VISIBLE MCD SPECTROSCOPY AND NATURE OF ROOM TEMPERATURE FERROMAGNETISM IN HYDROGENATED CO - AND (CO+AL) - DOPED ZNO FILMS

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Abstract. Co-doped ZnO and (Co+Al) - doped ZnO films were synthesized by the radio frequency magnetron sputtering in mixed atmosphere Ar+20% O_2 and Ar+20-50% H_2. The morphology, chemical composition, crystal structure, and magnetic circular dichroism of the films were investigated. It was established that the films thickness decreases several times when Ar replacing partly by hydrogen into the sputtering chamber. At the same time, the increase in relative Co content in the films with the increasing hydrogen concentration is observed. The hydrogenated films exhibit ferromagnetic behavior at room temperature. The nature of room temperature ferromagnetism in the hydrogenated Co - and (Co+Al) - doped ZnO films is discussed, as well as the mechanism of influence of hydrogen concentration on the magnetic properties of the samples.

1. Introduction

ZnO films doped with transition ions belong to the class of diluted magnetic semiconductors (DMS). Special attention is paid to the Co - and (Co+Al) - doped ZnO films due to possible room temperature ferromagnetism and high carrier concentration in the samples at a low content of the doped ions. However, it was established that the appearance of ferromagnetism in such materials depends strongly on the conditions of fabrication and treatment of the samples. To improve magnetic properties of the Co - and (Co+Al) - doped ZnO samples, many authors used the hydrogenation method, for example Refs. 1 and 2. However, in the works known to us, the hydrogen concentration in mixed-gas was up to 10-15%. In this work, the hydrogenated Co - and (Co+Al) - doped ZnO films are studied with 20-50% hydrogen concentration in mixed-gas.

2. Experimental procedure and sample preparation

The films were grown on glass substrate by the standard RF magnetron sputtering system using two inches $Zn_{0.95}Co_{0.05}O$ (CZO) and $Zn_{0.95}Al_{0.02}Co_{0.05}O$ (CAZO) targets. The CZO and CAZO targets were calcined at 1300 °C for 12 hours in atmosphere of flowing oxygen and 860 °C for 12 hours in atmosphere of flowing argon gas. The films were deposited at a total pressure of 30 mTorr and a forward RF power of 80W at the substrate temperature 450 °C for 20 minutes. Five samples of each composition were prepared with the following mixed gas in the chamber: Ar+20% O_2, Ar+(20%, 30%, 40%, 50%) H_2, samples CZO1, CZO2, CZO3, CZO4, CZO5, and CAZO1, CAZO2, CAZO3, CAZO4, CAZO5, respectively.

MCD was measured in the normal geometry: the magnetic vector and the light beam were directed normal to the films plane. The modulation of the polarization state of the light wave from the right-hand to the left-hand circular polarization relatively to the magnetic field direction was used. The MCD value was measured by the formula $MCD=(D_+–D_-)/d$, where D_+ and D_- are the optical density of the films for right and left polarized waves, and d is the films thickness. Measurements were carried out in the spectral range 1.2-4.5 eV in a magnetic field up to 13 kOe at the temperature 300 K.

3. Results

Data of the X-ray fluorescent analysis (XRFA) and electron probe microanalysis (EMP) for the CZO and CAZO films shown the increase of the Co content relative to the Zn content in the films. For the example, from 0.052 for CZO1 to 0.390 for CZO5 films. Such behavior is similar for the CAZO films. However, the growth of the Al content in them is also expected. At the same spraying time of the targets, a large difference in the thickness of the deposited films is noticeable. The films thickness decreases from 160 nm for CZO1 to 32 nm for CZO5, and from 99 nm for CAZO1 to 14 for CAZO5.

Special attention was paid to the MCD spectra measured in the visible range at the room temperature. The MCD spectra for the hydrogenated CZO and CAZO films are characterized by the intense signals of the different signs (for example, Fig. 1a). With increasing H_2 concentration a rearrangement of the MCD spectra is observed. At that, the MCD dependence on external magnetic

field is described by hysteresis loop in the whole investigated spectral range. Such behavior indicates the presence of room temperature ferromagnetism in the samples.

The MCD spectra and the MCD magnetic field dependencies for the Co - and (Co+Al) - doped ZnO films were compared with that for the Co particles [3] ion-synthesized in the amorphous matrix of silicon dioxide (Fig. 1b). The MCD spectra for the Co - and (Co+Al) - doped ZnO films were decomposed into several components. The intensity dependence of these components on hydrogen concentration was traced.

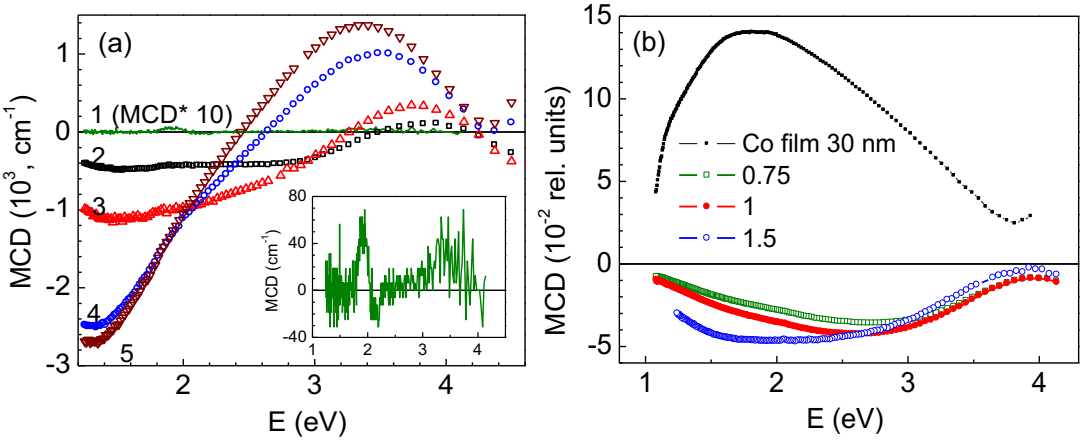

Fig. 1. a – MCD spectra for CZO1-CZO5 samples, curves 1-5, respectively, measured at H = 13 kOe and T = 300 K. Insert: the magnified MCD spectrum for CZO1. b – MCD spectra measured at H = 3 kOe and T = 300 K for the Co^+ implanted samples with ion current densities j=8 μA/cm^2. Black lines show MCD spectra for the thin films of Co measured at T = 300 K and H = 3 kOe.

Conclusions

An extremely strong effect of hydrogen on morphology, composition, and magnetic properties of the samples was revealed. The main tendency of the strong Zn content decrease in the films and their thickness with the growth H_2 concentration was observed. Unlike the CZO and CAZO films synthesized in atmosphere Ar+O_2, the hydrogenated CZO and CAZO films exhibit ferromagnetic behavior at room temperature. The complex nature of magnetism with a combination of the intrinsic ferromagnetism (due to the formation of the Co-H-Co complex) with the ferromagnetic inclusions is assumed in the investigated films. The nature of these ferromagnetic inclusions as well as the mechanism of influence of hydrogen concentration on the magnetic properties of the samples are discussed.

References

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