Available online at www.sciencedirect.com
ScienceDirect
Applied Surface Science 252 (2006) 8438–8441
applied surface science
www.elsevier.com/locate/apsusc

Optical properties of In_2O_3 oxidized from InN deposited by reactive magnetron sputtering

Lung-Chien Chen [a,*], Wen-How Lan [b], Ray-Ming Lin [c], Hue-Tang Shen [c], Hung-Chang Chen [a]

[a] *Department of Electro-Optical Engineering, National Taipei University of Technology, No. 1, Sec. 3, Chung-Hsiao E. Rd., Taipei 106, Taiwan, ROC*
[b] *Department of Electrical Engineering, National University of Kaohsiung, Kaohsiung, Taiwan, ROC*
[c] *Institute of Electro-Optical Engineering, Chang Gung University, 29 Wen-Hwa 1st Road, Kwei-Shan, Tao-Yuan 333, Taiwan, ROC*

Received 26 May 2005; received in revised form 27 October 2005; accepted 15 November 2005
Available online 18 January 2006

Abstract

Unintentionally doped and zinc-doped indium nitride (U-InN and InN:Zn) films were deposited on (0 0 0 1) sapphire substrates by radio-frequency reactive magnetron sputtering, and all samples were then treated by annealing to form In_2O_3 films. U-InN and InN:Zn films have similar photon absorption characteristics. The as-deposited U-InN and InN:Zn film show the absorption edge, ~1.8–1.9 eV. After the annealing process at 500 °C for 20 min, the absorption coefficient at the visible range apparently decreases, and the absorption edge is about 3.5 eV. Two emission peaks at 3.342 eV (371 nm) and 3.238 eV (383 nm) in the 20 K photoluminescence (PL) spectrum of In_2O_3:Zn films were identified as the free-exciton (FE) or the near band-to-band (B–B) and conduction-band-to-acceptor (C–A) recombination, respectively.

Keywords: InN; Reactive magnetron sputtering; In_2O_3; Photoluminescence

1. Introduction

Indium nitride (InN) which has a wurtzite structure with a direct band gap, is of considerable interest because it has potential applications in optoelectronic devices including light-emitting diodes in the visible region and low-cost solar cells with a high efficiency [1–5]. However, the band gap of hexagonal InN films grown on a *c*-plane sapphire (0 0 0 1) substrate remains a matter of dispute. InN is difficult to grow, because it has a very low dissociation temperature (~500 °C) [6–8]; its oxide is easily formed.

Recently, several authors have studied the formation of cubic In_2O_3 films by the oxidation of hexagonal InN films [8–10]. A cubic In_2O_3 film with a band gap of approximately 3.2 eV can be used in transparent electrodes in optoelectronic devices, including light-emitting diodes, photodetectors, thin-film solar cells, touch panels and flat panel displays [10–12]. However, there has been no study in optical properties of cubic In_2O_3 transformed from hexagonal InN. Therefore, in this study, an unintentionally doped In_2O_3 and a Zn-doped In_2O_3 thin film were deposited on a (0 0 0 1) sapphire substrate by radio-frequency (RF) reactive magnetron sputtering, and the formation of an In_2O_3 film by annealing was examined. The optical absorption and photoluminescence (PL) of the unintentionally doped In_2O_3 (U-In_2O_3) and zinc-doped In_2O_3 (In_2O_3:Zn) films were studied.

2. Experiment

In this study, InN and InN:Zn films (around 6000 Å thick) were grown on sapphire substrates by magnetron reactive sputtering deposition technology from high-purity indium and indium–zinc targets (In:Zn = 99.5:0.5) with a purity of 99.999% in nitrogen (N_2) gas at a flow rate of 9 sccm and a stable pressure of 3×10^{-3} Torr. The sputtering system consisted of a vacuum chamber with a target and a substrate copper holder, a turbo molecular pump parallel to a rotary pump that provides a high vacuum, a radio-frequency power supply at

* Corresponding author. Tel.: +886 2 2771 21713; fax: +886 2 8773 3216.
E-mail address: ocean@ntut.edu.tw (L.-C. Chen).

0169-4332/$ – see front matter
doi:10.1016/j.apsusc.2005.11.051

Table 1
Deposition conditions

Substrate	(0 0 0 1) sapphire
Substrate temperature	500 °C
Substrate-to-target distance	8 cm
RF power	50 W
Targets	In and InZn (99.5:0.5)
Gas	N_2
Residual pressure	$<5 \times 10^{-6}$ Torr
Sputtering pressure	3.1 mTorr
Deposition time	60 min

13.56 MHz, and mass flow controllers that maintain a steady gas flow rate. The target was cleaned by presputtering with Ar plasma for 5 min prior to each deposition process. The RF power and the gas pressure were kept constant at 50 W and 3.1×10^{-3} Torr, respectively, in all experiments. The temperature of the sapphire substrate during the deposition was monitored using a thermocouple and controlled at 500 °C using a heater behind the substrate. Table 1 presents the typical deposition conditions. Annealing treatment was performed at 500 °C for 20 min by rapid thermal annealing (RTA). Optical absorption coefficient was measured using a spectrometer in the range of 350–800 nm. The photoluminescence at temperatures from 20 to 200 K was measured using He–Cd laser excitation (326 nm line) at ranging from 330 to 700 nm and argon-ion laser excitation (514.5 nm line) at ranging from 700 to 1200 nm.

3. Results and discussion

Fig. 1 shows a typical X-ray diffraction (XRD) patterns of (a) as-deposited InN:Zn film and (b) InN:Zn film after 500 °C annealing for 20 min. A peak from (0 0 0 2) InN at 30.65° is observed for as-grown InN films. The peak is shifted from 30.65° [InN (0 0 0 2)] to 30.55° [In_2O_3 (2 2 2)] after annealing process. The In_2O_3 (2 2 2) peak is appeared, indicating that InN is dissolved and In_2O_3 formed.

A typical result of the absorption experiment is shown in Fig. 2, which shows plots of the absorption squared versus photon energy. In this figure, U-InN and InN:Zn films have similar absorption characteristics. The as-grown InN film yields an absorption edge at ~1.8–1.9 eV. Many groups have reported that the band gap energy of InN is around 0.7 eV. The oxygen caused a large absorption edge (~2 eV) because of the Burstein–Moss effect [2,4,13–15]. An extrapolation of the linear region to the horizontal axis gives the band gap energy of InN and In_2O_3. The as-deposited InN:Zn film shows the absorption edge, ~1.8–1.9 eV. After the annealing process at 500 °C for 20 min, the absorption coefficient at the visible range apparently decreases, and the absorption edge is about 3.5 eV, which is the band gap of indium oxide [16].

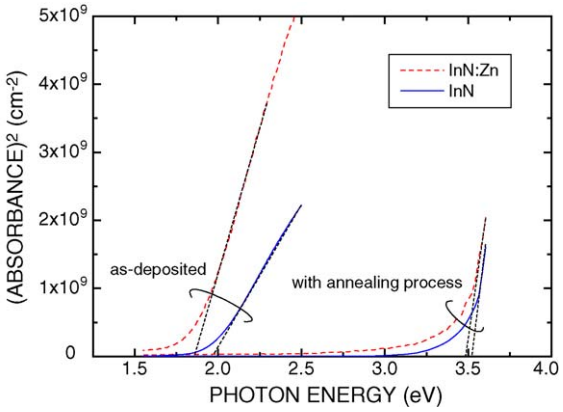

Fig. 2. Relationship between absorbance squared and photon energy at room temperature.

Fig. 3 shows the temperature dependence (T = 20–200 K) of PL spectra of the In_2O_3:Zn film at a sputtering power of 50 W following the 500 °C RTA process for 20 min. These spectra are normalized to the same main peak intensity and are obtained by exciting the wafer at 35 mW at ranging from 340 to 530 nm. The 20 K PL spectrum of the In_2O_3:Zn InN film is dominated by peak B at 3.238 eV (383 nm), but with one weak shoulder located at 3.342 eV (371 nm, denoted as A) on the high-energy side of peak B. Besides, a weak band at 3.062 eV (405 nm, denoted as C) on the low-energy side of peak B was observed.

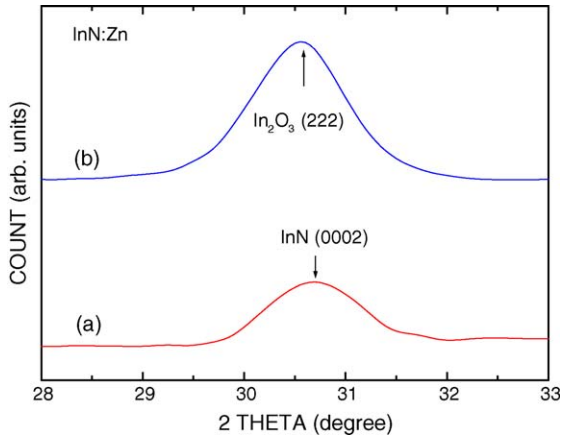

Fig. 1. Typical X-ray diffraction (XRD) patterns of: (a) as-deposited InN:Zn film and (b) InN:Zn film after 500 °C annealing for 20 min.

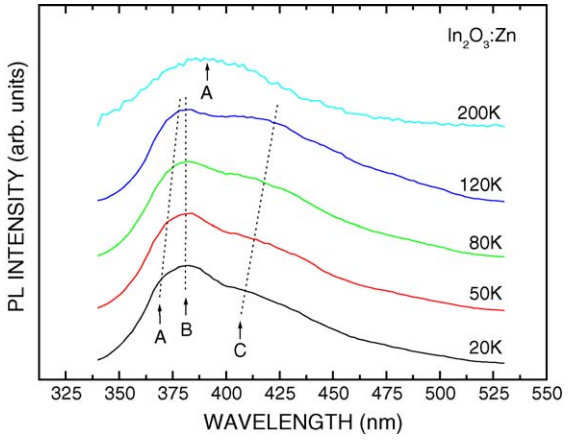

Fig. 3. PL spectra of the In_2O_3:Zn film at various temperatures in which the In_2O_3:Zn film was transformed from InN:Zn deposited at sputtering power of 50 W after 500 °C annealing for 20 min.