Combinatorial fabrication and magnetic properties of homoepitaxial Co and Li co-doped NiO thin-film nanostructures

U.S. Joshi [a,*], K. Itaka [b], Y. Matsumoto [c], H. Koinuma [b,d]

[a] Department of Physics, School of Sciences, Gujarat University, Ahmedabad 380 009, India
[b] Institute of Solid State Physics, University of Tokyo, Kashiwa, Kashiwanoha, Chiba 277-8581, Japan
[c] Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagastuta, Midoriku, 226-8503, Yokohama, Japan
[d] CREST, Japan Science & Technology Corporation (JST), 4-1-8 Honcho, Kawaguchi 332-0012, Japan

ARTICLE INFO

ABSTRACT

Magnetic properties of nanostructured epitaxial thin layers of a series of Co and Li co-doped NiO on MgO(1 0 0) substrate with NiO buffer layer have been investigated. Thin films were synthesized by combinatorial laser molecular beam epitaxy (CLMBE) in the continuous binary composition spread approach. Large and linear variation of x was achieved in the growth of $Co_xLi_{0.2}Ni_{0.8-x}O$ onto 9 mm of single substrate. Homoepitaxial growth with smooth surface morphology was confirmed by grazing incidence X-ray diffraction (GIXRD) and atomic force microscopy (AFM). Linear decrease in the band gap and optical transparency was observed with increasing cobalt concentration. The magneto-optical Kerr effect revealed a strong photon energy dependency with negative Kerr rotation for all the Co-concentrations in the film, suggesting intra-valence charge transfer (IVCT) between low spin state Co^{2+} with host Ni^{2+}. Ferromagnetic (FM)-like ordering was observed at low temperatures, while antiferromagnetism predominates at room temperature in the Co and Li co-doped nickel oxide epitaxial films.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Recently, the search for new functional nanomaterials has been directed towards more and more complicated compositions and structures. Nevertheless, in order to reach a targeted material, we need to make candidate materials and evaluate their properties much faster than by the conventional 'one-by-one' process. New concepts of 'combinatorial chemistry' in the form of continuous composition spread techniques have been employed for quick optimization of compositions in nanostructured thin-film fabrication. Excellent articles on combinatorial PLD thin-film fabrication can be found in the literature [1–3]. Combinatorial approach involves synthesis of vast number of compounds by reacting a set of components in the pre-designed combinations within a single experiment, and several key parameters such as temperature, pressure, atmosphere and thickness can be quickly adjusted for their optimal performance. Advanced electronic materials such as diluted magnetic semiconductors (DMS) have triggered an increasing interest due to their projected potential for the rapidly evolving field of spintronics [4–6]. Early efforts in this field focused on compound semiconductor materials doped with transition metal (TM) atoms, and ferromagnetism (FM) was indeed realized in some cases. The Curie temperatures in these systems have, however, been rather low prompting searches in other class of materials. In this context, oxides are a natural class to explore in view of their broad range of chemically tunable properties and reproducibility in the nanorange. Search for magnetism in transition element-doped ZnO and TiO_2 has shown considerable promise, [7–9] although the precise origin of ferromagnetism in these systems and the specific microstate of the materials are issues being debated in the literature [10–12]. Recent theoretical calculations showed half metallic behavior in the vacancy-induced NiO [13,14]. Such a half metallic behavior is considered to be an inherent property of almost all the well-known DMS compounds including transition metal-doped III–V semiconductors [15]. It is further predicted that carrier-induced ferromagnetism is more favorable in case if the carriers are holes, i.e., p-type oxides [10]. Moreover, in magnetically doped NiO system, the antiferromagnetic superexchange interaction can be suppressed by increasing the free carrier density so that the carrier-mediated RKKY interaction can surpass the AFM super-exchange interaction. The free carrier density can be increased through the co-doping method or further controlling the processing parameters, e.g. via chemical manipulation, such as in ZnO systems [16,17].

Although stoichiometric NiO is an insulator, its resistivity can be lowered by an increase of Ni^{3+} ions resulting from an addition of monovalent atom such as Li or by appearance of Ni vacancies

* Corresponding author. Tel.: +91 79 26303041; fax: +91 79 26306194.
E-mail address: usjoshi@gmail.com (U.S. Joshi).

and/or interstitial oxygen in NiO crystallites [18]. Considering these points, we have investigated the effect of cobalt substitution in Li-doped NiO grown on lattice-matched MgO(1 0 0) substrate with NiO buffer layer, in order to explore a possible magnetic ordering in p-type wide band gap oxides.

2. Experimental details

Single crystalline NiO epi layers of 15 nm thickness was deposited on MgO(1 0 0) substrate at room temperature under UHV. The films were post annealed in air at 800 °C by covering with another MgO(1 0 0) substrate. Details of the ultra-thin NiO buffer layer fabrication can be found in Ref. [19]. Atomically smooth NiO/MgO(1 0 0) substrates, with step and terrace morphology as shown in Fig. 1(b) were subsequently used for combinatorial laser MBE. The base pressure of the deposition chamber was 2×10^{-8} Torr. A composition spread thin film of $Co_{1-x}Li_{0.2}Ni_{0.8-x}O$ was deposited on single crystalline MgO(1 0 0) substrate with NiO buffer layer by the combinatorial pulsed laser deposition (PLD) technique in 10 mTorr of oxygen at a substrate temperature $T_s = 550$ °C. Ultraviolet KrF excimer laser ($\lambda = 248$ nm) pulses ablated ceramic targets of $Li_{0.2}Ni_{0.8}O$ and $Co_{0.1}Li_{0.2}Ni_{0.7}O$ alternately by switching the targets. Linear composition gradient across the spread was created by performing a series of shadow depositions through a rectangular moving mask, which moves back and forth over the substrate during the deposition [2]. The value of x in $Co_xLi_{0.2}Ni_{0.8-x}O$ was changed on NiO/MgO(1 0 0) substrate along one direction of the substrate with a span of 10 on 15 mm long substrate. Fig. 1(a) shows a schematic of the deposition process. Typical laser power and repetition rates were 1 J cm^{-2} and 10 Hz, respectively, and film growth rate was 0.36 Å/s. Film thickness was controlled to be approximately 80 nm.

Structural and surface morphology of the film was studied by grazing incidence X-ray diffraction (GIXRD) and atomic force microscopy (AFM) and the film thickness was determined by a stylus profiler (Veeco; Dektak3 ST). Elemental content in the samples were determined by the electron-probe micro analysis (EPMA). Magneto-optical Kerr spectra were recorded at room temperature in polar geometry in the photon energy range from 1.0 to 5.0 eV in an applied magnetic field of 20 kOe. Optical properties were studied by UV–visible spectrophotometer (UV-3100, Shimadzu Co., Japan). Magnetization measurements were performed by using SQUID magnetometer (Quantum Design, MPMS XL5) in a temperature range from 3 to 350 K by applying a field sweep of −6 to +6 T at an angle of approximately 30° to the plane of the film mounted in a vertical plastic straw.

3. Results and discussion

The AFM image of NiO buffer layer deposited on MgO(1 0 0) substrate is displayed in Fig. 1(b). An atomically flat surface morphology with steps and terrace structure is clearly seen. Each step height was found to be equal to the NiO unit-cell parameter (0.417 nm) [19]. These films were subsequently used as substrates for the combinatorial experiment. The growth conditions of the films were optimized by depositing $Li_{0.20}Ni_{0.80}O$ and $Co_xLi_{0.20-}Ni_{0.80-x}O$ films separately at substrate temperatures ranging from 450 to 650 °C under 10 mTorr of oxygen pressures, and deposition rates were optimized. Figs. 2(a) and (b) show the grazing incidence X-ray diffraction patterns and AFM images of samples with cobalt content $x = 0.0$, 0.05 and 0.08, respectively. GIXRD analysis revealed an epitaxial growth with appearance of only NiO(2 0 0) peak over entire Co substitution range in Li:NiO deposited at 550 °C. This is expected as both, MgO(1 0 0) and NiO(1 0 0) have the same cubic rock-salt structure with very small lattice mismatch of 0.85%. Although, the films deposited at 600 °C and higher temperatures were epitaxial in structure with smooth surface morphology but found to be nearly insulating due to significant Li evaporation [19]. The substrate temperature of 550 °C was therefore chosen for the composition spread experiments. GIXRD confirmed high-quality epitaxial growth for all Co-concentrations and the unit-cell parameter was estimated to be 0.42 nm. AFM images of Fig. 2(b) show a smooth surface morphology and the root-mean-square (RMS) roughness of the films were found to be 0.48 nm, which is comparable to the NiO unit cell. Average crystallite size estimated from the GIXRD and AFM for all the Co-concentrations was in the narrow range of 15–30 nm. Combined results of GIXRD and AFM indicate that the NiO buffer layer promoted strain-free homoepitaxial growth with uniform grain distribution. In our fabrication method, the Co composition in the film was intended to change linearly along positions in the film by using the moving masks and the synchronized laser pulses. One of the intriguing problem is the evaporation of Li which is very common in case of PLD deposition of Li:NiO films, particularly when grown in ultra-thin form [19]. The Co-concentration in the film was determined by the electron-probe micro analysis at five different positions along the film. EPMA results showed the expected compositional variation of Co and the atomic content of Co range from 1% to 12%. Thus, five samples with different Co-content were obtained from a single deposition run. No Co metal clusters were detected either by GIXRD or by SEM–EPMA in wider scan area. These structural, scanning probe and elemental analysis clearly suggest that Co substitutes for Ni up to the doping level of 10% without disturbing the cubic rock-salt Li:NiO structure.

Magneto-optical Kerr rotation (θ_k) as a function of photon energy for the Co and Li co-doped NiO films at room temperature are displayed in Fig. 2. All the samples show negative Kerr rotation with a systematic single dip in an applied magnetic field of 20 kOe. Photon energy dependency of Kerr rotation for various Co-content (x) is clearly evident in Fig. 2. The systematic shift in the dip is found to be in the photon energy range from 2.1 eV for $x = 0.02$ to 3.1 eV for $x = 0.08$, respectively in $Co_{1-x}Li_{0.2}Ni_{0.8-x}O$ film. Assuming that majority of the cobalt ions are in Co^{2+} oxidation state, these systematic results are attributed to broad nature of d–d intra-valence charge transfer (IVCT) transitions in which a d electron in a cation is transferred to a neighboring cation through optical excitation [20].

Fig. 3 shows the optical spectrograph of $Co_xLi_{0.20}Ni_{0.80-x}O$ films as a function of wavelength. The average transmittance remained to be more than 75% in the visible region and near-infrared region and it was improved systematically from the Co:Li:NiO-rich to Li:NiO-rich regions of the film, i.e., with decreasing Co-
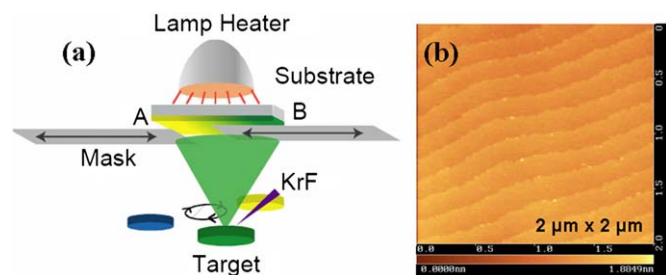

Fig. 1. (a) Schematic of the combinatorial composition spread fabrication technique using pulsed laser deposition and (b) AFM image of the 15-nm-thick NiO buffer layer deposited on MgO(1 0 0), which was used as substrate for the combinatorial experiment.