Applied Surface Science xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Structural and optical properties of highly (110)-oriented non-polar ZnO evaporated films on Si substrates

Shang-Dong Yang, Yu-Xiang Zheng*, Liao Yang, Zhun-Hua Liu, Wen-Jie Zhou, Song-You Wang, Rong-Jun Zhang, Liang-Yao Chen

Department of Optical Science and Engineering, Fudan University, Shanghai Engineering Research Center of Ultra-Precision Optical Manufacturing, 200433, Shanghai, China

ARTICLE INFO

Article history:
Received 31 July 2016
Received in revised form 6 February 2017
Accepted 9 February 2017
Available online xxx

Keywords:
Zinc oxide
Electron beam evaporation
Spectroscopic ellipsometry
Optical property

ABSTRACT

Zinc oxide (ZnO) films with thicknesses from (9.1 ± 0.7) to (145 ± 7) nm were deposited on silicon substrates by ion-assisted electron beam evaporation (EBE), and transformed to a highly (110)-oriented non-polar phase through thermal treatment at temperatures of 300, 500, and 700 °C. The structural, morphological and optical properties of the ZnO thin films were systematically characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), atomic force microscopy (AFM), spectroscopic ellipsometry (SE), and photoluminescence (PL). The XRD and AFM results illustrate that the deposited ZnO films evolved from an X-ray amorphous structure to the polycrystalline hexagonal wurtzite structure with increasing thickness and experienced a crystallographic plane improvement from (102) to the (110) non-polar phase during annealing. The dielectric functions of the whole layer are mainly affected by the dielectric responses near the surface of ZnO nanocrystals and show an upward trend with nanocrystal growth, induced by thickness and annealing temperature. The optical band gaps were also investigated and correlated with the structural properties. In the PL spectra, a strong ultraviolet luminescence (UVL) band and a weak visible green luminescence (GL) band were observed. The intensity ratio of UVL and GL—associated with crystal quality—agrees with the results acquired from other measurements. The two determinants for highly (110)-oriented non-polar ZnO films are the suppression of growth in the (002) direction by ion bombardment and the promotion of the (110) plane induced by diffusion energy during annealing.

1. Introduction

The II–VI semiconductor zinc oxide (ZnO) is a transparent conductive oxide (TCO) [1] that attracts attention because of its unique optical and electronic properties [2,3]. For example, its large exciton binding energy (60 meV) is an excellent property for building white or ultraviolet (UV) optoelectronic devices. Besides, ZnO has a wide energy band gap (3.37 eV) in the UV region [4,5]. It is widely used in the optoelectronic industry, such as in varistors [6], UV optoelectronic devices [7,8], window heaters [9], transparent high power electronics [10], optical coatings [11,12], and thin film solar cells [13]. As known, ZnO tends to crystallize along the (002) direction [14,15]. Structural, optical, electronic, and acoustic properties [16–20], and various deposition and post treatment methods of (002) ZnO single crystals and highly (002)-oriented polycrystalline ZnO have been widely studied [21–26]. ZnO in other orientations, for example (100) and (101), have also been theoretically predicted and experimentally investigated to possess special acoustic properties and photoluminescence behaviors [27,28]. In addition, the c-axis crystallographic direction (002) was found to cause quantum efficiency loss in ZnO-based optoelectronic applications as a result of spontaneous electric field and polarization induced by stress [29,30]. To improve the luminous performance of these devices, non-polar ZnO thin films with the c-axis parallel to the surface need to be adopted. Several methods, including pulsed laser deposition [31,32], metal-organic chemical vapor deposition [33,34] and capacitively coupled plasma deposition [35], have been utilized to prepare non-polar ZnO films on limited kinds of monocrystal substrates such as $SrTiO_3$ [36,37], Al_2O_3 [38,39], $LaAlO_3$ [40], and sapphire [41]. These complicated deposition methods and expensive monocrystal substrates restrict broad application of non-polar ZnO. The electron beam evaporation (EBE) method has the properties of high power, high purity, good uniformity, cost-effectiveness, suitability for high melting point materials, and large area contin-

* Corresponding author.
E-mail address: yxzheng@fudan.edu.cn (Y.-X. Zheng).

http://dx.doi.org/10.1016/j.apsusc.2017.02.069
0169-4332/

uous coating, and is widely used in the microelectronic industry, optical thin film coatings, solar cells, display devices, etc. [42]. Silicon (Si) dominates the large-scale integrated circuit and microelectronic industry, and is also used in optoelectronic devices [43]. Generally, the structural and optical properties of ZnO at the nanometer scale rely on the fabrication process. Therefore, a deep and systematic investigation of the properties of high-quality non-polar ZnO thin films deposited by EBE on Si substrates is essential and meaningful for the development of the optoelectronic industry [44–46]. To our knowledge, this type of study is very limited.

In this work, highly (110)-oriented non-polar ZnO thin films with different film thicknesses were prepared on silicon substrates through EBE and post-annealing treatment. The structures and morphologies of the samples were characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), and atomic force microscopy (AFM) to examine the formation mechanisms of non-polar ZnO. The optical properties of non-polar ZnO were investigated by spectroscopic ellipsometry (SE) and photoluminescence (PL) [47,48]. The effects of thickness and annealing temperature on the structural and optical properties are discussed.

2. Experiment

ZnO thin films were deposited on double-side-polished Si (100) wafers via ion-assisted EBE. Before deposition, the substrates were cleaned with acetone, ethanol, HF solution, and de-ionized water. During deposition, a broadband optical monitoring (BOM) method was used to monitor the optical thickness and deposition rate [49]. With a deposition rate of 0.1 nm/s and the deposition time ranging from 2 to 25 min, four samples of ZnO thin films with different thicknesses were prepared and named S1–S4. To observe the relationship between annealing temperature and properties of the ZnO film, each ZnO thin film was divided into four pieces and three of the four were annealed at three different temperatures: 300, 500 and 700 °C for 1h.

Sample thickness was measured by TEM (FEI Tecnai F20), the crystal structure was characterized by XRD (Bruker D8 advance), and the surface morphology was viewed by AFM (Vecco VT1000) in the non-contact mode. A home-built rotating-polarizer-analyzer ellipsometer (RPAE) was used to acquire the ellipsometric spectra (tan Ψ and cos Δ) of each thin film [50]. These parameters were measured every 5 nm in the wavelength range 300–800 nm at three different incident angles (65°, 70°, and 75°). The spectroscopic ellipsometer with the polarizer and analyzer rotating synchronously was developed to eliminate the uncertainty of phase shift and dc background signal in the rotating-analyzer-ellipsometer. Fig. 1 is an illustration of the optical system. A Hilger DU560 grating monochromator (1200 line/mm) with a 150 W xenon lamp provided the quasi-monochromatic light. The fixed polarizer with fixed azimuthal angle aims at reducing the residual polarization effect of the light source. The rotation ratio of the rotating polarizer and analyzer is 1: 2, i.e., $A = 2P = \omega_0 t$. The light intensity received by the detector is

$$\begin{aligned} I &= I_0 + I_1 \cos A + I_2 \cos 2A + I_3 \cos 3A + I_4 \cos 4A \\ &= I_0 + I_1 \cos \omega_0 t + I_2 \cos 2\omega_0 t + I_3 \cos 3\omega_0 t + I_4 \cos 4\omega_0 t, \end{aligned} \quad (1)$$

where

$$\begin{aligned} I_0 &= \frac{1}{4}\eta(7 + 3{\rho_0}^2 + 2\rho_0 \cos \Delta) + I_B, \\ I_1 &= \eta(3 + \rho_0 \cos \Delta), \\ I_2 &= \eta(2 - {\rho_0}^2), \\ I_3 &= \eta(1 - \rho_0 \cos \Delta), \\ I_4 &= \frac{1}{4}\eta(1 + {\rho_0}^2 - 2\rho_0 \cos \Delta), \end{aligned} \quad (2)$$

η is a light intensity related coefficient, $\rho_0 = \tan \Psi$, I_B is the dc background signal, I_0 is the dc component, and I_1–I_4 are all ac components. Since I_k ($k = 1, 2, 3, 4$) is determined by the Fourier transform,

$$I_k = \frac{2}{n}\sum_{i=1}^{n} I_i \cos(kA_i), \qquad k = 1, \quad 2, \quad 3, \quad 4. \quad (3)$$

The ellipsometric spectra (ρ_0 and cos Δ) can be obtained with self-consistency better than 0.5% by calculating any three of the four ac signals except the dc signal. PL spectra were detected with an Acton Spectra Pro 500i spectrometer excited with the 325 nm line of a He-Cd laser (Melles Griot 3074-M-X04).

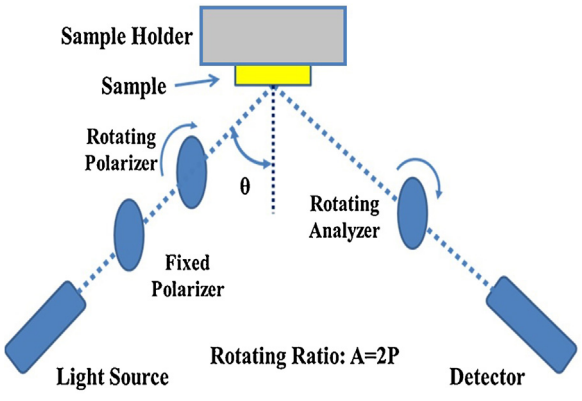

Fig. 1. Schematic diagram of the optical system of the RPAE.

3. Results and discussion

The estimated thicknesses of S1–S4 are (9.1 ± 0.7), (69 ± 4), (111 ± 5), and (145 ± 7) nm, respectively, which can be obtained from the TEM cross-sectional images in Fig. 2. Bulk ZnO has a hexagonal wurtzite structure with lattice constants a = 0.32498 nm and c = 0.52066 nm [51]. Fig. 3 shows the XRD results of the samples S1–S4. The patterns reveal that the ZnO thin films deposited are polycrystalline in nature [52], having strong (102) diffraction peaks and relatively weak (110) ones, except for the thinnest X-ray amorphous sample S1 that had no obvious diffraction peaks. With increasing thickness, the intensities of the diffraction peaks increased, implying better crystallization. ZnO often develops along the (002) orientation with the minimum surface energy. However, the unusual growth mode observed here, which was found in ion-assisted film deposition cases [53,54], is mainly due to the effects of ion assistance. In the low-pressure condition, accelerated ions are able to destroy the (002) direction, and so the target particles prefer to grow along other orientations with less ion bombardment damage, such as (102).

When the samples annealed, their crystallographic planes changed significantly. Fig. 4 shows the XRD patterns for sample S4 annealed at different temperatures and similar results were found for the other samples. The XRD patterns for samples annealed at 300 and 500 °C were almost identical, with the only strong (110) diffraction peaks between 30° and 60° in 2θ; however the original strong (102) peaks of the as-deposited ZnO films vanished, suggesting that the preferred orientation of ZnO nanocrystals changed from (102) to (110) after thermal treatment. The activation energy provided in the annealing process is a key factor for this structural improvement. Particles at high temperature with extra diffusion mobility tend to crystallize in a crystallographic plane with rather lower free surface energy, stimulating (110) direction growth.

Please cite this article in press as: S.-D. Yang, et al., Structural and optical properties of highly (110)-oriented non-polar ZnO evaporated films on Si substrates, Appl. Surf. Sci. (2017), http://dx.doi.org/10.1016/j.apsusc.2017.02.069