Pure UV photoluminescence from ZnO thin film by thermal retardation and using an amorphous SiO\textsubscript{2} buffer layer

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**Abstract**

ZnO/SiO\textsubscript{2} thin films were fabricated on Si substrates by E-beam evaporation with thermal retardation. The as-prepared films were annealed for 2 h every 100 °C in the temperature range 400–800 °C under ambient air. The structural and optical properties were investigated by X-ray diffraction (XRD), atomic force microscopy (AFM) and photoluminescence (PL). The XRD analysis indicated that all ZnO thin films had a highly preferred orientation with the \textit{c}-axis perpendicular to the substrate. From AFM images (AFM scan size is 1 \textmu m \times 1 \textmu m), the RMS roughnesses of the films were 3.82, 5.18, 3.65, 3.40 and 13.2 nm, respectively. PL measurements indicated that UV luminescence at only 374 nm was observed for all samples. The optical quality of the ZnO film was increased by thermal retardation and by using an amorphous SiO\textsubscript{2} buffer layer.

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**1. Introduction**

Recently, a great deal of attention has been paid to ZnO as its properties offer great potential, i.e. a large band-gap energy of 3.37 eV for the wurtzite structure at room temperature and large exciton binding energy of \textasciitilde 60 meV. ZnO has also been employed in a vast range of devices including short wavelength light emitting diodes [1], and photodetectors [2]. Substrate selection is a crucial issue in ZnO growth. Silicon (Si) is the most suitable substrate not only because of its low cost but also for its additional advantages in integrated photonic electronic devices. However, direct growth of ZnO films on Si is extremely difficult and often results in amorphous or polycrystalline films due to the mismatch of large lattice and thermal expansion coefficients between ZnO and Si. Films deposited on a buffer layer are better than those grown directly on the Si substrate. Many different buffer layers such as MgO [3], SiC [4] and MgF\textsubscript{2} [5] have been employed. ZnO is a promising material for light emitters in the UV region. The optical quality of ZnO, which is expressed as the ratio of the peak intensities of near band-edge emission \((I_{NBE})\) to that of deep-level emission \((I_{DL})\), that is \(I_{NBE}/I_{DL}\), is a key aspect for studying the applications of ZnO film in the UV region. Kumano et al. [6] obtained a ratio as high as 60 even at room temperature. Zhao et al. [7] reported an intensity ratio of 122 for thin films prepared at 650 °C by pulsed laser deposition (PLD).

In this paper, ZnO films were fabricated on Si substrates by E-beam evaporation using SiO\textsubscript{2} as the buffer layer. Thermal retardation for 30 min at a temperature of 300 °C, higher than the deposited temperature of 250 °C, was used to increase the optical quality of the ZnO film. UV emission was observed at only 374 nm. Furthermore, the influence of the annealing temperature on the as-prepared ZnO/SiO\textsubscript{2} film has been investigated in detail.

**2. Experimental**

ZnO/SiO\textsubscript{2} films were grown on Si substrates by E-beam evaporation (PMC90S, Protech Korea Ltd). SiO\textsubscript{2} and ZnO were...
deposited at 250 °C. The chamber was evacuated to a base pressure of 2.0 × 10^{-5} Torr, then Ar (purity: 99.999%) at 18 SCCM (cubic centimeter per minute at STP) was used to etch the substrates for 5 min. Then, a flow of O₂ (purity: 99.999%) at ~17 SCCM for SiO₂ and ~20 SCCM for ZnO was turned on. The electron gun voltage was 7.10 kV for depositing both ZnO and SiO₂. The current was 30 mA for ZnO and 89 mA for SiO₂. The deposited sources of ZnO and SiO₂ were 99.999% pure. SiO₂ films were deposited at a rate of 5.2 Å/s, while 3.2 Å/s was used for ZnO films. Each layer was ~200 nm thick. Finally, the chamber temperature was raised from 250 to 300 °C for 30 min after the films were deposited. Subsequently, the as-deposited films were annealed in a tube furnace for 2 h every 100 °C for 30 min.

The structures of the films were characterized by a Bruker D8-advance X-ray diffractometer with Cu Kα (λ = 1.5406 Å) radiation. The 2θ range used in the measurements was 10–70° in steps of 0.02° s⁻¹. AFM images were collected using a CSPM4000 scanning probe microscope system (Benyuan Nano-Instruments Co. Ltd., Beijing, China). PL spectra were acquired with a FluoroMax-2 fluorescence spectrometer (JOBIN YVON-SPEX) at 350–600 nm, with a 325 nm (Xe lamp) excitation light. The photoluminescence excitation (PLE) spectra were measured in the interval 300–400 nm with a detection wavelength of 374 nm. All measurements were performed in air at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of the ZnO thin films. Whether the films were annealed or not, only the (0 0 2) peaks were observed, which shows that the ZnO thin films have a highly preferred orientation with the c-axis perpendicular to the substrate. No SiO₂ diffraction peaks were observed in the films. This means that SiO₂ is amorphous in those samples. Unlike ZnO films on crystalline substrates, there is no epitaxial relationship between the ZnO thin films on the SiO₂ buffer layer. From the full-width at half-maximum (FWHM) and the peak position of the (0 0 2) peak, the grain sizes in the films can be estimated with the Scherrer formula. Calculation of the film stress is based on the biaxial strain model [8]. Grain sizes and biaxial stresses, calculated from (0 0 2) peak positions, are shown in Table 1. The interplanar spacing parameters are smaller than d₀ (2.6035 Å, is the strain-free interplanar spacing) and compressive stresses are induced due to the interplanar spacing between the ZnO thin films on the SiO₂ buffer layer. The strain-free interplanar spacing (and compressive stresses are

<table>
<thead>
<tr>
<th>Sample</th>
<th>2θ (deg.)</th>
<th>Interplanar spacing d (Å)</th>
<th>FWHM (deg.)</th>
<th>Graininess (Å XRD)</th>
<th>Graininess (Å AFM)</th>
<th>σ₃σ₀ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-prepared</td>
<td>34.481</td>
<td>2.5990</td>
<td>0.383</td>
<td>218</td>
<td>215.6</td>
<td>0.4027</td>
</tr>
<tr>
<td>400 °C</td>
<td>34.480</td>
<td>2.5990</td>
<td>0.314</td>
<td>266</td>
<td>243.6</td>
<td>0.4027</td>
</tr>
<tr>
<td>500 °C</td>
<td>34.581</td>
<td>2.5917</td>
<td>0.355</td>
<td>235</td>
<td>205.8</td>
<td>2.7494</td>
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<tr>
<td>600 °C</td>
<td>34.641</td>
<td>2.5873</td>
<td>0.330</td>
<td>253</td>
<td>215.0</td>
<td>3.7746</td>
</tr>
<tr>
<td>700 °C</td>
<td>34.561</td>
<td>2.5931</td>
<td>0.311</td>
<td>269</td>
<td>263.3</td>
<td>2.4232</td>
</tr>
<tr>
<td>800 °C</td>
<td>34.561</td>
<td>2.5931</td>
<td>0.300</td>
<td>278</td>
<td>432.0</td>
<td>2.4232</td>
</tr>
</tbody>
</table>

Fig. 1 shows the XRD patterns of the ZnO thin films on Si substrate using SiO₂ as buffer layers and at different annealing temperatures.

Table 1 Data evaluated from XRD and AFM for samples with different annealing temperatures.
4. Conclusions

ZnO/SiO₂ thin films on Si substrates were fabricated by E-beam evaporation. Thermal retardation for 30 min at a temperature of 300 °C, higher than the deposited temperature of 250 °C, was used to increase the optical quality of the ZnO film. XRD demonstrated that the as-prepared and annealed ZnO thin films have a highly preferred orientation with the c-axis perpendicular to the substrate. The SiO₂ buffer layer is amorphous. AFM images illustrated that the surfaces of the thin films were very smooth. The RMS roughnesses of the films were 3.82, 5.18, 3.65, 3.58, 3.40 and 13.2 nm, respectively. PL spectroscopy showed that UV luminescence at only 374 nm is observed for all samples. The intensity of the UV emission at 374 nm increased with increase in annealing temperature up to 700 °C. The optical quality of the ZnO film has been improved by thermal retardation and by using an amorphous SiO₂ buffer layer.
Acknowledgment

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References