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Effects of growth temperature on structural and optical properties of ZnO thin films grown chemically on porous silicon substrate

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ABSTRACT

Seed layer-free ZnO thin films were synthesised by chemical bath deposition method on porous silicon substrates. The effects of growth temperature on the structural and optical properties of ZnO thin films were systematically investigated by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM) and photoluminescence (PL) spectroscopy. The grain size of the ZnO thin films gradually increases with increased growth temperature. The FESEM images displayed that the thickness of ZnO thin films increased with the increase in growth temperature. Meanwhile, photoluminescence measurements demonstrated a sharp and highly intense UV emission peak at growth temperature of 95 °C. This finding indicates that the optical and crystallographic properties of the ZnO thin films were improved with growth temperature of 95 °C.

1. Introduction

Semiconductor nanostructures possess good characteristics pertaining to their electronic and optical properties due to quantum confinement effect, which can emit tunable light depending on size. ZnO thin films with a direct wide band gap of 3.37 eV and large exciton binding energy of 60 meV are widely applied for developing novel optoelectronic and electronic devices such as light emitting diodes [1], gases sensors [2], acoustic devices [3], UV photodetectors [4] and solar cells [5]. A number of deposition techniques such as molecular beam epitaxy (MBE) [6], radio frequency sputtering [7], atomic layer deposition (ALD) [8], pulsed laser deposition (PLD) [9], chemical vapour deposition (CVD) [10] have been used to produce ZnO thin films. ZnO nanostructures grown on Si-based substrates have attracted significant interests in the past few decades because silicon substrate is a stable and high temperature resistant material and a very popular substrate in IC technology [11,12]. However, it is difficult to directly grow or deposit high quality ZnO nanostructures on silicon substrates since there is a huge stress between ZnO and Si substrate due to the mismatch in their thermal expansion coefficients and lattice constants [13]. Therefore, it is necessary to look for a better substrate for growing high quality ZnO nanostructure. Among porous semiconductors, porous silicon (PS) has opened a new possibility for Si-based integrated circuits due to its remarkable optical and electronic properties. It has been used for various adsorptive substances due to its low cost, large internal surface-to-volume ratio, sponge-like structure, adjustable roughness and strong absorbability. Moreover, PS prepared by the silicon is compatible with silicon IC technology, which provides a possibility to integrate PS-based optical devices [14]. The porous silicon layer can reduce the large mismatches in the lattice constants and thermal expansion coefficients between the ZnO and Si substrates as well as the large stress between the ZnO nanostructures and Si substrate [15]. So far, the ZnO thin films have been widely fabricated by numerous techniques [16–20], but chemical bath deposition (CBD) technique is one of the appropriate chemical syntheses to produce ZnO thin films on various substrates because of its low temperature, non-requirement of

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sophisticated instruments, simplicity, capability for large-scale production as well as its affordability. It has been known that the growth temperature used for chemical bath deposition synthesis can affect the formation of the ZnO thin films. A detailed understanding on structural and optical properties of ZnO thin films is essential for using them in the optoelectronics industry since the carrier relaxation processes strongly affect optoelectronic and electronic characteristics of ZnO thin films. However, few systematic studies have considered the effects of the growth temperature on both the structural and optical properties of ZnO thin films grown by chemical bath deposition technique especially using PS substrates. To the best of the author's knowledge, this study is the first to examine the effects of growth temperature on the structural and optical properties of seed layer-free ZnO thin films synthesised on PS substrate using CBD technique. Furthermore, in this study, the XRD, FESEM and PL spectroscopy were utilised to study the effects of growth temperature on the structural and optical properties of fabricated ZnO thin films on PS substrates.

2. Experimental

ZnO thin films were prepared on PS substrate by chemical bath deposition technique. There are several major steps in this experiment, which are the preparation of the PS substrate, deposition and characterisation process of ZnO thin films. The porous structure was formed on an n-type Si (100) substrate using the photo electrochemical etching method. The process for this method was carried out in a Teflon cell containing a mixture of hydrofluoric acid and 96% ethanol with a volume ratio of 1:4. The PS layer was formed with a constant current density of 20 mA/cm^2 for 5 min at room temperature using the Pt wire and Si wafer as cathode and anode, respectively. The sample was illuminated with a 60 W visible lamp during etching process. The prepared PS substrates were rinsed with deionised (DI) water and dried with nitrogen gas [21]. A 0.050 M/L of zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$ and an equal molar concentration of hexamethylenetetramine $C_6H_{12}N_4$ were dissolved in DI water at 80 °C separately. The two solutions were combined and the samples were vertically placed in a beaker. To determine the influence of growth temperature, the beaker was placed in an oven at different temperatures (55, 70, 85, and 95 °C) for 5 h to grow ZnO thin films. Then, the samples were rinsed with DI water and dried with nitrogen (N_2) gas.

The crystal structure of the ZnO thin films was obtained using X-ray diffraction (XRD) (PANalytical X'Pert PRO MRD PW3040). The surface morphology of ZnO thin films was investigated using field emission scanning electron microscopy (FESEM) (model FEI/Nova NanoSEM 450). Furthermore, photoluminescence (PL) spectroscopy (Jobin Yvon HR 800 UV, Edison, NJ, USA) was used to characterise the optical properties of the ZnO thin films at room temperature.

3. Results and discussion

Fig. 1(a) displays the XRD patterns of ZnO thin films grown on Si and PS substrates. Meanwhile, the XRD patterns of ZnO thin films with different growth temperatures are shown in Fig. 1(b). For all the ZnO thin films, only a strong diffraction peak (0 0 2) with polycrystalline hexagonal wurtzite crystal structure (the standard data for ZnO; ICSD 01-074-0534) were observed, thus indicating that the preferred orientation due to the lowest surface free energy is along the c-axis perpendicular to PS substrates [22]. The XRD peak position, full width at half maximum (FWHM), lattice constant (c), stress, grain size and degree of orientation of the ZnO (002) planes for ZnO thin films grown on Si substrate and PS substrates with different growth temperatures are summarised in Table 1.

As depicted in Fig. 1(a), a higher intensity and narrower FWHM of the (002) diffraction peak demonstrated that the ZnO thin film grown on PS substrate has a good crystallinity compared to that of Si substrate. This result insinuates that the PS had some impact on enhancing the crystal quality of the ZnO thin films. The XRD patterns in Fig. 1(b) show that the intensity of (002) peak gradually increased as the growth temperature increases to 95 °C. The small FWHM and stronger diffraction intensity of growth temperature at

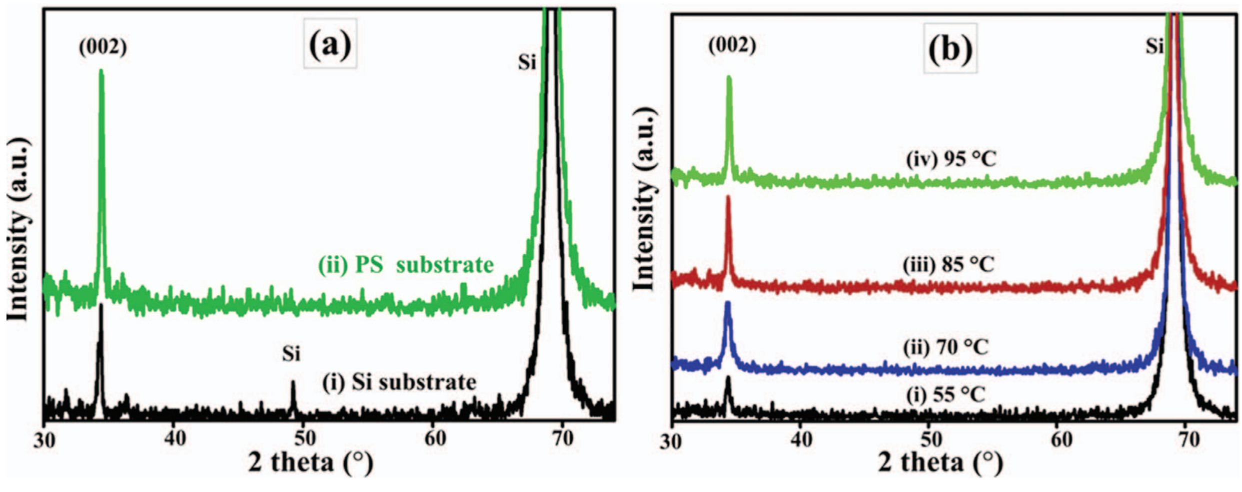

Fig. 1. (a) Typical XRD patterns of ZnO thin films grown on Si and PS substrates at 95 °C for 5 h, (b) XRD patterns of ZnO thin films grown on PS substrate with different growth temperatures for 5 h.