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Thickness dependent ferromagnetism in thermally decomposed NiO thin films

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ABSTRACT

We report the effects of film thickness, annealing temperature and annealing environments on thermal decomposition behavior and resulting magnetic properties of NiO (t=50–300 nm) thin films. All the NiO films were prepared directly on thermally oxidized Si at ambient temperature using magnetron sputtering technique and post annealed at different temperatures (T_A) under vacuum and oxygen atmospheres. As-deposited films exhibit face centered cubic structure with large lattice constant due to strain induced during sputtering process. With increasing T_A, the lattice constant decreases due to the release of strain and thickness dependent thermal decomposition reaction of NiO into Ni has been observed for the NiO films annealed at 500 °C under vacuum condition. As a result, the antiferromagnetic nature of the as-deposited NiO films transforms into ferromagnetic one with dominant thickness dependent ferromagnetic behavior at room temperature. In addition, the existence of both Ni and NiO phases in the annealed NiO films shows noticeable exchange bias under field cooling condition. The behavior of thermal decomposition was not observed for the NiO films annealed under oxygen condition which results in no detectable change in the magnetic properties. The observed results are discussed on the basis of thickness dependent thermal decomposition in NiO films with increasing T_A and changing annealing conditions.

1. Introduction

Recently nanostructured nickel oxide (NiO) materials have received enormous interest due to their novel properties, which are considerably different from those observed in bulk material, and their potential applications in a wide variety of technological areas such as spin valves, magnetic recording, resistive random access memory, electrochromic, supercapacitors, alkaline batteries, etc [1–6]. The proper control of size, shape, morphology and surface of nanostructures remains a challenge as the properties are strongly depending on the structures at the nanoscale. In particular, the development of magnetism in NiO based thin films was focused to obtain ferromagnetism above room temperature such that these oxides with cubic structure could easily facilitate integration of spintronic devices. As a result, different fabrication methods such as sol–gel [7], vacuum evaporation [8], pulsed laser deposition [9], magnetron sputtering [10–13] and reactive ion beam sputtering [14] were employed for the preparation of NiO films.

It is well known that the bulk NiO is an antiferromagnetic (AFM) material with a Néel temperature (T_N) of 523 K and transforms from cubic to rhombohedral structure below T_N [15,16]. However, NiO thin films interestingly show unusual properties due to the occurrence of structural disorder, vacancies of nickel and/or oxygen, aligned dislocations into NiO crystal, finite size effect, etc. For instance, Sugiyama et al. [9] demonstrated that dislocations in NiO crystals show unique magnetic properties with high coercivity due to the strong interaction between the ferromagnetic dislocations and surrounding AFM bulk phase. While Jang et al. [17] reported that the enhanced electrical properties of sputtered NiO thin films are mainly due to the nickel vacancy based defects, Yang et al. [18] shown that the non-stoichiometric NiO thin films should contain excess oxygens at interstitial positions, which diffuse out during the annealing process and hence tune the electrical, chemical and optical properties. Bruckner et al. [19] reported that the sputtered NiO films having non-stoichiometric NiO decompose during heating at high temperatures (T_A) into thermally stable oxygen poorer NiO and/or metallic Ni. Similarly, Kawai et al. [20] reported that annealing of NiO films above 400 °C under high vacuum environment produces conducting filaments in single crystalline NiO, which results in memory cell. Recently, Jang et al. [21] reported that the decomposition reaction of NiO films strongly depends on T_A and thickness of the films (t). These results reveal that the thermal decomposition of sputtered NiO is very much important for selected practical applications such as

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resistive random access memory and spintronic devices. However, the related mechanism of thermal decomposition as a function of thickness and annealing temperature, and the resulting magnetic properties are still unclear. Therefore, in this study, we report the thickness dependent thermal decomposition behavior and the resulting magnetic properties of NiO thin films deposited using magnetron sputtering technique at ambient temperature directly on thermally oxidized Si substrate and post annealed at different T_A under high vacuum environment. The observed results are also compared with the results obtained by annealing the as-deposited NiO films under oxygen condition.

2. Experimental details

NiO (t nm) single layer thin films with various thicknesses (t=50–300 nm) were deposited directly on thermally oxidized Si substrate by sputtering NiO target (50.8 mm diameter and 3 mm thickness) using magnetron sputtering technique with various process parameters. NiO sputtering target was prepared by ball milling the high purity NiO (99.9% Sigma Aldrich, USA) powders using high energy planetary ball mill followed by sintering process. Before starting the deposition, the base pressure of the chamber was evacuated below 5×10^{-7} Torr. Sputtering was carried out at ambient temperature in an argon atmosphere of 21 mTorr. The optimization of argon gas pressure was done mainly by analyzing the formation of NiO thin films with AFM nature. The deposition rate of NiO films was pre-calibrated using ex-situ surface profilometer (Vecco, Dektak 150 model). Accordingly, the deposition rate for NiO thin film under the above sputtering conditions was optimized to be 1.67 nm/min. All the as-deposited films were post annealed ex-situ in a separate high vacuum ($< 10^{-6}$ Torr) annealing setup at different T_A: 300 °C, 400 °C and 500 °C for 70 min duration. In order to compare the resulting properties, the NiO films were also annealed at 500 °C under oxygen atmosphere. The annealing temperature and annealing time were optimized based on the thermal decomposition behavior of NiO thin films.

Crystal structure and microstructure properties of the as-deposited and annealed films were analyzed through X-ray diffraction (XRD) obtained using high-power X-ray diffractometer (Rigaku TTRAX III, 18 kW) with Cu-K$_\alpha$ radiation (λ=1.54056 Å) and transmission electron microscopy (TEM, JEOL 2100) techniques, respectively. XRD data were collected at a slow scan rate of 0.005°/s for analyzing the structural parameters. Magnetic properties of the films were analyzed by using vibrating sample magnetometer (VSM, Lake Shore Model 7410) by performing magnetic hysteresis loops ($M-H$) along the film plane at different constant temperatures in the temperature range of 30–300 K.

3. Results and discussion

3.1. Structural properties of NiO thin film

Fig. 1 depicts the room temperature XRD patterns of the as-deposited and annealed NiO (t nm) thin films at different temperatures under vacuum and oxygen annealing conditions. In order to compare the XRD patterns of the thin films with the bulk counterpart, XRD pattern of the bulk NiO powder with rescaled intensity is also included in Fig. 1a. The XRD patterns show the following features: (i) All the NiO films grown with different thicknesses exhibit face centered cubic (*fcc*) structure and highly oriented along (200) plane. The intensity of the (200) peak increases with increasing NiO film thickness. The absence of any other impurity peaks within the detection limit of X-ray diffractometer confirms the formation of high purity NiO thin films. (ii) However, a careful comparison between the as-deposited films and bulk NiO powder confirms that the peaks are substantially broadened and the peak positions are shifted noticeably to lower angles. This suggests that the as-deposited films have fine crystallites and large lattice constant as compared to the bulk NiO. (iii) With increasing T_A up to 400 °C, the peak broadening decreases gradually along with a considerable shift in the peak position to higher angles as shown in Fig. 1b and c. This confirms that the average crystallite size increases and lattice constant decreases with increasing T_A. (iv) On further increasing T_A to 500 °C, the NiO films with $t \leq 100$ nm exhibit no detectable peaks related to *fcc* phase of NiO, but display only the peak corresponding to Ni phase. This reveals that the NiO films decompose into Ni. With increasing $t > 100$ nm, we observed the existence of two peaks corresponding to (200) peak of NiO and (111) peak of Ni. Interestingly, the relatively intensity of the NiO(200) peak increases with increasing NiO film thickness from 200 nm to 300 nm. This suggests that the amount of decomposition reaction from NiO into Ni decreases with increasing NiO film thickness [21]. These results clearly suggest that the thermal decomposition reaction of NiO into Ni

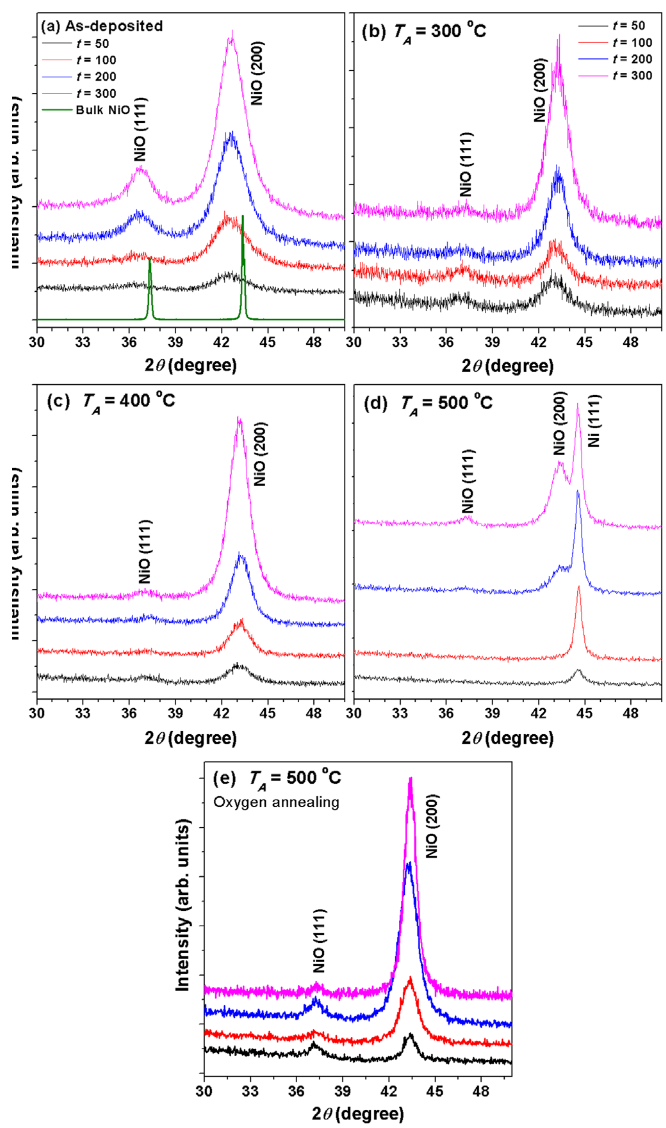

Fig. 1. Room temperature XRD patterns of as-deposited (a) and annealed NiO thin films with different thicknesses at different temperatures under vacuum (b,c,d) and oxygen (e) conditions.