Structure and properties of Mn–Co–Ni–O thin films

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Abstract. Mn1.56Co0.96Ni0.48O4 (MCN) thin films were prepared by chemical solution deposition method on the silicon substrate. The spinel structure and the dense surface morphology of the MCN thin films were characterized by X-ray diffraction, scanning electron microscopy and atomic force microscopy, respectively. The optical constants of the MCN thin films in the mid-infrared wavelength range were determined by measuring the ellipsometry parameters and modelling through the Drude-Lorentz oscillator dispersion formula. The refractive index decreases while the extinction coefficient increases with the increase of wavelength. The electrical resistance of the MCN thin films decreases rapidly with increasing temperature, indicating an NTC characteristic. It is expected that MCN thin films will show considerable application potential in the infrared detection.

1. Introduction

Transition metal oxides have been of great interest due to the abundant physical phenomena, such as metal-insulator transitions, spin glasses, high-temperature superconductors, giant magnetoresistance and so on[1, 2]. These diverse electrical and magnetic properties come from the complex interactions among spins, charges, lattices and orbitals. Due to these special characteristics, spinel-type transition metal oxides have great potential for applications in electronic, optoelectronic and spintronic devices [3]. Mn-Co-Ni-O is one of these transition metal oxides, which is known as a spinel compound with negative temperature coefficient (NTC) property and is usually used in temperature compensation device, temperature sensor device, surge protection device and uncooled infrared detector[4, 5]. Mn1.56Co0.96Ni0.48O4 (MCN) is considered to be a prominent component because its resistivity is close to the lowest resistivity of these ternary compounds[6]. Dense polycrystalline MCN thin films exhibit good crystallization and electrical properties, such as low resistance, high sensitivity and stability, compared to their bulk counterparts [7, 8]. Additionally, MCN and its complexed thin films have relatively large absorption coefficients and can be promising candidates for electrode and thermal absorption layers in detectors [3]. Therefore, revealing the optical and electrical properties of MCN thin films would greatly contribute to their applications in oxide optoelectronics. In this work, MCN thin films have been synthesized using a wet chemical process and the structural, optical and electrical properties have been characterized and discussed in detail.

2. Experimental

MCN thin films were deposited on silicon (100) substrate using the chemical solution deposition (CSD) method. Mn(CH3COO)2·4H2O (AR, 99.0%), Co(CH3COO)2·4H2O (AR, 99.5%), and
Ni(CH$_3$COO)$_2$·4H$_2$O (AR, 99.5 %) were chose as raw materials with molar ratios of Mn: Co: Ni = 13: 8: 4. Dissolved these acetates in glacial acetic acid and adjusted the concentration to 0.2 mol/L. The solution was then spin-coated on a silicon substrate at a speed of 3000 rpm for 30 seconds. Each layer of wet film was dried for 6 minutes at 350 °C. The above spin coating and heat treatment processes were repeated 10 times. Finally, the resulting films were annealed at 750 °C for 2 hours to improve crystallinity.

The phase structure of the MCN thin films was investigated by X-ray diffraction (XRD, Bruker D8). The morphology and surface roughness of the MCN thin films were observed by scanning electron microscopy (SEM, Supra55VP, Zeiss) and atomic force microscopy (AFM, Asylum Research MFP-3DTM), respectively. The optical constants of the MCN thin films were obtained by spectroscopic ellipsometry (SENTECH SE850) in the mid-infrared wavelength range of 2 to 12 μm. The relationship between the resistance and test temperature was measured on a heating stage using a digital multimeter (Agilent 34410A).

3. Results and discussion

Figure 1 shows the XRD pattern of the MCN thin films deposited on the silicon substrate. All diffraction peaks are labelled with Miller indices ($hkl$) and can be attributed to a cubic spinel structure with a space group of $Fd-3m$ (according to JCPDS-ICDD 84-0542). The strong and narrow diffraction peaks indicate the formation of well-crystallized polycrystalline films. The crystallite size of the MCN thin films is approximately calculated by the Scherrer equation and obtained as 30.2 nm.
Figure 2. (a) SEM image and (b) three-dimensional (3D) AFM image of the MCN thin films.

The SEM image of the MCN thin films is shown in figure 2 (a). As can be seen, the surface of the MCN thin films is extremely dense and consists of many uniform grains around 200 nm. The dense film morphology can reduce the influence of ambient conditions, such as a variation of ambient humidity [9]. As shown in figure 2 (b), the surface morphology of the MCN thin films is also confirmed by AFM measurements on an area of 4×4 μm². The surface roughness value of the MCN thin films is measured to be 7.8 nm, which also indicates that the surface of the MCN thin films is very smooth due to the uniform and small particles.

For spectroscopic ellipsometry measurement, the Drude-Lorentz (DL) oscillator dispersion formula is used to simulate the dielectric functions of the thin films. A three-layer model (air/MCN/substrate) is developed to accurately characterize the dielectric properties of the MCN thin films. The DL dispersion function can be expressed as follows [10]:

\[ \varepsilon = \varepsilon_1 + i\varepsilon_2 = \varepsilon_{\infty} - \frac{\omega_p^2}{\nu^2 + i\omega_p\nu} + \sum_{k=1}^{n} \left( \frac{\Omega_p^2}{\Omega_p^2 - \nu^2 - i\Omega_p\nu} \right) \]  

where \( \nu = \omega / 2\pi c = (1/\lambda)\varepsilon_{\infty} \) is the high-frequency dielectric constant, representing the effect of the internal electric field on the Lorentz oscillator. The \( \Omega_p, \Omega_o \) and \( \Omega_d \) of the Lorentz oscillator part represent the strength, center frequency, and damping of the oscillator, respectively. \( \omega_p \) depends on the concentration of free carriers \( N \) and the effective mass \( m^* \): \( \omega_p = \sqrt{N\varepsilon_{\infty}} ^{\varepsilon_2 / \varepsilon_1} \). \( \omega_o \) depends on the mobility of free carriers \( \mu \) and the effective mass \( m^* \): \( \omega_o = \frac{e}{m^*} \mu \). Meanwhile, the refractive index \( n \) and extinction coefficient \( k \) are determined by the following equations[11]:

\[ n = \frac{1}{\sqrt{\varepsilon_1}} \sqrt{\varepsilon_1^2 + 2\varepsilon_2^2} \]
\[ k = \frac{1}{\sqrt{\varepsilon_1}} \sqrt{\varepsilon_1^2 + 2\varepsilon_2^2} \]
From the best fit obtained between the measured and fitted data, the evaluated optical constants of the MCN thin films are presented in figure 3. The refractive index \( n \) first decreases rapidly with increasing wavelength and then increases slowly. For the extinction coefficient \( k \) value, it increases rapidly with increasing wavelength in the range of 2-12 \( \mu \)m. The similar results have been observed by W. Zhou et al[12]. The refractive index of the sample reaches a maximum value of about 2.06 at 2 \( \mu \)m, and a maximum \( k \) value of about 0.14 at 12 \( \mu \)m. It is generally believed that optical constants are mainly influenced by crystal quality, thermal mismatch strain, electronic band structure, lattice point defects, annealing temperature and so on[13]. In particular, the relatively high \( k \)-value indicates that the MCN thin films have a strong optical absorption capacity and are suitable for use in infrared detectors[14].

Figure 3. Refractive index \( n \) and extinction coefficient \( k \) of the MCN thin films.

Figure 4. Relationship between the resistance and test temperature of the MCN thin films. The inset is the schematic diagram of the electrode structure.
Figure 4 shows the resistance of the MCN thin films as a function of test temperature. The resistance decreases with increasing temperature, indicating an NTC characteristic. The resistance value measured at 30 °C is 4.80 MΩ, which drops to 0.99, 0.30, and 0.05 MΩ at 60, 90 and 150 °C, respectively. The small resistance obtained in this work can be primarily attributed to the uniform grain size and dense structure of the sample. A smaller number of insulating grain boundaries means a lower electron conduction barrier, which leads to a lower resistance[15]. On the other hand, the rapid decrease in resistance as the temperature increases indicates that the MCN thin films can be used as NTC thermistors.

4. Conclusions
In summary, the MCN thin films were synthesized through the CSD method and the structure, optical and electrical properties were characterized. The thin films have the uniform grain size and the dense surface. In the mid-infrared band, the refractive index of the MCN thin films decreases and the extinction coefficient increases with increasing wavelength. The resistance of the MCN thin films decreases rapidly with increasing temperature. These results indicate that the MCN thin films are suitable for the fabrication of infrared detectors.

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