice parameter of ZnO is 0.325mm and the FWHM of the peaks in the $\Phi$–scan of ZnO is small (0.68°). This value is close to previous value reported in the literature. In order to obtain additionnal information, on the structural properties of the ZnO films, we have determined the thin film strains. This technique used the distance between atomic plane of a crystalline specimen as an internal strain gage. The plane spacing $d_{hkl}$ is normal to the diffraction vector $\hat{L}$. One can define a strain $\varepsilon$, along this diffraction vector $d_{hkl}$, $\varepsilon = (d_{hkl} - d_0)/d_0$ where $d_0$ is the unstressed plane spacing of the $(hkl)$ planes (i.e the value of the bulk). To measure the stress, we used the $\sin^2\Psi$ technique. Briefly, in this model, the strain is defined as follows: $\varepsilon = \alpha \sin^2 \Psi + \beta$ (where $\alpha$ and $\beta$ are constantes that depends on the strain along the the surface direction, the Young’s modulus, Poisson’s ratio and the stress along the direction, for details see Ref.15). Fig.3 shows the evolution of the strain $\varepsilon$ as a function of $\sin^2\Psi$ for ZnO films grown at different temperatures. The strain increases with the temperature, indicating that the film is more strained along the
in-plane direction (since the out-of-plane lattice parameter is practically constant whatever the growth conditions). A similar conclusion is obtained when $\varepsilon$ is plot for various oxygen pressure (not shown). To minimize the substrate-induced strain of the ZnO, we deposited the film at 600°C under 0.1 Torr of $O_2$ (under these conditions $\varepsilon$ is almost constant as a function of $\sin^2 \Psi$).

These conditions will be used hereafter to synthesise Co-doped ZnO films. We used the following procedure. For example, in order to grow a Co-doped ZnO film, we fired $m$ pulse on Co and $n$ pulses on Zn. The sequence is repeated until the desired thickness is obtained. Various compositions have been grown with different $m/n$ ratios given the same results and indicating a good reproducibility of the films. Moreover, in each case the film is a single phase, highly crystallized (the FWHM is always around 0.25°). In the XRD patterns, only the diffraction peaks corresponding to the Co:ZnO phase are observed suggesting that the Co clusters are not present. This is confirmed by the x-rays topography recorded in a scanning transmission electron microscopy (JEOL 2010F) of the Co:ZnO films where an homogenous repartition of the Co is observed. The details of the structural and microstructural characterizations will be present elsewhere. Moreover, it has been shown that the high pressure of oxygen (0.1 Torr in the present case) reduces the Co clusters formation\(^\text{17}\). The out-of-plane lattice parameter of the Co:ZnO films increases almost linearly as a function of the Co doping and nearly obeys the Vergard’s law (Fig.4). Regarding this curve, it seems that the limit of the solution is close to 9%, since for higher Co content, the lattice parameter do not change.

We investigated the magnetic properties of these thin film samples using a SQUID magnetometer. Fig.5 shows the $M(T)$ recorded for a 5% Co-doped ZnO film\(^\text{18}\). The ferromagnetic behavior is observed on the $M(H)$ in the whole temperature range between 5-300K (inset of Fig.5). The hysteresis of the magnetization is very small (about few Gauss). $M(T)$ curves (Fig.5) clearly evidences that the film is ferromagnetic with a Curie temperature around 300K. The transition from the ferromagnetic state to the paramagnetic state is clearly seen, suggesting that the mettalic Co clusters (the $T_C$ of the metal Co clusters is above 1000K) are
not responsible for the effect observed at 300K\textsuperscript{9,10}. Moreover, the saturation moment (0.7 $\mu_B$/mole Co) is very weak compared to 1.7$\mu_B$ of metallic Co\textsuperscript{0}, suggesting that the Co state should be close to Co\textsuperscript{2+}. The increase of the out-of-plane lattice parameter as the cobalt content increases is also in favor of Co\textsuperscript{2+}\textsuperscript{19}. We believe that this is due to the technique used in the study where not only the conditions of the deposition minimize the strains but also the alternately deposition from the two targets favors the homogeneity of the doped films. Moreover, it has been seen that the low temperature of deposition leads to homogenous films\textsuperscript{9}.

In conclusion, we have developed an alternative method for the growth of pulsed laser deposited thin films. This method permits an accurate control of the dopant in the matrix. To illustrate this procedure, we firstly synthesized high quality ZnO thin films on Al\textsubscript{2}O\textsubscript{3} (0001) substrates and minimized the substrate-induced strain by optimizing the growth conditions. Secondly, we utilized this process to deposit high quality Co-doped ZnO films with a Curie temperature close to room temperature. The growth of these ferromagnetic films opens the route for the fabrication of spin-based electronics since this original method can be used to grow various oxide thin films.

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We try to investigate the magnetic properties of samples with a lower content of Co (<5%). But in this case, the signal of the substrate is higher than the film signal which makes impossible to conclude about a magnetic state of 2% or 4% Co-doped ZnO films.
Figures Captions:

Figure 1: Room temperature Θ – 2Θ XRD pattern of typical ZnO film. The inset depicts the rocking curve (ω-scan) of (002) reflection of the film. Note the sharpness and the high intensity of the peaks.

Figure 2: Φ-scan of the {103} family peaks of a typical ZnO film showing a very good in-plane orientation of the film.

Figure 3: ε vs. sin^2Ψ for a ZnO films grown at different deposition temperatures. The values of (hkl) planes corresponding to the measured sin^2Ψ is indicating. The dot lines are only a guide for the eyes.

Figure 4: Evolution of the d_{002} in Co:ZnO films as a function of the Co content. The line is a guide for the eyes. The plateau above 15% indicates that the limit of the solid solution is around 9%.

Figure 5: M(T) of the Co:ZnO films (5% of Co) recorded under 2000G. The inset depicts the M(H) at 30K and 350K. The 350K signal is due to the background component of the substrate. The anomaly at 30K ±7000G corresponds to the difficulty in fitting the signal when crosses zero.
Figure 1

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