Effect of pressure on the elemental composition and magnetic properties of lithium-doped ZnO thin films

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Abstract. The paper presents the results of a study of the effect of pressure in a vacuum chamber on magnetic characteristics of Zn$_{1-x}$Li$_x$O$_y$ thin films obtained by pulsed laser deposition on sapphire substrates as well as the results of elemental analysis across thickness of the samples. Secondary ion mass spectrometry demonstrated that the method of pulsed laser deposition allows for the synthesis of zinc oxide based thin films characterized by a high uniformity of elemental composition across thickness. It was established that different pressure in the vacuum chamber affects the number of oxygen vacancies in thin films, but not the distribution of elements across thin film thickness. Weak room temperature ferromagnetism was observed in Zn$_{1-x}$Li$_x$O$_y$ thin films synthesized at a pressure of 3.15·10$^{-5}$ Torr; it increases upon the increase in lithium concentration. Interstitial lithium atoms are considered to play an important role in its occurrence. The results of the study allow for expansion of the body of knowledge about the nature of room temperature ferromagnetism in zinc oxide based thin film structures as well as for developing technologies for high-quality thin film materials for recording and storing information.

1. Introduction

Thin film diluted magnetic materials based on a wide-band semiconductor - zinc oxide - are of great interest to scholars across the world as these materials display a unique combination of magnetic, electrical, magnetotransport, and magneto-optical properties [1-3]. However, based on a modest amount of research on room temperature ferromagnetism in zinc oxide based thin films, the use of lithium as an alloying element for obtaining ferromagnetic ordering has been limited [4-6]. The discovery of room temperature ferromagnetism in lithium-doped ZnO thin film structures may open up the possibility of controlling electrical and magnetic properties of the material using magnetic and electric fields respectively. Zn$_{1-x}$Li$_x$O$_y$ films can be used both as channels of field-effect transistors and ferroelectric elements for recording information. According to [7], the structure of a memory element based on Zn$_{1-x}$Li$_x$O$_y$ is fatigue-resistant during repeated readouts, which is expected to significantly increase resources of big data storing and recording devices. Despite numerous attempts were made to create such devices, the issues regarding stability of the elemental composition across thickness as well as the physical nature of ferromagnetic properties of Zn$_{1-x}$Li$_x$O$_y$ are still to be fully addressed. All things considered, further theoretical and experimental research into the matter is of the utmost importance.

The purpose of this work is to obtain high-quality Zn$_{1-x}$Li$_x$O$_y$ thin films ($x = 0$−0.06; 0.89 < $y$ < 1) by pulsed laser deposition as well as to study the effect of pressure in a vacuum chamber on their elemental composition across thickness and ferromagnetic ordering at room temperature.
2. Experimental procedure and methods.

Zn\(_{1-x}\)Li\(_x\)O\(_y\) thin films (thickness = 100 nm) with a lithium concentration of 0, 2, 4, 6 at % were synthesized by pulsed laser deposition (PLD) on c-sapphire substrates. The process of PLD is shown in figure 1. The heating temperature of the samples in the vacuum chamber was set at 500 °C, the pulse repetition rate of the KrF laser was 2 Hz, and the pulse energy was equal to 300 mJ. Thin films were synthesized at residual pressures of 3.15·10\(^{-5}\) Torr and 7.5·10\(^{-3}\) Torr in the chamber. Ceramic targets (m = 40 g) were obtained from mixtures of high purity ZnO and Li\(_2\)CO\(_3\) powders by applying the pressing force of 10 ton/cm\(^2\). The targets then were annealed at a temperature of 950 °C for 3 hours. X-ray phase analysis performed using an XRD 7000 diffractometer showed that all Zn\(_{1-x}\)Li\(_x\)O\(_y\) samples contain a single ZnO phase with a wurzite structure (P6\(/mc\)) oriented along the (001) direction. Surface roughness of the synthesized films was 2-7 nm. Magnetic measurements were obtained in the field range from -1000 Oe to +1000 Oe at room temperature using Quantum Design Physical Property Measurement System (PPMS 9). The results of the magnetic studies were processed based on the Langevin function after subtracting the values of the substrates and the sample holder. The method of secondary ion mass spectrometry (SIMS) based on the analysis of ionized sputtering products (element detection limit = 10\(^{-4}\)%), was employed for depth profiling of the elemental composition of the samples. The study was carried out in ultra-high vacuum using a time-of-flight secondary ion mass spectrometer 7200 ToF-SIMS Physical Electronics that applies a sputtering beam of Cs\(^+\) ions (\(E = 3\) keV; \(I = 27\) nA) and a pulsed analytical beam of Bi\(^+\) ions (\(E = 25\) keV; \(I = 1\) Pa). The primary ion density was set at 10\(^{13}\) ions/cm\(^2\) for sputtering the surface of Zn\(_{1-x}\)Li\(_x\)O\(_y\) thin films.

3. Magnetic properties of thin films

The study indicated that Zn\(_{1-x}\)Li\(_x\)O\(_y\) thin films (\(x = 0-0.06\)) synthesized at a pressure of 7.5·10\(^{-3}\) Torr do not exhibit ferromagnetic ordering while demonstrating paramagnetic properties. However, the field dependencies of the magnetic moments of the doped images, which were obtained at 3.15×10\(^{-5}\) Torr, showed the presence of weak room ferromagnetism (at \(x = 0\), the films demonstrated paramagnetic properties). Despite rather weak magnetic signals (~ 10\(^{-6}\) emu), paramagnetic course of the curves is clearly visible (figure 2). Magnetic characteristics of Zn\(_{0.98}\)Li\(_{0.02}\)O\(_y\) and Zn\(_{0.96}\)Li\(_{0.04}\)O\(_y\) samples are very similar. For these thin films, magnetic saturation moments are 4.3·10\(^{-6}\) emu and 4.8·10\(^{-6}\) emu respectively, and coercive force values are 28 Oe and 40 Oe accordingly. The most pronounced room temperature ferromagnetism is observed for Zn\(_{0.94}\)Li\(_{0.06}\)O\(_y\). It is characterized by a wider hysteresis loop with coercive force of 72 Oe and the largest magnetic saturation moment among the studied samples - 7·10\(^{-6}\) emu. This value is very close to the value of coercive force (80 Oe) obtained for Zn\(_{0.94}\)Li\(_{0.06}\)O\(_y\) in [8]. Increasing the concentration of lithium from 2 to 6 at. % allows for an almost proportional increase in coercive force in Zn\(_{1-x}\)Li\(_x\)O\(_y\) films (~3.2 times). Thus, the rise in ferromagnetic signal at room temperature is observed upon an increase in lithium concentration in ZnO thin films, which is associated with an increase in the number of interstitial defects (Li\(_i\)) in the samples [9].
4. Profiling of the element composition across thin film thickness

Positive- and negative-ion SIMS profiles of the element distribution across thickness of Zn$_{0.94}$Li$_{0.06}$O$_y$ films obtained at pressures of $3.15 \times 10^{-5}$ Torr and $7.5 \times 10^{-3}$ Torr, and the substrates on which they are synthesized, are shown in figures 3 and 4 respectively. The ordinate axis, by which the mass analyzer of the spectrometer determines the elemental composition, indicates the intensity of secondary ions, and the abscissa axis indicates the measurement time, which is interpreted as the depth of the films. Thus, the starting time corresponds to the first layer of surface atoms, and the time $\tau_1 = 500$ s corresponds to the total thickness of the studied films (100 nm). A conditional vertical line through $\tau_1$ indicates the film-substrate interface. The thickness of the investigated substrate depth cannot be determined distinctly, since the time spent bombarding primary ions of the film depth (for example, 1 nm) differs from the time required for bombarding the same depth of the substrate. Even then, it is deemed possible to analyze the distribution of substances to observe the mutual diffusion of film and substrate elements.

According to the positive ion SIMS profiles, zinc and oxygen are evenly distributed across thickness of the films (figure 3), which indicates uniformity of the ceramic targets as well as stability of the...
parameters of the PLD process with regard to time. At the film-substrate interface, the concentration of Zn and O decreases sharply due to complexity of diffusion of atoms into the crystal structure of the \( c \cdot Al_2O_3 \) substrate. Penetration of aluminum from the substrates into the thin film is expected to be smoother. It is worth noting that concentration of lithium on the film surface (thickness \(< 18 \text{ nm} \)) and at the film-substrate interface is significantly higher than its concentration in the film volume. Surface defects and dislocations formed by a relatively high degree of lattice mismatch between films and substrates are likely to contribute to the transfer of lithium atoms from the volume of the films, characterized by the structure of a greater crystal perfection, to its boundaries.

In the negative ion SIMS profiles, the surface of the films indicates an increased content of carbon adsorbed from the atmosphere before surveying (figure 4). An insignificant amount of carbon in the film volume can be attributed to the use of lithium carbonate for the synthesis of ceramic targets. Comparing the SIMS profiles, we can conclude that the pressure during the synthesis has little effect on the concentration of elements and their thickness distribution. According to SIMS, PLD allows for the synthesis of thin films characterized by a high uniformity of elemental composition across thickness.

![Figure 4](image)

**Figure 4.** Negative ion SIMS profiles of distribution of elements across thickness in \( \text{Zn}_{0.94}\text{Li}_{0.06}\text{O}_y \) thin films synthesized at pressures of \( 3.15 \cdot 10^{-5} \text{Torr} \) (left) and \( 7.5 \cdot 10^{-3} \text{Torr} \) (right).

5. Conclusions

The article presents the results of magnetic measurements of \( \text{Zn}_{1-x}\text{Li}_x\text{O}_y \) thin films \((x = 0-0.06)\) synthesized by pulsed laser deposition at pressures of \( 3.15 \cdot 10^{-5} \text{Torr} \) and \( 7.5 \cdot 10^{-3} \text{Torr} \), as well as the results of depth profiling of the elemental composition of the samples. It was established that different pressure in the vacuum chamber affects the number of oxygen vacancies in thin films, but not the distribution of elements across thin film thickness. A weak ferromagnetic signal was detected at room temperature in \( \text{Zn}_{1-x}\text{Li}_x\text{O}_y \) films \((x = 0.02-0.06)\) synthesized at a pressure of \( 3.15 \cdot 10^{-5} \text{Torr} \), which increases with the rise in atomic concentration of lithium.Interstitial lithium atoms are considered to play a special role in its occurrence.

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References
[1] Kuz’mina A S, Lotin A A, StrokIN N A, Kuz’min M P and Kazantsev A V 2019 Mater. Res. Express. 6 086523
[2] Wang X L, Shao Q, Zhuravlyova A S, He M, Yi Y, Lortz R, Wang J N and Ruotolo A 2015 Sci. Rep. 5 9221
[3] Kuz’mina A S, Lotin A A, Novodvorsky O A, Perov N S, Gan’shina E A, Makarova L A, Semisalova A S, Shneider A G, Kuz’min M P and Kolesnikov S S 2017 Mater. Chem. Phys. 198 291-6
[4] Pazhanivelu V, Selvadurai A P B and Murugaraj R 2015 Mater. Lett. 151 112-4
[5] Awan S U, Hasanain S K, Anjum D H, Awan M S and Shah S A 2014 J. Appl. Phys. 116 164109
[6] Vettumperumal R, Kalyanaraman S and Santoshkumar B 2014 Mater. Res. Bull. 50 7-11
[7] Aghamalyan N R, Aslanyan T A, Vardanyan E S, Kafadaryan E A, Hovsepyan R K, Petrosyan S I and Poghosyan A R 2013 Proceedings of NAS RA Physics 48 193-202
[8] Yi J B et al. 2010 Phys. rev. lett. 104 137201
[9] Awan S U, Hasanain S K, Bertino M F and Jaffari G H 2012 J. Appl. Phys. 112 103924