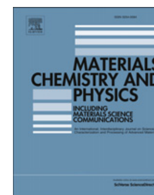
Materials Chemistry and Physics 135 (2012) 88–93

Contents lists available at SciVerse ScienceDirect

Materials Chemistry and Physics

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



Blue-shifted stimulated emission from ZnO films deposited on SiO_2 by atomic layer deposition

Ming Chih Lin [a], Mong-Kai Wu [a], Miin-Jang Chen [a,b,c,*], Jer-Ren Yang [a], Makoto Shiojiri [d]

[a] Department of Materials Science and Engineering, National Taiwan University, Taipei 10617, Taiwan, ROC
[b] Center for Emerging Material and Advanced Devices, National Taiwan University, 1 Rooseverlt Rd. Sec. 4, Taipei 10617, Taiwan, ROC
[c] National Nano Device Laboratories, Hsinchu 30078, Taiwan, ROC
[d] Professor Emeritus of Kyoto Institute of Technology, 1-297 Wakiyama, Kyoto 618-0091, Japan

A R T I C L E I N F O

Article history:
Received 4 September 2011
Received in revised form
5 April 2012
Accepted 14 April 2012

Keywords:
Atomic layer deposition
ZnO film
Photoluminescence
Stimulated emission

A B S T R A C T

ZnO films were prepared by atomic layer deposition upon a SiO_2 layer on a Si substrate and treated by rapid thermal annealing. The optically-pumped random lasing actions with low threshold values were observed in the ZnO films on SiO_2/Si substrates. With the decrease in ZnO film thickness or the increase in post-annealing duration, the stimulated emission shifted toward the shorter wavelength and the lasing threshold increased. The results can be attributed to the inter-diffusion between ZnO and SiO_2, which causes the modification of bandgap renormalization in ZnO.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

ZnO is one of the most promising materials with many specific features. It has a high excitonic binding energy of 60 meV as well as a direct and wide bandgap of 3.37 eV at room temperature, resulting in strong ultraviolet (UV) spontaneous emission and low-threshold stimulated emission [1,2]. It has been observed that even the polycrystalline ZnO could exhibit coherent random lasing action [3]. However, we have learned from an experiment on SiC–ZnO heterojunctions that high-quality ZnO epilayers grown on the SiC substrates can hardly exhibit stimulated emission, due to the high refractive index of SiC ($n = 2.8$ at $\lambda = 380$ nm) [4] which results in the lack of the optical confinement [3]. The SiO_2/Si might be a suitable substrate to induce the stimulated emission from ZnO because of the lower refractive index of SiO_2 ($n = 1.56$ at $\lambda = 380$ nm) than ZnO ($n = 2.37$ at $\lambda = 380$ nm) [5]. The random lasing action has been observed in ZnO deposited on SiO_2 by the catholic vacuum arc technique [6,7], suggesting that the optical confinement is necessary for the onset of stimulated emission. It has been reported that the stimulated emission in ZnO depends on the compressive or tensile strain, which might influence the Mott density, resulting in two specific lasing regions associated with free exciton emission or electron-hole plasma (EHP) emission [7]. In the present paper, we have applied the atomic layer deposition (ALD) technique to prepare preferentially $(10\bar{1}0)$ oriented ZnO films on the Si substrates covered with a SiO_2 layer. A blue shift of stimulated emission from the ZnO films is demonstrated, which is dependent on the film thickness and the post-deposition annealing condition.

2. Experimental

The (002) Si wafers used as substrates in this study were cleaned by acetone, methanol, and de-ionized water, successively, and then dried by blowing N_2 gas. After the clean procedure, SiO_2 layers ~180 nm thick were grown by surface oxidation of the Si substrates at 950 °C in a furnace. Subsequently, ZnO thin films were deposited on the SiO_2/Si substrates by ALD (Savannah S100, Cambridge Nanotech). The self-limiting and layer-by-layer growth of ALD provides many benefits such as easy and accurate thickness control, high uniformity over a large area, low defect density, conformal step coverage, good reproducibility, and low deposition temperatures. The pulse times of precursors, $Zn(C_2H_5)_2$ (Diethylzinc, DEZn) and H_2O vapor, were 0.05 and 0.1 s, respectively. The N_2 purge time was 5 s. The growth temperature was 180 °C, which is within the "ALD window" for the deposition of ZnO [8]. The growth rate of ZnO was about 0.17 nm cycle^{-1}. After the deposition, the ZnO films were treated by rapid thermal annealing (RTA) at

* Corresponding author. Department of Materials Science and Engineering, National Taiwan University, Taipei 10617 Taiwan, ROC. Tel.: +886 2 3366 5301; fax: +886 2 23634562.
E-mail address: mjchen@ntu.edu.tw (M.-J. Chen).

0254-0584/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2012.04.027

900 °C for 10 min in N_2 ambient to improve their crystal quality. The ZnO films of different thicknesses were prepared with 350, 500, 600 and 1000 ALD cycles, for which the samples were named T350, T500, T600, and T1000, respectively.

A fourth harmonic Q-switched Nd:YAG laser ($\lambda = 266$ nm, pulse width ~10 ns, repetition rate = 15 Hz, LOTIS TII LS-2134UTF) was used as the excitation source to study the stimulated emission from ZnO. The laser beam was focused into a small spot with a diameter about 0.8 mm. The photoluminescence (PL) spectroscopy was measured in the standard backscattering configuration where the light emission from top surface of the sample was collected. A computer-controlled SpectroPro 2300i monochromator together with a photomultiplier and the conventional lock-in technique were used to record the PL spectra. The crystallinity was characterized by X-ray diffraction (XRD, PANalytical X'Pert PRO) and the scanning range (2θ) was from 30° to 40° with a step size of 0.01°. The surface morphology was examined by atomic force microscopy (AFM, Autoprobe M5) and the scanned sample area was 1 μm^2 with a scanning speed of 1 Hz.

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples. Curve (a) is the XRD pattern of sample T500 before annealing. It shows small $(10\bar{1}0)$, (0002), and $(10\bar{1}1)$ peaks. Curve (b) is the XRD pattern of the same sample T500 after the RTA treatment. The crystallinity is greatly improved and the $(10\bar{1}0)$ peak becomes stronger than the (0002) peak. Curve (c) is the XRD pattern of sample T1000 after the RTA treatment. With the increase in film thickness, the $(10\bar{1}0)$ orientation becomes strongly dominant, exhibiting preferentially the *c* axis parallel to the substrate surface. Fig. 2 shows the AFM images of the samples after the RTA treatment, indicating that the average grain sizes of samples T500 and T1000 are 65 and 250 nm, respectively. The grain size of the thick ZnO film is larger than that of the thin one, being consistent with the result of XRD pattern.

The ALD-deposited ZnO films on the SiO_2/Si substrates are very different from the ZnO films grown by other conventional techniques such as metal–organic chemical–vapor deposition (MOCVD) or sputtering, where the [0001] orientation (with the *c* axis normal to the substrate surface) usually dominates. Since the most densely packed plane of ZnO is (0001), the [0001] orientation must be the most preferable. Therefore, the dominant $(10\bar{1}0)$ orientation of the ALD-deposited ZnO films is attributed to the low deposition temperature and layer-by-layer deposition on the SiO_2/Si substrate [9–11]. In addition to the (0002) peak, a small peak appears at $2\theta = 34.2°$ in both the curves (b) and (c) as shown in Fig. 1. This can be identified as the (140) reflection of Zn_2SiO_4, indicating that the inter-diffusion between SiO_2 and ZnO occurs during the RTA treatment.

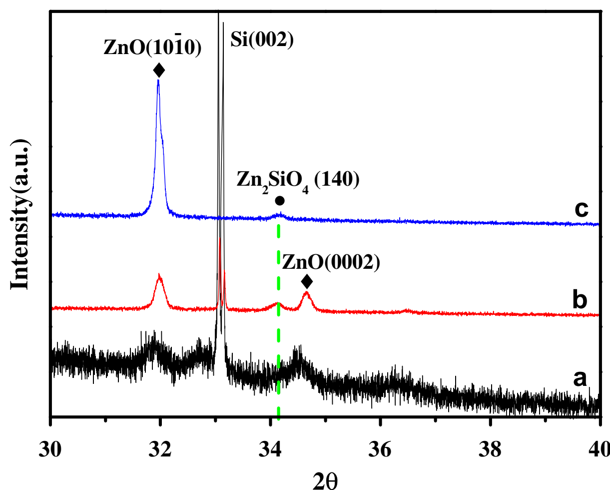


Fig. 1. XRD patterns of the samples (a) T500 without annealing, (b) T500 after the RTA treatment and (c) T1000 after the RTA treatment.

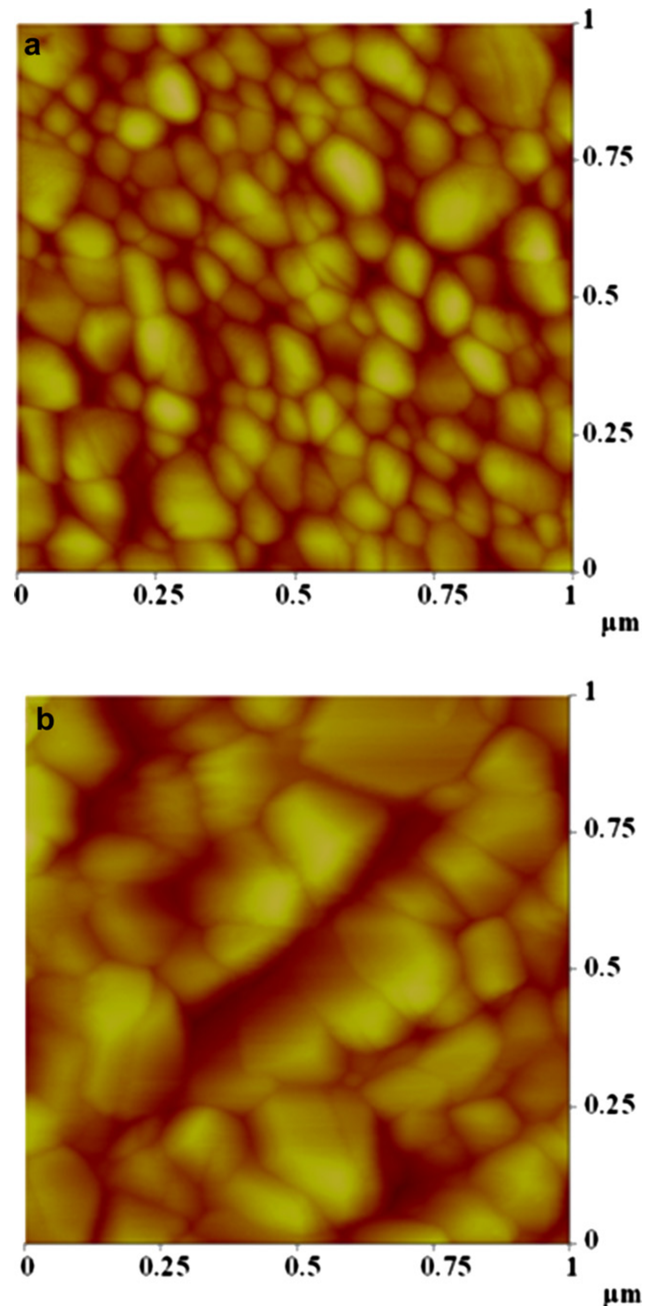


Fig. 2. AFM images of the surfaces of the samples (a) T500, and (b) T1000.

Fig. 3 shows the PL spectra of sample T1000 under various pumping intensities at room temperature. At low pumping intensities, the PL spectrum exhibits only a UV spontaneous emission around 3.27 eV, which can be ascribed to the radiactive recombination of free or bound excitons. At the pumping intensity up to a critical value, several narrow spectral peaks appear around 3.16 eV. The full-width at half-maximum (FWHM) of these spectral peaks are smaller than 0.4 nm, which may result from the random lasing action [12,13]. The resonant cavities of random lasing are self-

Download English Version:

https://daneshyari.com/en/article/1523417

Download Persian Version:

https://daneshyari.com/article/1523417

Daneshyari.com