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Binary composition spread approach for parallel pulsed laser deposition synthesis and highthroughput characterization of transparent and semiconducting oxide thin films

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Conventional ‘one by one’ synthesis approach has been a major rate limiting step in the systematic exploration of increasingly complex materials for the demanding new technologies. Derived from the new concepts of combinatorial chemistry, recently introduced continuous binary composition spread technique based on the non-uniformity of the deposition rate typically observed in pulsed laser deposition (PLD) is applied to the parallel growth of transparent and semiconducting oxides $Li_xNi_{1-x}O$. A large variation of x in $Li_xNi_{1-x}O$ was achieved on a single MgO(100) substrate. Details of the synthesis technique are discussed. Microstructural, transport and optical studies were done to optimize the Li concentration in the film. XRD and AFM confirmed an epitaxial growth and smooth surface for all the Li contents. SIMS data revealed a non-linear Li variation along the film with a minimum of 0.01% of Li content. High conductivity of 1.42 ohm^{-1} cm^{-1} was obtained in sufficiently high Li concentration regions. Optical transparency beyond 80% was obtained in the 40 nm thick films. The combinatorial binary composition spread technique results in significant time and energy savings for rapidly optimizing the thin film growth parameters to explore new TCOs for future optoelectronic applications.

Keywords: Pulsed laser deposition, Semiconducting oxide thin films, Thin films

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1 Introduction

Recently, the search for new functional materials 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 form of the continuous composition spread techniques have been employed for quick optimization of compositions in thin film fabrication. Excellent research papers on combinatorial PLD thin film fabrication can be found in Refs (1–3). A case study on the transparent conducting oxides (TCO), which are the focus of attention in recent years due to its wide range of applications in oxide as well as opto-electronics[4-6] has been reported. Most of the presently known TCO films, for example, indium tin oxide (ITO), impurity doped tin oxides and impurity doped zinc oxides are *n*-type semiconductors with free electrons resulting from extrinsic donors as well as intrinsic donors. However, for large scale opto-electronic device applications, transparent conducting *p*-type semiconductors are required. NiO is an interesting candidate of this class with a wide band gap of 3.6 to 4.0 eV and exhibits very low *p*-type conductivity[7-9]. Although, stoichiometric NiO is an isulator, 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 and/or interstitial oxygen in NiO crystallites[8].

Often wide band gap, hence, optical transparency and conductivity prove to be difficult to achieve in a single functional material. Combinatorial composition spread is an ideal tool for optimizing and elucidating such type of novel property in oxide systems[1]. In conventional one by one synthesis by PLD of pure NiO and Li doped NiO thin films, the former shows high optical transparency but electrically insulating behaviour, whereas the Li:NiO is highly conductive with degraded transparency. We have synthesized a series of $Li_xNi_{1-x}O$ films on a single substrate through combinatorial composition spread approach[2] and investigated their microstructural, electrical and optical properties in order to find an optimum balance between transparency and conductivity in the film as a function of Li concentration.

2 Experimental Details

A composition spread thin film of $Li_xNi_{1-x}O$ was deposited on single crystalline MgO(100) substrate by the combinatorial pulsed laser deposition (PLD) technique in 10 m Torr of oxygen at a substrate temperature T_s = 600°C. The base pressure of the deposition chamber was 2×10^{-8} Torr. Ultraviolet KrF excimer laser (λ= 248 nm) pulses ablated ceramic targets of NiO and $Li_{0.20}Ni_{0.20}O$ alternatively 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 $Li_xNi_{1-x}O$ was changed on MgO(100) substrate along one direction of the substrate with a span of 9 mm on 15 mm long substrate. Fig. 1 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 40 nm.

Surface morphology of the film was studied by the Atomic Force Microscopy (AFM) and the film thickness was determined by a stylus profiler (Veeco; Dektak3 ST). Resistivity measurements were performed by using the Quantum designed PPMS. Au/Ni were thermally evaporated through metal shadow masks for making the electrodes. Li concentration in the film was determined by Secondary Ion Mass Spectroscopy (SIMS) measurements with the mass set: ^6Li, C, O, $^6Li^+$, ^{26}Mg, Al, Si, Ni, and ^{60}Ni, using O^{2+} primary beam intensity. Optical properties were studied by UV-Visible Spectrophotometer (UV-3100, Shimadzu Co, Japan).

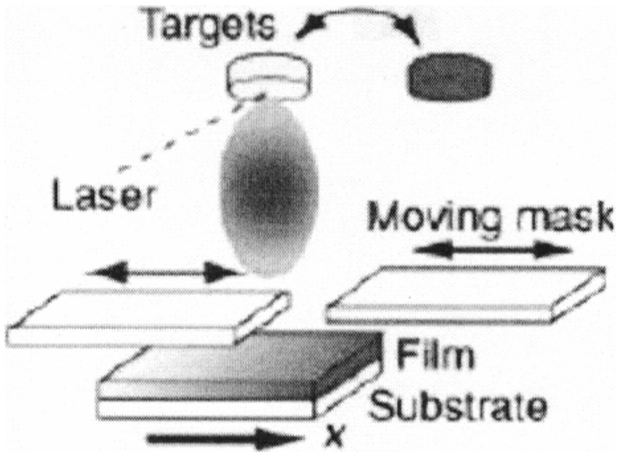

Fig. 1—Schematic of combinatorial binary composition spread fabrication technique using pulsed laser ablation

3 Results and Discussion

At first, the growth conditions of the film were optimized by depositing $Li_{0.20}Ni_{0.80}O$ films at substrate temperatures from 500 to 700°C under 10 mTorr of oxygen pressures. Fig. 2(a) shows typical X-ray diffractograph of the film deposited at T_s=600°C under 10 mTorr oxygen. An epitaxial growth of Li:NiO is evident with no other peaks than the NiO (200) in the XRD pattern of Fig. 2(a). This is expected as both, MgO (100) and NiO have the same cubic rock-salt structure with very small lattice mismatch of 0.85%. Although, the films deposited at 650°C and higher temperatures, were epitaxial in structure with smooth surface morphology but found to be electrically insulating due to a significant Li evaporation. The substrate temperature of 600°C was, therefore, chosen for the composition spread experiments. Fig. 2(b) shows AFM images at two different positions of the composition spread film. A smooth surface can be seen with an RMS roughness of 0.21 nm, which is smaller than the NiO unit cell value (0.417 nm). The average particle size estimated from the AFM images was in the range 40-50 nm. We have recently shown that higher annealing temperatures can lead to an atomically flat, step and terrace surface morphology for this compound, however, at such a temperature due to severe Li evaporation no conductivity was observed[10]. In our fabrication method, the composition of the film is

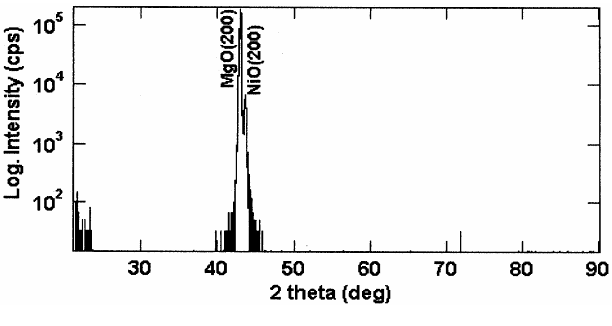

Fig. 2—(a) XRD of the Li:NiO film deposited at 600°C under 10 mTorr oxygen

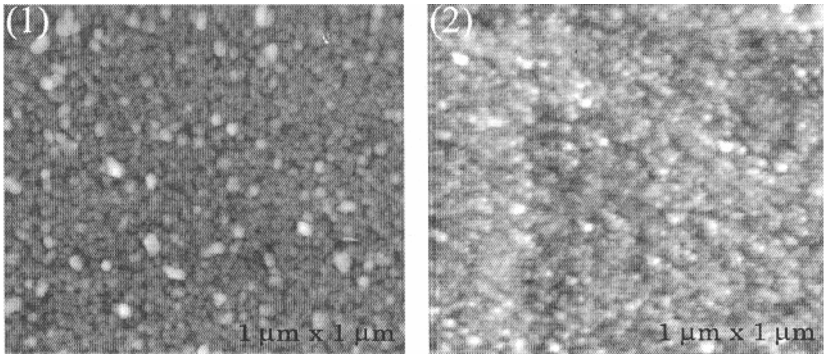

Fig. 2—(b) AFM images of composition spread films (1) Li:NiO-rich region (2) NiO rich region

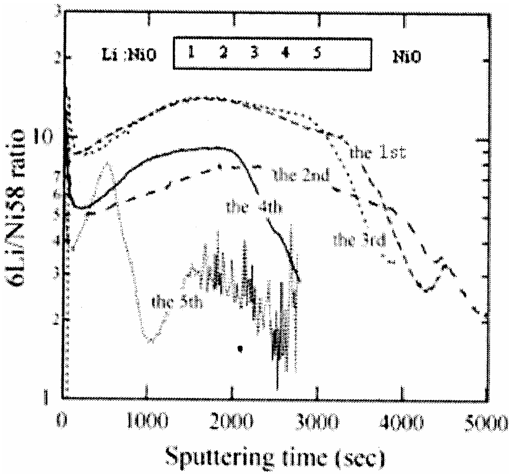

Fig. 3—Results of the SIMS analysis for the $Li_xNi_{1-x}O$ composition spread film: $^6Li/^{58}Ni$ ratio as a function of sputtering time, measured at five different points as schematically indicated in the inset

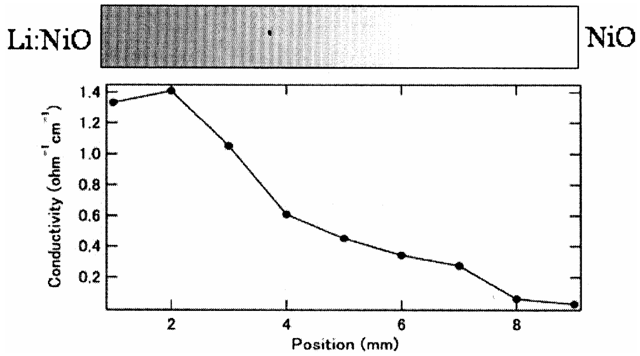

Fig. 4—Room temperature conductivity as a function of position from the Li:NiO to NiO ends of the film

intended to change linearly along positions in the film by using the moving masks and the synchronized laser pulses, one of the intriguing problems is the evaporation of Li which is very common in case of PLD deposition of Li:NiO films[11]. This makes it difficult to precisely control the exact value of x in $Li_xNi_{1-x}O$ at a given position in the film. The Li concentration in the film at five arbitrarily chosen points was determined by Secondary Ion Mass Spectroscopy (SIMS) and the results are presented in Fig. 3. The $^6Li/^{58}Ni$ ratio was found to decrease nonlinearly from Li:NiO-end to NiO-end of the film, giving a maximum 10% and a minimum 0.01% of Li content, respectively. At the intermediate Li contents, the $^6Li/^{58}Ni$ ratio exhibited remarkable discontinuities with increasing Ni ion sputtering time (Fig. 3). The observed variations and discontinuity in the SIMS spectra clearly indicate an inhomogeneous Li evaporation even at the substrate temperature of 600°C. Fig. 4 shows the conductivity results on the composition spread film measured at room temperature. Starting from as high as 1.42 $ohm^{-1}cm^{-1}$, the conductivity was almost linearly decreased with decreasing Li concentration. However, a slight non-linearity in the conductivity is attributed to the non-linear Li deficiency in the film, which is consistent with the observed SIMS spectra. The carrier concentration, which is directly related to the number of Li^{1+} ions for each Ni^{2+} in the crystal, should also be changing non-linearly, resulting in the observed conductivity behaviour of Fig. 4. Hall effect measurements[12] showed the conduction to be of *p*-type. The average hole concentration in the intermediate region of Li doped NiO film was estimated to be 3×10^{18} cm^{-3} and the carrier mobility[12] was calculated to be 0.27 cm^2/V s . These values were consistent with reported values for the bulk NiO samples[9].

Optical spectrographs of the $Li_xNi_{1-x}O$ film in the Li rich, intermediate and Li deficient regions are shown in Fig. 5. The average transmittance remained

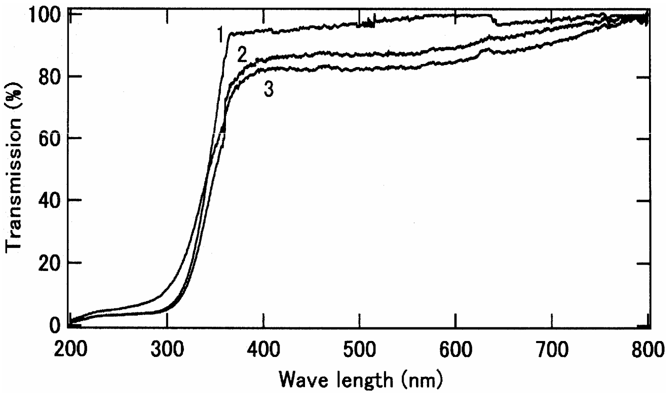

Fig. 5—UV-Vis transmission spectra collected in the three different regions of the film (1) NiO-end (2) intermediate and (3) Li:NiO-end

to be more than 0.80 in the visible region and it was improved systematically from the Li rich to Ni rich regions of the film. The absorption edges were found to be slightly shifted towards higher wavelength with increasing Li content in the film. The optical band gap calculated from the UV-Vis spectra found to decrease from NiO-end to Li:NiO-end by approximately 0.30 eV, with a maximum of 3.624 to 3.321 eV (Fig. 5, curve 1 and 3) and the optical transparency was correspondingly decreased. The observed decrease in the band gap indicates that Li substitution for Ni significantly enhances the hole concentration in the NiO complex, a result well established in the literature for the bulk[8] Li doped NiO.

4 Conclusions

Epitaxial thin films of transparent and semiconducting oxides $Li_xNi_{1-x}O$ were synthesized by combinatorial pulsed laser deposition with the binary composition spread approach. High conductivity of 1.42 $ohm^{-1}cm^{-1}$ was obtained in sufficiently high Li concentration regions. SIMS data revealed a non-linear Li variation along the film. The conductivity was found to decrease with decreasing Li concentration in a slightly non-linear fashion due to the insufficient hole concentration caused by Li evapotation. High optical transparency beyond 80% was obtained in the 40 nm thick film. Present findings demonstrate that the combinatorial composition spread technique is a powerful tool for quickly optimizing the growth parameters to explore new TCOs for future optoelectronic applications.

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