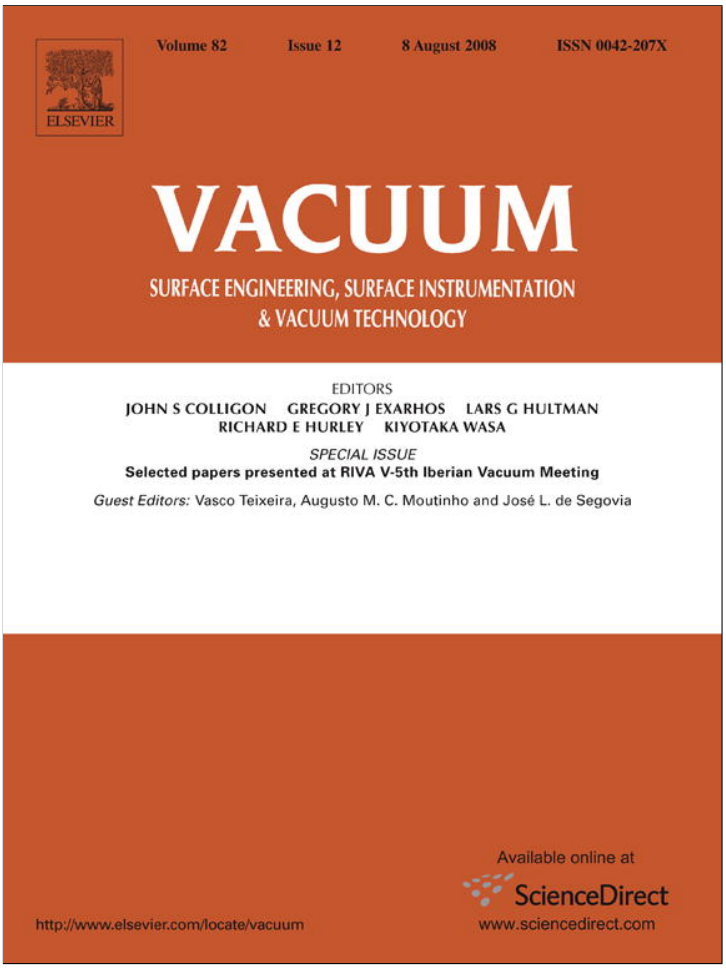

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The role of the Zn buffer layers in the structural and photoluminescence properties of ZnO films on Zn buffer layers deposited by RF magnetron sputtering

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A B S T R A C T

Highly *c*-axis oriented ZnO thin films were grown on Si (100) substrates with Zn buffer layers. Effects of the Zn buffer layer thickness on the structural and optical qualities of ZnO thin films were investigated for the ZnO films with the buffer layers 90, 110, and 130 nm thick using X-ray diffraction (XRD), photoluminescence (PL) and atomic force microscopy (AFM) analysis techniques. It was confirmed that the quality of a ZnO thin film deposited by RF magnetron sputtering was substantially improved by using a Zn buffer layer. The highest ZnO film quality was obtained with a Zn buffer layer 110 nm thick. The surface roughness of the ZnO thin film increases as the Zn buffer layer thickness increases.

1. Introduction

ZnO has been intensively studied in recent years because of its potential applications in optoelectric and electronic fields such as light emitting diodes (LEDs), laser diodes (LDs), photodetectors, solar cells, displays, gas sensors, varistors, and surface acoustic wave (SAW) resonators [1]. However, the ZnO films have demonstrated recently the giant second-order optical susceptibilities during the photoinduced optical second harmonic generation [2]. These results substantially change an interest to the films which now are promising the non-linear and quantum electronic materials comparable with the typical inorganic crystals. However, due to the cheaper technology compared to the traditional crystals the film production of all the ZnO film technology should take this fact into account.

In these studies ZnO thin films have been mostly grown on sapphire substrates. It is evidently more desirable to grow ZnO thin films on Si substrates since cheap large Si single crystal wafers with a high quality are available. Nevertheless, it is not easy to grow ZnO films with a high quality epitaxially on silicon substrates directly because of formation of an amorphous SiO_2 layer at the interface of ZnO and Si [3]. Various materials such as Zn [4], ZnS [5], MgO [6], ZnO [7] and SiO_2 [8], GaN [9],GaF_2 [10] have been tried to enhance the quality of ZnO thin film grown on Si substrates. However, more effort is needed to obtain ZnO films with a quality high enough to realize real devices. In this paper, we report effects of the Zn buffer layer thickness on the crystallinity, surface roughness and optical properties of ZnO thin films grown by RF magnetron sputtering.

2. Experimental

A Zn buffer layer and a ZnO thin film were deposited sequentially by RF magnetron sputtering on the Si (100) substrate. The Ar gas flow rate was 20 sccm. The chamber pressure, sputtering power substrate temperature, and Ar gas flow rate during deposition of both the Zn buffer layer and ZnO film were fixed to be 5×10^{-2} Torr, 30 W, 150 °C and 20 sccm, respectively. The thickness of the Zn buffer layer was varied by using different deposition times such as 7.0, 8.5 and 10.0 min; the sputter-deposited films were annealed in an oxygen atmosphere at 700 °C for 1 h by rapid thermal annealing (RTA).

X-ray diffraction (XRD), photoluminescence (PL) and atomic force microscopy (AFM) analyses were performed to investigate the crystallinity, optical properties, and surface morphologies of ZnO thin films, respectively. X-ray diffraction (XRD) analyses were performed in a Philips X'pert diffractometer using Cu Kα radiation with a thin film goniometer. The optical properties of ZnO thin films were characterized by photoluminescence with He–Xe laser as a light source using an excitation wavelength of 325 nm and a power of 200 mW.

3. Results and discussion

Fig. 1 shows the θ–2θ X-ray diffraction spectra for ZnO/Zn/Si (100) samples with different Zn buffer layer thicknesses. A strong ZnO (002) diffraction peak as well as several very small peaks are

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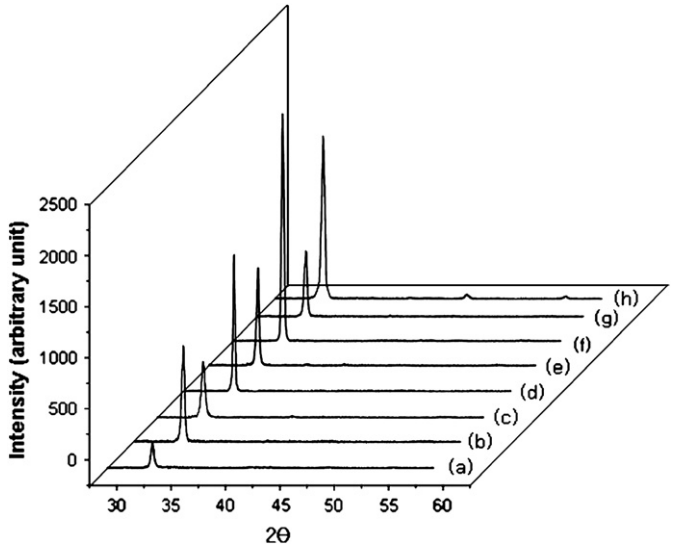

Fig. 1. X-ray diffraction spectra of as-deposited and annealed ZnO thin films grown on Si substrates with buffer layers of different thicknesses. (a) As-deposited, without a Zn buffer layer; (b) annealed, without a Zn buffer layer; (c) as-deposited, with a Zn buffer layer 90 nm thick; (d) annealed, with a Zn buffer layer 90 nm thick; (e) as-deposited, with a Zn buffer layer 110 nm thick; (f) annealed, with a Zn buffer layer 110 nm thick; (g) as-deposited, with a Zn buffer layer 130 nm thick; and (h) annealed, with a Zn buffer layer 130 nm thick.

observed in the spectrum of each sample, which indicates that ZnO thin films are all *c*-axis oriented but that they are polycrystalline rather than epitaxial even after annealing. The (002) reflection intensity for the sample with the Zn buffer layer 110 nm thick is stronger than that for any other sample. The full widths at half maximum (FWHMs) of (002) reflection for as-deposited and annealed ZnO/Zn/Si (100) samples measured from Fig. 1 are given in Table 1 for various Zn buffer layer thicknesses.

Table 1
The FWHMs of the (002) diffraction peaks for ZnO thin films grown with Zn buffer layers of different thicknesses on Si (100) substrates

Sample	Zn buffer layer thickness (nm)	As-deposited or annealed	FWHM
A	0	As-deposited	0.30
B	0	Annealed	0.25
C	90	As-deposited	0.36
D	90	Annealed	0.25
E	110	As-deposited	0.27
F	110	Annealed	0.24
G	130	As-deposited	0.36
H	130	Annealed	0.31

The Zn buffer layer 110 nm thick shows the smallest FWHM for both as-deposited and annealed ZnO films. This analysis result on FWHM is consistent with that on the (002) reflection intensity. Another thing to note is that the intensity increases and the FWHM decreases markedly by annealing, which suggests the crystallinity of a ZnO film is substantially improved by annealing. Fig. 2(a)–(d) shows the AFM images of annealed ZnO/Zn/Si (100) samples with the Zn buffer layers of different thicknesses. The RMS surface roughnesses of the samples measured from Fig. 2(a)–(d) are plotted as functions of the Zn buffer layer thickness in Fig. 3. One can see from Fig. 3 that both the surface roughnesses of ZnO/Zn/Si (100) samples tend to increase with increasing the Zn buffer layer thickness, which indicates that the surface roughness of the ZnO thin film is strongly related to that of the underlying Zn layer. Therefore, the Zn buffer layer should not be too thick to obtain a smooth ZnO film surface, the RMS surface roughness of the ZnO/Zn/Si (100) sample with the Zn layer thickness of 110 nm was

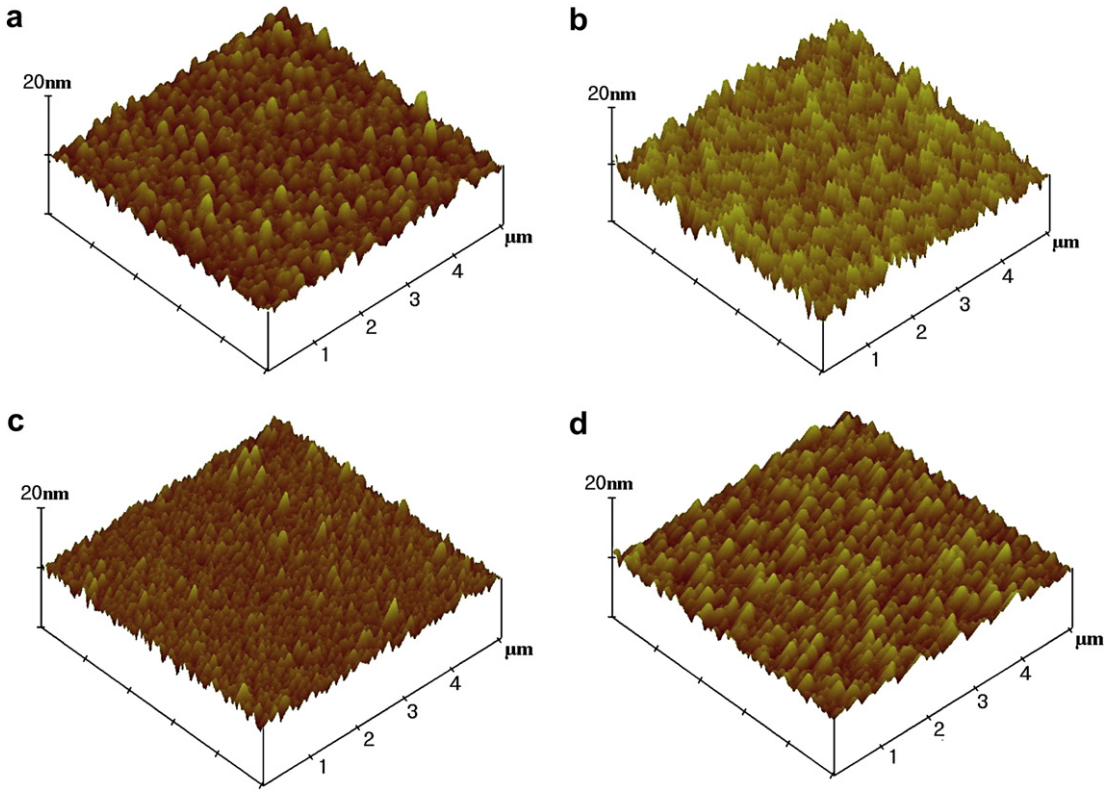

Fig. 2. AFM images of annealed ZnO/Zn/Si (100) samples with Zn buffer layers. (a) 0 nm, (b) 90 nm, (c) 110 nm, and (d) 130 nm thick.

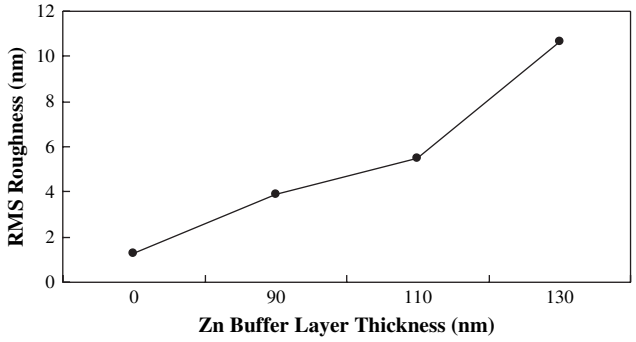

Fig. 3. Dependence of the RMS surface roughness of the ZnO thin film on the Zn buffer layer thickness.

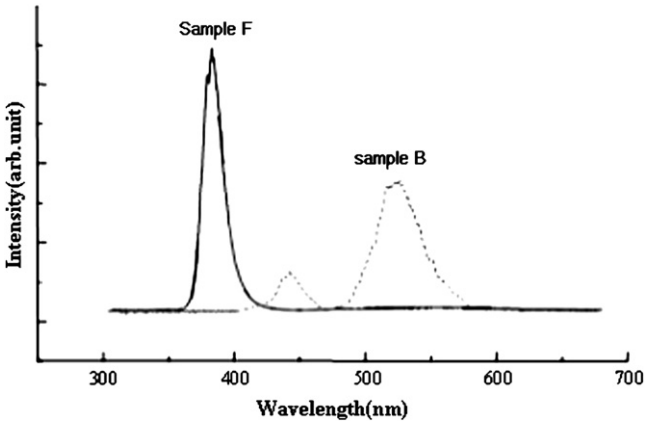

Fig. 4. PL spectra for ZnO thin films with and without a Zn buffer layer.

measured to be 5.47 nm. It is a general trend that the surface roughness of a film increases as the underlayer thickness increases because the difference in height between the highest part and the lowest part of the underlayer increases with an increase in the underlayer thickness.

Fig. 4 shows the room temperature photoluminescence (PL) spectra of annealed ZnO/Zn/Si (100) samples with and without a Zn buffer layer. A strong green band (520 nm) and a weak blue band emission (430–460 nm) appear in the sample without a Zn buffer layer (sample B) whereas only a strong ultraviolet band emission (380 nm) appears in the sample with a Zn buffer layer (sample F). The UV peak at around 380 nm is attributed to two different emission sources. One is the spontaneous radiation of the free exciton and the other is electron-hole plasma (EHP) radiation caused by a high excitation density [11]. According to previous studies [12,13], the green band at ~525 nm is formed by the transitions from shallow donors to deep acceptors, such transition is accompanied by phonon replica process. The deep acceptor has a ground state and excited states. Therefore, it is clear that the appearance of the ultraviolet emission is an evidence of the improvement in the crystallinity of the ZnO film by using a Zn buffer layer. As mentioned earlier, it is difficult to grow epitaxial ZnO films directly on Si substrates owing to amorphous SiO_2 formation and large lattice mismatch between ZnO and Si.

The reason why the crystallinity of ZnO films can be substantially improved by using ZnO buffer layers as follows: Zn has a hexagonal closed-packed (hcp) structure with lattice constants of $a = 2.665$ Å and $c = 4.95$ Å. ZnO also has an hcp structure with lattice constants of $a = 3.252$ Å, $c = 5.213$ Å and Si has a diamond cubic structure with lattice constants of $a = 5.430$ Å. Therefore, if Zn and ZnO films grow on the Si (100) substrate in such a way as ZnO (0001)//Zn (10110)//Si (100), lattice mismatches between Zn and Si are 1.7% along the Si [010] direction and 9.7% along the Si [001] and those between Zn and ZnO are 5.4% along the Zn [1210] direction and 1.5% along the Zn [0001] direction, which are much smaller than those between ZnO (0001) and Si (100) [4].

Another element which must be considered in choosing a buffer layer is thermal expansion coefficient. The thermal expansion coefficients of ZnO, Zn, and Si are $a = 2.9 \times 10^{-6}$/K and $c = 4.75 \times 10^{-6}$/K for ZnO, $a = 30.2 \times 10^{-6}$/K for Zn, and 2.6×10^{-6}/K (at 313 K) and 4.6×10^{-6}/K (at 400 K) for Si, respectively. Therefore, thermal strain field will form at the interfaces during annealing, if a Zn buffer layer is used because the thermal expansion coefficient of Zn is much smaller than those of ZnO and Si.

Concerning the interface reaction during annealing there is little possibility that Zn–Si–O compounds form at the interface between the Zn buffer layer and the Si substrate because the surface of the Si substrate was cleaned to remove native oxides at the surface with diluted HF dipping and then in-situ Ar ion sputter etching prior to Zn sputter deposition. We cannot find any diffraction peak of Zn–Si or Zn–Si–O compounds in the XRD diffraction pattern for the sample annealed at 700 °C (Fig. 1b, d, f, and h), which suggests that no chemical reaction between Zn and Si at the interface of the Zn layer and the Si substrate at 700 °C, that is, the Zn buffer layer is thermally stable on Si (100). However, it should be noted that a Zn buffer layer is rather unfavorable from the viewpoint of thermal expansion.

4. Conclusion

It was confirmed by XRD and PL analysis results that the crystallinity of a ZnO thin film deposited by RF magnetron sputtering is substantially improved by using a Zn buffer layer. However, the surface roughness of the ZnO film tends to increase with increasing the Zn buffer layer thickness. The highest ZnO film quality is obtained with a 110 nm thick Zn buffer layer and the surface roughness of the ZnO film deposited on the Zn buffer layer 110 nm thick is 5.47 nm.

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