Superlattices and Microstructures 86 (2015) 134–142

Contents lists available at ScienceDirect

Superlattices and Microstructures

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

The influence of growth temperature on structural and optical properties of sputtered ZnO QDs embedded in SiO_2 matrix

Alireza Samavati [a,*], Zulkafli Othaman [a], S.K. Ghoshal [b], M.K. Mustafa [c]

[a] Ibn Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia, Skudai, Johor 81100, Malaysia
[b] Advanced Optical Material Research Group, Department of Physics, Faculty of Science, Universiti Teknologi Malaysia, Skudai, Johor 81100, Malaysia
[c] Faculty of Science Technology and Human Development, Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Johor, Malaysia

ARTICLE INFO

Article history:
Received 9 July 2015
Accepted 10 July 2015
Available online 11 July 2015

Keywords:
ZnO QDs
RF magnetron sputtering
Structural properties
Optical behavior

ABSTRACT

We report the influence of growth temperature on surface morphology, structural and optical properties of ZnO QDs embedded with SiO_2/Si matrix fabricated by radio frequency (RF) magnetron sputtering method. The fragmentation due to elastic strain relaxation compensate adatom diffusion length at higher temperature causes the decrement of the ZnO QDs sizes from ~41 nm to ~12 nm and number density enhancement from ~0.2 to ~15.4 × 10^{10} cm^{-2} by increasing the growth temperature. ZnO QDs shows a well-defined hexagonal close packed wurtzite structure with lattice parameters close to those of bulk ZnO, confirming their high crystalline quality. Increasing growth parameters causes to decrease the lattice parameters due to change in interatomic distances explained by elimination of defects and structural relaxation. The room temperature photoluminescence (PL) spectra shows strong UV accompanied by weaker green peak originated from recombination of free excitons and dominative deep-level emissions respectively. As the growth temperature increased to 500 °C, an emission intensity in the ultraviolet and green region enhanced which is due to increment in the numbers of photo-carriers by increasing the number density of QDs. Calculated band gap using an optical transmittance measurement indicates that the bandgap shift to higher energies is not taken placed because of large size of dots. The Urbach energy increases considerably in samples with increasing growth temperature which is attributed to higher degree of surface disorder in smaller QDs. The excellent features of the results suggest that our systematic analysis method may constitute a basis for the tunable growth of ZnO QDs suitable in nanophotonics.

1. Introduction

Synthesis and characterization of II–VI semiconductor materials at nanometer scale has received much attention in the scientific community, because of their great potential to test fundamental concepts of quantum mechanics and their various applications [1,2]. However, there have been few studies on the formation of a ZnO QDs structure using a conventional semiconductor growth method in spite of many extensive studies on compound semiconductors such as InAs [3] and CdSe [4]. ZnO QDs embedded in SiO_2 thin films is promising for various applications including ultraviolet (UV) single-photon and opto-spintronic applications [5], gas sensors [6], nanoelectronics [7] photodetectors and solar cell [8]

* Corresponding author.
E-mail address: alireza.samavati@yahoo.com (A. Samavati).

http://dx.doi.org/10.1016/j.spmi.2015.07.026
0749-6036/

due to their direct, wide band gap and large exciton binding energy (60 meV). An essential surface modification needs to be done for each of the desired applications because surface effects radically influence the functionality of semiconductor nanocrystals. For preparing ZnO QDs on SiO_2 thin films a variety of methods have been employed such as pulsed laser deposition (PLD), sol–gel, sputtering, and molecular beam epitaxy (MBE) [9–11]. The sputtering technique is the most widely used among the above methods, because of its various advantages, such as a low deposition temperature, preferred orientation and high deposition rate on an amorphous substrate and large deposition area. It is found that ZnO QD embedded in SiO_2 matrix give emission peak in the visible range [12]. ZnO has high surface-to-volume ratio at nanometer scale and hence surface defects play an important role in its properties. The sputtering process parameters such as rf power, working pressure, substrate temperature, substrate target distance and gas flow ratio influence on structural, morphological and optical characteristics of ZnO/SiO_2/Si hetero-structure. In particular, the supply of appropriate thermal energy enhances the mobility of the adatoms on the substrate surface, and accelerates the migration of adatoms to the suitable site, resulting in the enhancement of the crystallinity. Therefore, growth temperature is an important factor to obtain high-quality thin films. Using rf magnetron sputtering in the presence of in situ substrate heating at temperature lower than 400 °C during deposition, Kang et al. reported that 200 °C temperature is suitable for preparing smooth surface, good crystallinity with best piezoelectric constant [13]. However, the structural and morphological evolution of ZnO/SiO_2/Si and their optical behavior on higher temperature is not thoroughly scrutinized.

Therefore, in this study, we investigate the growth temperature (350–500 °C) dependent surface morphology and optical properties of ZnO QDs deposited on SiO_2/Si (SiO_2 layer on Si) substrates by radio frequency (RF) magnetron sputtering.

2. Experimental procedures

ZnO/SiO_2/Si hetero-structure deposited by RF magnetron sputtering using high purity ZnO and SiO_2 target of 3 in. diameter. The substrates used are n-type Si with (1 0 0) orientation. The hetero-structure is grown as follows: initially a layer of SiO_2 on Si substrate, and then a thin layer ~20 nm of ZnO on top of the SiO_2 layer ~30 nm are sputtered. The RF power and deposition time for SiO_2 deposition are 250 W and 40 min and for ZnO are 175 W and 5 min respectively and the Ar flow rate is kept constant at 10 sccm. The working pressure in the growth chamber is 4×10^{-3} Torr. The substrates are initially cleaned with acetone and isopropanol in an ultrasonic bath for 10 min and rinsed with deionized water, before being fixed to a rotating substrate holder of the HVC Penta Vacuum. The substrates are fixed at a distance of 10 cm above the targets. Mechanical rotary pump and turbo pump are used to evacuate the sputtering chamber to its ultimate pressure of about 5×10^{-6} Torr. The ZnO QDs are deposited at different growth temperature of 350, 400, 450 and 500 °C. The samples are kept inside the chamber to cool to room temperature after growth.

An AFM built by Seiko Instrument Inc. (SPI3800) is used to study the surface morphology, whereas a structural details of the samples are studied by X-ray diffraction (XRD) (D8 Advance Diffractometer, Bruker, USA) using Cu Kα radiation (0.154 nm) at 40 kV and 100 mA. The 2θ range is set to 0–90° with a step size of 0.02° and a resolution of 0.011°. Photoluminescence (PL) spectra are recorded at room temperature using a luminescence spectrometer (LS 55, Perkin Elmer, USA) under 285-nm excitation. The Field-emission scanning electron microscope (FESEM, JEOLJSM 6380LA) attached with EDX are employed for observing layer formation and elemental analysis. Optical measurements are performed at room temperature with Shimadzu UV-3101PC double-beam spectrophotometer.

3. Results and discussion

Figs. 1 and 2 represent the AFM images and the corresponding size distribution of samples at different growth temperatures with intervals of 50 °C in the range of 350–500 °C. As shown in Table 1, the island density increases and the island size, RMS roughness and FWHM of size distribution decreases with the increase of growth temperature. Uniform islands with a narrow size distribution and a high density of 15.4×10^{10} cm^{-2} are achieved at the growth temperature of 500 °C as shown in Fig. 1e. The increase of growth temperature usually increases the adatom diffusion length, leading to the increase of the island size. However, the fragmentation due to elastic strain relaxation appears to compensate this effect at higher temperature [14]. As a result, the island density increases and the average size decreases as shown in Figs. 1 and 2. These experiment results are different from some early reports, for example, the deposition of ZnO on SiO_2 using MOCVD by Zhou et al. [15]. Their experiments showed that islands width and height increased and the density decreased with growth temperature increasing. In addition, it should be considered that when the lateral size reaches the inter-dot mean distance [16], the density of islands will decrease. So it can be confirmed that the typical mean inter-island distance is not reached at the growth temperature between 350 °C and 500 °C. But this effect at higher temperature can be compensated by the fragmentation due to elastic strain relaxation [17], if it is large enough. As a result, their experiments results showed different phenomena. Above 550 °C, an island is hardly detected by AFM, probably due to enhanced evaporation of adatoms.

The step structure is observed on a substrate without depositing ZnO by AFM, shown by arrows in Fig. 1a. This step height is about 0.8 nm. The AFM images show that ZnO QDs are all grown well along each step of the substrate. The nucleation mechanism of these dots is controlled by kinetics of nucleation and will pertain if the diffusion lengths of the adatoms are sufficient to allow them reach the steps before nucleation on the terraces. These dots have been measured by AFM, and the average interval of dots on each step is about 60–80 nm. These data are in the same ranges with the interval of center line on each step measured by AFM.