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Photoluminescence properties of Zinc Oxide nanostructures on different substrates obtained by an immersion method

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ABSTRACT

This paper present ZnO nanostructures deposited on various substrates by a low-temperature synthesis method in mixture of zinc acetate dehydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$] solution and urea [$CH_4N_2O$]. The effects of the substrates used in this study; glass, Si, Si/Au and porous silicon (PSi) were evaluated. Depending on the substrate, different ZnO nanostructures morphologies were produced. Based on this, an understanding of the unique development of size and growth orientations of ZnO has been achieved. The optical properties of zinc oxide at room-temperature were determined using a photoluminescence (PL) measurement. As-prepared PSi substrate emit strong red light, so the PL spectra before and after deposition of ZnO nanostructures were measured. The PL emission of PSi was discovered by ZnO emission in the visible region.

1. Introduction

In the semiconductor industry, many types of materials such as silicon, gallium arsenic, TiO_2 and zinc oxide (ZnO) are used as base materials. ZnO is a unique material that has a wide bandgap of 3.37 eV and large exciton energy of 60 meV [1]. ZnO nanostructures may have novel applications in optoelectronics [2], sensors [3], transducers and biomedical science. ZnO nanostructures grown on Si-based substrate receive significant attention because silicon is widely used in semiconducting devices. Silicon is a stable and high temperature resistant material that is suitable for device fabrication. The problem growing ZnO nanostructures directly on silicon substrates is the introduction of large lattice mismatches. A large stress exists between the ZnO layer and the Si substrate that prevents the ZnO layer from being deposited on the Si substrate. The Si surface must be modified to prepare a suitable site to which ZnO nanostructures can adhere. Porous silicon (PSi) has a rough surface morphology, which is a good template for growing ZnO nanostructures without using metal catalysts [4] because a rough surface provides a good site for ZnO to grow with minimum stress applied between the ZnO and PSi layer. ZnO nanostructures have been synthesized by various methods such as chemical vapour deposition (CVD) [5], electrochemical method [6], RF magnetron sputtering [7] and the sol–gel method [8]. Among these methods, the sol–gel selected because of its simplicity, safety, low cost, low-temperature deposition and large area coating capability. In a previous study, it was found that the sol solution partially entered into the pores of the porous silicon substrate during the sol–gel process, thus improving the structural stability of PSi [7].

The structure of ZnO growth depends not just on the growth parameters, but also on the chosen substrate, both of which play an important role in determining the dimension of ZnO [9,10]. In this study, we used urea (as a stabilizer) and zinc acetate dehydrates (as a precursor) to synthesize ZnO nanostructures on four different substrates. A solution-immersion method was adopted with the intention of developing a large area deposition at low temperature and low cost. Normally, to deposit ZnO using zinc acetate dehydrates as a source, it must be dissolved in an alcohol solution however, in this study, we used distilled water as a solvent. ZnO deposited on Si formed a flower-like structure, but easily peeled off from the Si substrate. As a result, we have determined the nucleation process for the formation of flower-like structures. A glass substrate was used as a control sample to determine the single- layer ZnO optical and electrical properties. The as-grown ZnO nanostructures were characterized by using FESEM and photoluminescence (PL).

2. Methodology

In this study, the ZnO nanostructures were synthesized on different substrates using a hydrothermal immersion method. A 0.2 molar concentration of $Zn(CH_3COO)_2.2H_2O$ solution was mixed with urea solution at a 1:1 concentration ratio. The solution was

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stirred at 60 °C for 1 hour and aged 24 hours at room temperature until it was completely homogeneous. PSi was prepared using p-type silicon (100) as a starting material. Silicon wafer cut with dimensions 2 cm × 2 cm was mounted in an electrochemical cell with aluminium foil placed on the backside of the wafer to increase the conductivity between aluminium base and the silicon wafer (Fig. 1(a)). Hydrofluoric acid (48%) and absolute ethanol (99.7%) in a 1:1 ratio were used as the electrolyte and completely filled Teflon cell. The tungsten rod acted as the cathode and the aluminium based acted as the anode in the electrochemical etching process. The current density and etching time were 20 mA/cm^2 and 30 minutes, respectively. After the PSi was successfully fabricated, it was cleaned by DI water and dried using hydrogen gas.

For the immersion step, a glass substrate, a Si wafer, Si coated with Au (6 nm) and PSi were put in a test tube containing (Fig. 1(b)) a previously prepared acetate solution. The temperature of the vessel was maintained at 90 °C for 4 hours, and then the samples were dried at 160 °C for 1 hour before annealed at 500 °C for 1 hour. The ZnO nanostructures were observed using field emission scanning electron microscope (FESEM-JEOL) and their optical properties were characterized using a Modu-Laser photoluminescence (PL) spectrometer, which used a He–Cd Laser at 325 nm as a source at room temperature.

3. Results and discussion

3.1. Structural Properties

FESEM (JEOL) was used to investigate the surface structure of the PSi and ZnO nanostructures. Fig. 2 displays an FESEM micrograph of the surface of the porous silicon surface produced by electrochemical etching at 200 k magnification and an Atomic Force Microscope (AFM) image in 3D imaging. The FESEM results in (Fig. 2(a)) show nanometre-sized pores formed on the surface of p-type silicon with irregular columnar pores (Fig. 2(b)). These pores were assumed to be nano pores because their sizes were between 15 ~ 30 nm; they are represented by the dark areas in the (Fig. 2(a)). The porous structures on the Si wafer minimized the mismatch bertween the ZnO nanostructures film and substrate by decreasing the stress. As a result, the structural and optical properties of ZnO thin films have been improved [11].

Fig. 3 shows the morphology of ZnO deposited on PSi, quartz glass, Si and Si coated with Au. These images show that ZnO nanostructures were successfully synthesized on four different templates. It is evident that ZnO nano flower-like clusters were deposited on the glass substrate in low volume; because we ZnO nanostructures did not fully cover the glass surface. Fig. 3(a) demonstrates that the nanoflowers clustered with a diameter about 60 μm in a certain areas on the quartz. The small inset in Fig. 3(a) showing the ZnO at high magnification indicate that the ZnO nanoparticles attached together to form a chain of particles and produced a leaf-like form. The ZnO particle size was calculated by the equation (1) below [12] and is summarized in Table 1.

$$E_g(eV) = E_g + \frac{h^2}{8d^2}\left[\frac{1}{m_e^*} + \frac{1}{m_h^*}\right] \quad (1)$$

Here, E_g (eV) = the energy band gap of PSi calculated from the PL peak position, $E_g = 3.3 \sim 3.4$ eV, eV is the energy band gap of ZnO, h = Planck's constant = 4.13×10^{-15} eV s, R is the radius of the particles, $m_e^* = 0.19\ m_e$ is the electron effective mass, $m_h^* = 0.16\ m_e$ is the hole's effective mass, $m_e = 9.10 \times 10^{-31}$ kg and d is the diameter of the spherical particle.

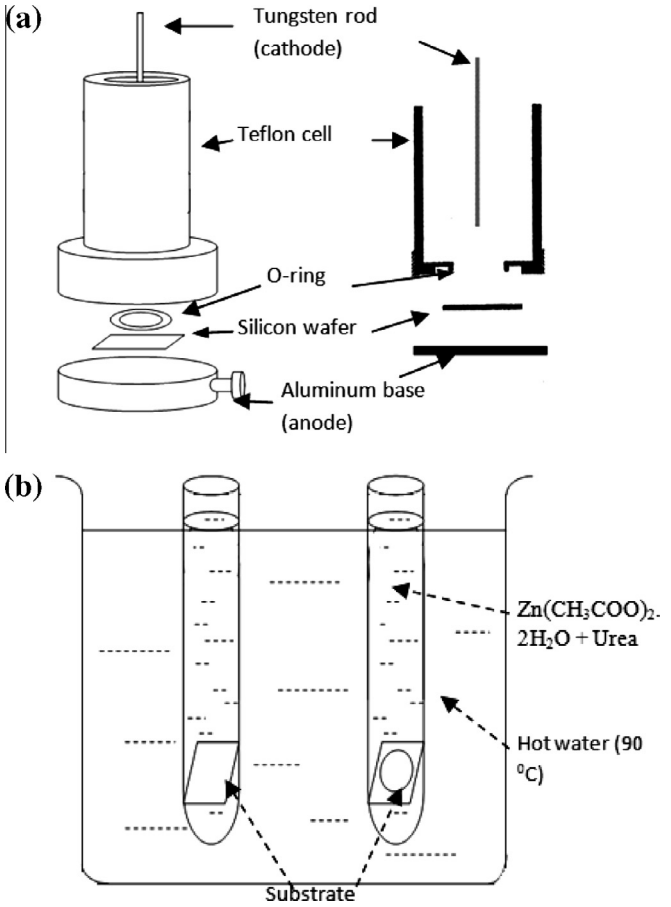

Fig. 1. Experimental set-ups to produce (a) porous silicon nanostructures by electrochemical etching and (b) ZnO nanostructures by thermal immersion method.

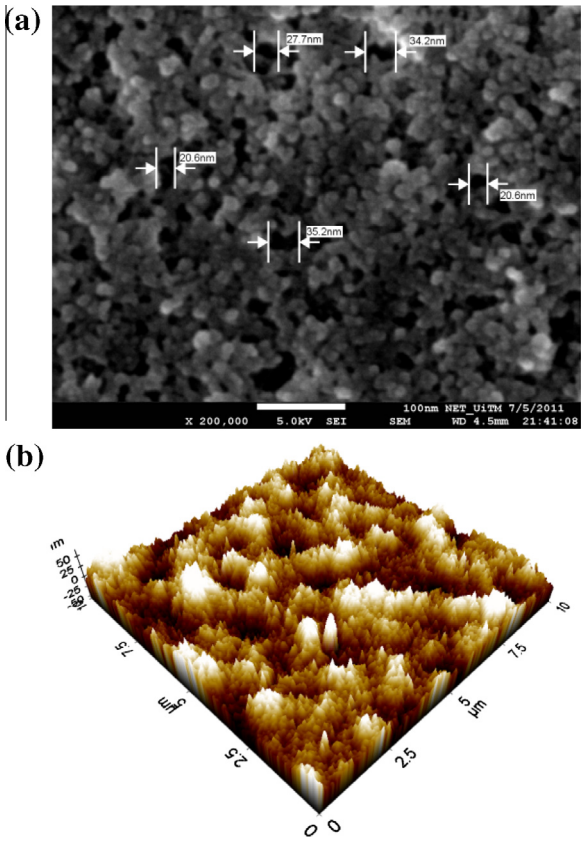

Fig. 2. Porous silicon (a) morphology and (b) surface topography by AFM prepared by electrochemical etching.