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Enhanced performance of NiMgO-based ultraviolet photodetector by rapid thermal annealing

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ABSTRACT

$Ni_{1-x}Mg_xO$ thin films for metal–semiconductor–metal (MSM) ultraviolet (UV) photodetector were deposited by pulsed laser deposition. The effects of rapid thermal annealing (RTA) on both structural and optical properties of the thin films were studied. After RTA treatment, the $Ni_{1-x}Mg_xO$ films showed better crystalline quality with a larger optical band gap. Moreover, the effect of RTA on the current–voltage characteristics of MSM UV photodetector fabricated on the $Ni_{1-x}Mg_xO$ thin film was investigated, too. The results revealed that the series of dark current is significantly reduced from 390.50 nA (as-deposited) to 19.96 nA (RTA treated at 1000 °C), which can lead to higher signal-to-noise ratio of the photodetector. Thus the performance of the photodetector was enhanced by RTA to the $Ni_{1-x}Mg_xO$ thin films.

1. Introduction

Nickel oxide (NiO) is a direct bandgap semiconductor with a band gap of about 3.7 eV. It has good thermal and chemical stability [1]. In recent years, NiO has received renewed attention and is being explored for a wide range of applications, including ultraviolet (UV) detectors [2], chemiresistive sensors [3,4], and photocathodes of dye-sensitized solar cells [5–7]. Conductive or semiconductive NiO thin films have been obtained via several methods, such as reactive sputtering [8], spray pyrolysis [9], and electrodeposition [10].

NiO and MgO have similar rock-salt cubic structures and lattice constants (0.4177 nm for NiO, 0.4209 nm for MgO) [11–13], hence they could form a perfect solid solution within which the entire MgO mole-fraction ranges from 0 to 1. The band gap of $Ni_{1-x}Mg_xO$ alloys, therefore, vary from 3.7 to 7.8 eV depending on the value of x. [14].

Therefore, the absorption edge of $Ni_{1-x}Mg_xO$ alloys can be extended from 160 nm to 335 nm, making high efficiency solar-blind UV detector based on $Ni_{1-x}Mg_xO$ thin films a promising application for the future. Recently, there are a number of reports of preparing $Ni_{1-x}Mg_xO$ thin films using radio frequency sputtering method [15], sol–gel method [16], electron beam evaporation [17], and molecular beam epitaxy [18]. $Ni_{1-x}Mg_xO$ thin films have been exploited for deep UV detectors [15,17,18]. However, there are still several problems hindering its developments, such as the poor crystallization of the film [16], the difficulty of widening the band gap to expected values [17] and the low response efficiency [18]. The solution to above problems is a huge interest of our research. Rapid thermal annealing (RTA) processing, widely used in semiconductor processing [19], can improve the crystalline quality [20], reduce the defects [21,22] and relax the residual stress of the film [23]. We applied the RTA process to $Ni_{1-x}Mg_xO$ thin films and related devices. The improvement of the performance of the NiMgO-based UV photodetector is expected.

In our previous report [24], we have deposited $Ni_{1-x}Mg_xO$ thin film on ZnO thin film using pulsed laser deposition (PLD) and measured the valence band offset of the n-ZnO/p-$Ni_{1-x}Mg_xO$ heterojunction, which plays a key role in the design and application of n-ZnO/p-$Ni_{1-x}Mg_xO$ heterojunction for UV photodetector. The aim of this work is to find the ways to investigate the performance of NiMgO-based metal–semiconductor-metal (MSM) UV photodetector, including the preparation parameters of $Ni_{1-x}Mg_xO$ thin films, the effects of RTA on structural and optical properties of $Ni_{1-x}Mg_xO$ films and the dark current of NiMgO-based UV photodetector.

2. Experimental details

We deposited $Ni_{1-x}Mg_xO$ thin films with Mg composition of around 20 atom% on quartz substrates at 400 °C by PLD method. The $Ni_{1-x}Mg_xO$ target was fabricated using NiO (99.99% purity) mixed

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with MgO (99.99% purity) powders. The mole content of Mg in the target is around 20%. $Ni_{1-x}Mg_xO$ thin films were prepared by PLD at 5 Hz, with a 25 ns, 300 mJ, 248 nm KrF excimer laser (Complex 102) for the ablation and grown at 400 °C under 20 Pa. The as-deposited films were annealed in N_2 atmosphere at 600, 700, 800, 900 and 1000 °C for 120 s, respectively. It only cost 20 s to heat from room temperature to the set temperature. The cooling rate was about 20 °C/s from the set temperature to 100 °C, and about 5 °C/s from 100 °C to room temperature.

The structure of $Ni_{1-x}Mg_xO$ thin films was characterized by an X-ray diffraction (XRD) technique using a Bede D1 system (Powder diffraction with Bragg–Bretano geometry) with a Cu Kα radiation (λ = 0.1541 nm) (PANALYCICAL X'PROX). The surface morphology of the samples was derived from the Scanning Electron Microscopy (FE-SEM; HITACHI S-4800) with the working voltage of 20 kV. The film composition was characterized by energy-dispersive X-ray (EDS, GENESISI4000) attached to the SEM with the working voltage of 20 kV and the working distance of 10.5 mm. UV–visible (U-4100; 300–1000 nm) spectral analysis was utilized to measure the transmission and energy band gap. A MSM structured photodetector was fabricated by depositing interdigital Au electrodes on the $Ni_{1-x}Mg_xO$ thin film. The current–voltage (*I*–*V*) characteristics were evaluated by using an Agilent E5270B system.

3. Results and discussion

3.1. Effect of RTA on the structure of $Ni_{1-x}Mg_xO$

Fig. 1 shows the XRD patterns of both the as-deposited $Ni_{1-x}Mg_xO$ thin film and the annealed samples by RTA at different temperatures. For the as-deposited one, there are two peaks corresponding to the NiO(111) and (200) planes, respectively, indicating that the film has reasonable crystallization with a preferential orientation of cubic NiO structure. The intensity of (200) peak decreased with rising annealing temperature and eventually disappeared when the annealing temperature reached 800 °C, which proved that RTA can improve the crystallization of $Ni_{1-x}Mg_xO$ thin films by enhancing their preferred orientations and erasing another growing planes.

According to Scherer formula, the values of the full-width at half-maximum (FWHM) of the (111) peaks are used to estimate the crystallite size [25,26]. Fig. 2 shows the FWHM and the grain size as a function of annealing temperatures. It is obvious that the as-deposited $Ni_{1-x}Mg_xO$ film has the largest FWHM and the smallest crystallite size. The FWHMs

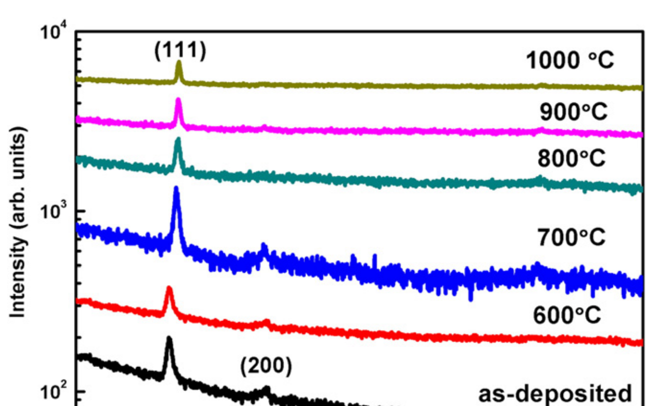

Fig. 1. The XRD patterns of the as-deposited $Ni_{1-x}Mg_xO$ film and those subjected to RTA at different temperatures.

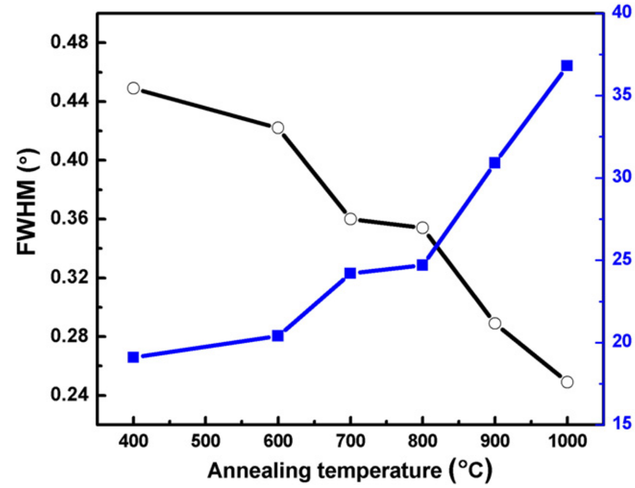

Fig. 2. Dependences of the FWHM (black hollow circles) and the grain size (blue solid squares) of the XRD (111) peak on RTA temperature for the $Ni_{1-x}Mg_xO$ films.

become smaller and the grain size gets larger as the annealing temperature elevates from 600 °C to 1000 °C. This indicates that the crystalline quality of the $Ni_{1-x}Mg_xO$ film is greatly improved after RTA treatment. It is inferred that the interstitial Mg (0.086 nm) locating on the position of Ni (0.083 nm) vacancy is the main reason for the structural improvement. Besides, the removal of structural defects in the films, such as non-stoichiometric nickel vacancies [27], and strain relaxation between the $Ni_{1-x}Mg_xO$ thin film and quartz substrate can also improve the crystal structure.

Fig. 3 shows the SEM images of the surface morphology of the corresponding films in Fig. 1. It can be seen that the grains become larger as the annealing temperature increases, which is consistent with XRD results.

3.2. Optical band gap

Fig. 4 displays the optical transmittance spectra in the wavelength range of 200–800 nm for both the as-deposited $Ni_{1-x}Mg_xO$ thin film and those annealed at various temperatures. The average optical transmittance values of each $Ni_{1-x}Mg_xO$ thin film were about 80% in the visible range (400–800 nm), indicating that annealing temperature does not influence the optical transmittance in the visible region obviously. However, we can clearly see from Fig. 4 that the absorption edge of $Ni_{1-x}Mg_xO$ film was below the wavelength of 310 nm, which is obviously shorter than the pure NiO (335 nm) [15]. Besides, it could be seen that the absorption edges of samples shifted slightly toward the shorter wavelength as the annealing temperature increased.

The optical band gaps of these thin films were deducted by using the extrapolation from the plots of $(\alpha h\nu)^2$ versus $h\nu$ [28] shown in Fig. 5. It can be seen that the band gap of the as-deposited sample was 3.78 eV, the band gap increased with increasing annealing temperature, and a band gap of 3.90 eV was achieved when the temperature reached 1000 °C. Compared with other reports which supposed that the Mg composition affects the band gap of $Ni_{1-x}Mg_xO$ films, we observed the effect of annealing process on band gap [7,16].

To further prove our discovery, we carried out EDS measurements on all samples. It was found that the films were composed of Mg, Ni and O. The calculated content ratios of Mg/Mg + Ni in the films were shown in Fig. 5. It could be seen that the Mg contents in the films increased from 0.26 to 0.31, with increasing annealing temperature. Therefore, the change of band gap resulted from the spontaneous movement of interstitial Mg toward Ni vacancy, which is due to the higher