Magneto-optical characterization of ZnO / Ni nano-laminate obtained via Atomic Layer Deposition

K Buchkov¹,², A Galluzzi³,⁴, B Blagoev¹, A Paskaleva¹, P Terziyska¹, T Stanchev¹, V Mehandzhiev¹, P Tzvetkov⁵, D Kovacheva⁵, I Avramova⁵, E Nazarova¹, M Polichetti³,⁴

¹ Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., BG-1784, Sofia, Bulgaria
² Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, Acad. G. Bonchev Str, Bl. 109, Sofia, BG-1113, Bulgaria
³ Department of Physics “E.R. Caianiello”, University of Salerno, via Giovanni Paolo II, 132, Fisciano (SALERNO), I-84084, Italy
⁴ CNR-SPIN Salerno, via Giovanni Paolo II, 132, Fisciano (SALERNO), I-84084, Italy
⁵ Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., bl.10, BG-1113 Sofia, Bulgaria

E-mail: buchkov@issp.bas.bg

Abstract. The magneto-optical (MO) properties of ZnO / Ni transition metal oxide (TMO) nano-laminate structures prepared by Atomic Layer Deposition (ALD) have been investigated. The structural (XRD) and chemical composition (XPS) analysis confirm the ZnO formation and corresponding effect of Ni incorporation in the crystal lattice. The XPS identification of Ni I²+ state, reveals also some minor traces of Ni(OH)₂ inclusions. By using a MO Kerr effect microscopy, we have studied the local magnetic coercivity and its distribution and mapping of the ZnO/Ni nano-laminate sample on a microscale level. The statistical dispersion of the measured \(H_c\) values ranges between 100 and 400 Oe (peak value of ~ 200 Oe) with minor inhomogeneity inclusions.

Introduction

The development of diluted magnetic semiconductors (DMS) [1] materials and particularly the investigation of their general magnetic and magneto-optical properties is one of the main topics in the fundamental and applied research fields of spintronics [2], photonics [3,4] and information storage technology [5].

The universal and diverse semiconducting properties of Zinc Oxide (ZnO) [6,7]: wide direct band gap of 3.37 eV), high optical transmittance and electrical conductivity - together with the possibilities of chemical modifications with (3d) ferromagnetic transition metal elements (and TM oxides) as Ni, Co etc., makes it a primary magneto-optic DMS material [1,2]. In this context, a major requirement is that a DMS material should exhibit a ferromagnetic ordering at (or above) room temperature as in the case of Ni doped ZnO [8].

Another main magneto-chemistry challenge for ZnO / TM oxide compounds is the stochastic formation (segregation) of additional phase nanoclusters (magnetic inclusions) which obscure the
intrinsic magnetic nature. The non-uniformity also changes the electronic band structure and consequently affect negatively on spin polarized, charge and photon mediated processes.

The modification of the structural and physical properties of the ZnO / TM (Ni/ZnO in our case) compound depends both on the doping level [9] and the specifics of the technique as magnetron sputtering [10], pulsed laser deposition [11] and chemical (physical) vapor deposition [12].

The Atomic Layer Deposition (ALD) is effective technique for preparation of high quality (low temperature, uniformity, orientation and thickness control) films, since it uses a deposition cycle process with atomic layer precision level allowing nanostructure engineering [13–15]. This is one of the modern and innovative technological approach for realization of DMS ZnO/Ni nanostructures.

In this study we present basic structural and chemical composition of ALD grown ZnO / Ni nano-laminate using X-ray diffractogram (XRD), X-ray photoelectron spectroscopy (XPS) and Spectroscopic Ellipsometry (SE) for thin film quality verification analysis.

The investigation focus is on the magneto-optical properties and preliminary analysis of the magnetic response of the nano-laminate. The local (microscale magnetic homogeneity) distribution map of the magnetic coercivity ($H_c$) has been constructed by means of MO Kerr microscope magnetometry. The statistical dispersion of the coercivity values is also presented. This research trend is rarely explored [16] and to our knowledge not applied so far for ALD ZnO TMO nano-laminates. In addition, the analysis will provide more direct view for the optimization of deposition protocols and further ways to improve film architecture.

**Experimental Details**

The ZnO/Ni nano-laminate films using thermal ALD reactor (Beneq TFS-200) were grown [17]. The ALD protocol was performed by 24 supercycles repetition consisting from alternating of 16 ZnO and 5 Ni-O subcycles (total repetition of 504 subcycles). Diethylzinc(DEZ)/water and Nickelocene(NiCp2)/O3 precursors for ZnO and Ni-O subcycles were used respectively. The precursor/purging pulse durations were 0.2/2, 0.2/2, 2/4 and 1/5 s for DEZ, water, NiCp2 and O3 respectively. ZnO thin films were deposited on p-Si(100) substrates at reactor temperature ~ 180°C. The powder form NiCp2 was heated up to 80 °C to maintain an appropriate vapor pressure.

The thickness of the nano-laminate films is determined to be ~ 70 nm by fitting the experimental data for $\Psi$ and $\Delta$ acquired using a Woollam M2000D rotating compensator spectroscopic ellipsometer (in a spectral range 193 nm to 1000 nm).

The XRD analysis is performed on a Bruker D8 Advance diffractometer (Cu Kα radiation) and a LynxEye detector. The structural data were identified with Diffracplus EVA using ICDD-PDF2 crystallographic database.

A Kratos AXIS Supra spectrometer with a non-monochromatic Mg X-ray source was used for the X-ray photoelectron spectroscopy (XPS) analyses under vacuum greater than $10^{-8}$ Pa at 90 degree take-off angle. The C1s photoelectron line at 285 eV was used for calibration of the spectra.

The field-dependent (up to 4.5 kOe) magneto-optical measurements have been performed at room temperature using Scanning Laser Microscope (660nm wavelength) as a part of MO Kerr magnetometer system (NanoMOKE3). The magnetic field was applied in longitudinal configuration considering the in-plane magnetic anisotropy of the ZnO/Ni nano-laminate film.

**Results and discussion**

The XRD crystallographic analysis (figure 1) and the direct data comparison with a pure ZnO sample, confirms that the ZnO/Ni oxide nano-laminate has a typical (for ZnO), hexagonal wurtzite-type structure with nano-sized polycrystalline morphology. Traces of TMO oxide phases were not detected, possibly due to lower TMO concentrations used, presumably below the certain sensitivity limit of XRD. For pure ZnO, the dominant XRD reflection is in (002) crystallographic orientation. Doping with Ni changes the dominant crystallographic orientation from (002) to (100). The lattice parameters for ZnO/Ni are determined as follows: $a = 3.24(3)$ Å and $c = 5.21(4)$ Å. It is seen that the structural incorporation of Ni, effectively modifies the crystal lattice as revealed by the slight shift of
the reflection peaks (compared to pure ZnO). The results follow a systematic structural tendency similar to the previous studies of ZnO/Ni nano-laminates where different ALD protocols have been applied [17] and different doping with TMO elements (Ni, Co and Fe) and various substrates were tested.

![XRD comparision analysis of ZnO/Ni oxide and pure ZnO nano-laminate](image1)

**Figure 1.** XRD comparision analysis of ZnO/Ni oxide and pure ZnO nano-laminate

The qualitative chemical composition (element oxidation states and corresponding binding energies) of ZnO:Ni nano-laminate was verified also by the XPS spectra. The identification of Zn\textsubscript{2p} photoelectron spectral line confirms the ZnO formation, together with the Zn L\textsubscript{3}M\textsubscript{45}M\textsubscript{45} Auger line, since the chemical shift of Zn 2p\textsubscript{3/2} peak (specifically in ZnO) is minimal and difficult to identify the Zn chemical state. The XPS spectral data are presented in figure 2 (a). Minor signal for Ni 2p in 2\textsuperscript{+} oxidation state is also detected – figure 2 (b). The Auger parameter for ZnO/Ni nano-laminate is identical as for hydroxide, possibly Ni(OH)\textsubscript{2} [18].

![XPS spectral data for Zn 2p and Auger peak for Zn L\textsubscript{3}M\textsubscript{45}M\textsubscript{45} (A). Peak detection](image2)

**Figure 2.** XPS spectral data for Zn 2p and Auger peak for Zn L\textsubscript{3}M\textsubscript{45}M\textsubscript{45} (A). Peak detection
for Ni $^{2+}$ oxidation state (B).

The magneto-optical characterisation of the nano-laminate ZnO/Ni is based on constructing of the 2D (gradient colour) map of the local coercivity values by measuring the Kerr hysteresis loops (in sweeping magnetic field) at specific 5 $\mu$m sized sector of the film surface and scanning spatially over 200$\mu$m x 120$\mu$m area. The data are presented in figure 3 with corresponding colour bar of the coercivity variation. The distribution is relatively homogenous with few sectors with higher $H_c$ values ($H_c > 1000$ Oe) which is most likely due to clustering of Ni dopants. In addition, the presence of sectors with negative (diamagnetic) values is also an interesting observation.

![Figure 3. 2D Map of $H_c$ coercivity gradient distribution for ZnO/Ni nano-laminates](image)

The statistical dispersion and log-normal distribution of the coercivity is presented via histogram in figure 4 and as it is seen is quite wide even reaching values beyond 1500 Oe, corresponding to strong magnetic behaviour. In general, the $H_c$ takes predominantly values between 100 Oe and 400 Oe (peak average of $\sim$ 200 Oe) which is within appropriate (low magnetic field) practical limit for spin control applications.

![Figure 4. The histogram represents the cluster density distribution (number) depending on the measured coercivity values](image)
In conclusion, we have investigated the magneto-optical properties of ZnO/Ni TMO nano-laminate structures obtained by Atomic Layer Deposition. The structural and chemical composition analysis verify the successful ZnO formation with consequent modification of the crystal structure due to Ni incorporation.

By using a MO Kerr effect microscopy, we have studied the local magnetic coercivity and its microscopic distribution and mapping. The results reveal that the distribution of magnetic response is relatively homogeneous and is in the range between 100 and 400 Oe (peak average of ~200 Oe) which is within the preferred range for spin control applications. The observed areas with stronger magnetic response (up to $H_c = 3000$ Oe) are most likely due to formation of Ni clusters. Therefore, further optimisation of deposition process (including possible annealing steps) will be needed to improve the homogeneity of Ni distribution in ZnO matrix.

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