ZnO Films Deposited on Porous Silicon by DC Sputtering

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Abstract

ZnO is now a fascinating semiconductor oxide material for light emission or transparent electronic conductors. We deposited ZnO films on porous silicon, which is known as a light emitting material based on silicon, by means of a direct current sputtering technique. The deposition was performed at room temperature, and the samples were annealed afterwards to improve the ZnO crystalline quality. The discussion to compare our results with that formed on Si wafer, reveals that the ZnO on porous silicon has the better crystalline quality in the scope of an X-ray diffraction measurement.

Keywords

ZnO Film, DC Sputtering, Annealing, X-Ray Diffraction Analysis, Porous Silicon

1. Introduction

ZnO attracts much attention [1]-[8] as a light emitting material or a transparent electronic conducting material. It is generally challenging to form compound semiconductor because the control of both elemental ratio and structural defects is inevitable. Nowadays, various deposition techniques have been applied to deposit ZnO films: radio frequency (RF) sputtering [9] [10], molecular beam epitaxy [11] [12], pulsed laser deposition [13] [14] and chemical vapor decomposition [15] [16]. Especially we have been challenging the deposition using a direct current (DC) sputtering technique [17]-[23] that is not used so often for oxide material. It was reported that the post-deposition annealing can well enhance the crystalline quality of ZnO both on the Si and glass substrates.

Porous silicon has a long history of its development. The remarkable issue is
found in 1990: visible photoluminescence even observed by naked eye. The strong photoluminescence is fascinating because silicon is an indirect transition semiconductor and so light emission had not been thought to occur to such an extent. The emission from porous silicon is usually observed in the red or infrared region [24] [25]. The blue photoluminescence has been also reported from porous silicon, but it derives from silicon oxide formed on the surface of porous silicon. The electroluminescence has been also observed so far. It costs so little to form porous silicon where the relatively low reproducibility is, on the other hand, a big obstacle to make use of porous silicon as a commercial device.

ZnO has a wide direct band gap of 3.37 eV and a large exciton binding energy of 60 meV [26]. So ZnO has the ability to emit light in a blue or ultraviolet region. If ZnO is deposited on porous silicon, both blue and red light are supposed to be generated and combined. Actually Kayahan reported white light luminescence from ZnO deposited on porous silicon. Their interest was mainly focused on the luminescence. They showed X-ray diffraction pattern just for the purpose of monitor ZnO crystals.

In this article, we study the ZnO film quality with regard to an X-ray diffraction pattern, if it is deposited on porous silicon. Our discussion will address to the comparison with the ZnO film on silicon wafer reported before. Porous silicon is a kind of disorder system in itself, and therefore the ZnO state on porous silicon is not clarified yet. In order to obtain basic information about ZnO structure, we investigated X-ray diffraction spectra from ZnO deposited on porous silicon closely.

2. Experimental Details

We prepared two kinds of porous silicon. We used (100) boron-doped p-type silicon wafer with a resistivity between 1 and 10 Ω·cm for both kinds of porous silicon samples. A Si wafer (anode) and a Pt counter electrode (cathode) were installed in an electrolyte. An anodization of Si wafer was done at the current density of 20 mA/cm². The anodized area is just less than 2 cm². The other condition is different in the two kinds of samples. One is formed in the most well-known procedure. The electrolyte consists of HF (50 wt%):ethanol = 1:1 (volume ratio) and anodization time was 30 min. for one kind of sample (S1). For the other sample (S2), the electrolyte consists of HF (50 wt%):H₂O = 1:4 (volume ratio) and anodization time was 5 min. The latter anodization condition is not as popular as the former one. The appearance of the anodized surface is quite different as shown in the next section. The photoluminescence was checked only by naked eye using a handy mercury UV lamp for the excitation.

The obtained porous silicon samples were used as a substrate, and ZnO was deposited onto it. We used a ZnO ceramic target disk (4N) with 70 mm in diameter. The target was situated at a distance of 30 mm from the porous silicon substrate. The deposition was performed for five hours under the ambient pressure of 7.5 Pa and input power of 24 W. The substrate was not intentionally heated during the deposition. After the deposition, annealing was performed by
an electric furnace at 950°C for an hour in the air. The annealing condition is the same as the report by Kayahan.

The obtained samples were examined by means of an X-ray diffraction (XRD) measurement. The XRD pattern was taken with a spectrometer (Ultima IV, Rigaku) equipped with a Cu target and a Ni filter. X-ray tube was loaded with 40 kV and 40 mA in the experiment. The surfaces of the samples were observed by a scanning electron microscope (SEM) of JSM-6510LA by JEOL Ltd.

3. Results

The appearance of the porous silicon is shown in Figure 1. Both samples show the circular porous silicon region that can be clearly recognized. The appearance is quite different: S1 has a dark brownish color uniformly and S2 has a yellowish spotted pattern. The diameter of the circle is about 1 cm. In this photograph, slight photoluminescence of orange color is seen near the periphery of the circle area because of the white light irradiation for taking a photograph. Figure 2 shows the photoluminescence irradiated with a UV lamp. The photoluminescence intensity is distinctly stronger in S2 for visible light.

![Figure 1](image1.png)

**Figure 1.** The optical photographs of the two kinds of samples. Inside the central circular area, porous silicon is formed on the surface.

![Figure 2](image2.png)

**Figure 2.** The optical photographs of the two kinds of samples excited with a mercury lamp.
The SEM photographs taken from S1 and S2 samples are shown in Figure 3 and Figure 4, respectively. Figure 3 was taken from 65 degree to the normal direction, and shows the surface in the upper side and the cross section in the lower side. The white part at the most upper layer that is seen white in the figure corresponds to the ZnO layer: the cross sectional image of several μm in thickness and the surface area. Under ZnO layer, we can observe obvious two layers of porous silicon layer (middle) and silicon substrate layer (bottom). The obtained ZnO layer has a smooth and uniform structure. The SEM photo of the sample S2 in Figure 4 shows island structure of porous silicon surface. The edges at all islands show doubled lines, which indicate that the porous silicon islands are capsulated with ZnO films.

![Figure 3](image1)  
**Figure 3.** The SEM photographs of the sample S1: surface (upper) and cross section (lower).

![Figure 4](image2)  
**Figure 4.** The SEM photographs of the sample S2 (surface).
The XRD patterns taken from ZnO/S1 and ZnO/S2 are shown in Figure 5 and Figure 6, respectively. These patterns do not include the reflection from the substrates because the ZnO film was thick enough. Both figures consist of two patterns: as deposited sample (bottom) and annealed sample (top). In both figures, the pattern from the annealed samples consists of 5 structures diffracted from (100), (002), (101), (102) and (110) crystalline planes. As-deposited samples show only (002) diffraction that is broader and shifted to the lower 2θ side compared with that of annealed samples.

4. Discussion

According to the XRD data for ZnO (JCPDS data) tells us that the diffraction from (101) plane is the strongest. Contrary to the data, (002) diffraction is the strongest in both samples. It stems from the fact that the deposited ZnO film is preferentially oriented along to (101). The preference is stronger in the ZnO/S1 sample.

We reported on the ZnO film deposited on Si substrate [23] and glass sub

![Figure 5](image1.png)

**Figure 5.** The XRD patterns taken from the sample S1.

![Figure 6](image2.png)

**Figure 6.** The XRD patterns taken from the sample S2.
strate [27]. As-deposited sample has shown only (002) diffraction in both cases, similar to the results above. And then, the both samples, after annealed, have also shown only one structure corresponding to (002) diffraction without any other structures. However the ZnO deposited on porous silicon have shown the occurrence of the other four orientations by the annealing. The reason for the occurrence may be due to the surface structure of porous silicon, which does not have a smooth surface but a numerous pits or holes at a nano scale region. It allows a variety of crystal orientations of growing. **Figure 4** shows the obvious bumpy surface of many terraces. It is easily understood from the point of view. On the other hand, **Figure 3** shows a smooth surface apparently, but the annealing effect was different compared with the sample on Si wafer or glass substrates. It derives from the nanostructures of porous silicon that cannot be observed SEM photographs in the figures here.

We discuss here the (002) peak structure quantitatively comparing four samples with each other. The full width at half maximum (FWHM) of the peak corresponding to the (002) diffraction is considered here. **Table 1** shows those of ZnO/S1 and ZnO/S2 as well as ZnO/Si and ZnO/glass reported in the literature. The table shows the data both before and after the annealing. The annealing condition for ZnO/glass is 600°C and 0.5 hours, which is different from the others (950°C and 1 hour). It was because the glass cannot endure and melt above 600°C. In all cases, the FWHM was reduced by the annealing. It is well accepted that the deposited ZnO restores from the crystallographic view by the annealing. In addition, **Figure 3** and **Figure 4** show that all samples before annealing have a slight shift to the lower angle side. This means the ZnO has tensile stress normal to the surface. In other words, compressive stress exists along the surface. Summarizing the above, the as-deposited ZnO film includes a uniform strain and non-uniform compressive stress, eased by the successive annealing.

For the as-deposited, all samples showed (002) reflection peaks regardless of the substrates. It is quite attractive phenomenon. The fact indicates that the very initial procedure of deposition is presumed to be the same. The (002) orientation is surely preferred to be grown even if the surface is rough at the nano scale. This can be related to a deposition mechanism of ZnO.

Interesting point is the difference among the samples. The annealing condition is peculiar for ZnO/glass, so the other three kinds of samples are compared here. The peak position before the annealing and the shift amount by the annealing is quite similar for the three kinds of samples. The peak at 34.0° or 34.1° is shifted to 34.5° in all cases. Contrarily, the FWHM of the peak does not show the same value. As-deposited sample shows the largest FWHM for ZnO/S2 and then ZnO/S1 and ZnO/Si to become smaller. It is assumed that the uniform

<table>
<thead>
<tr>
<th>Degree</th>
<th>ZnO/S1</th>
<th>ZnO/S2</th>
<th>ZnO/Si</th>
<th>ZnO/Glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>0.801</td>
<td>0.825</td>
<td>0.725</td>
<td>0.91</td>
</tr>
<tr>
<td>After</td>
<td>0.24</td>
<td>0.187</td>
<td>0.262</td>
<td>0.798</td>
</tr>
</tbody>
</table>

**Table 1.** The FWHM’s of samples before and after annealing.
strain is the biggest for ZnO/S2 because the ZnO/S2 has the roughest surface in the three. However, this tendency is turned over by the annealing. Surprisingly ZnO/Si has the largest FWHM and then ZnO/S1 and ZnO/S2. The FWHM of the peak is the narrowest for ZnO/S2 after the annealing. It suggests that the ZnO/S2 has the least strains in the film, even compared with ZnO on a Si single crystalline wafer. It leads to the conclusion that an S2 type of the substrate is helpful for growing a ZnO film with less uniform strain inside the film. This is also supported by the FWHM of the (101) diffraction peak. After the annealing, the values for ZnO/Si and ZnO/S2 are 0.221° and 0.165°, respectively. The reason why rougher surface of S2 can provide better ZnO crystal is the next interesting point.

5. Conclusion

ZnO films were deposited onto porous silicon by a DC sputtering method and investigated mainly by means of XRD measurements. Two kinds of porous silicon were engaged in this research. One was formed by the anodization with an electrolyte including ethanol (S1), and the other without ethanol (S2). The surface morphology is quite different in the two: S1 looks apparently smooth by the SEM observation while S2 obviously consists of many terrace-like structures and then rough surface in the same-scale view. As-deposited ZnO films are oriented along (002) on the surface in both cases. The FWHMs of the (002) diffraction peaks are broader than that of ZnO deposited on single crystal Si wafer, and sharper than that of ZnO deposited on a glass substrate. The S2 sample provided broader peak than the S1 sample. The peak shift away from the JCPDS data is very similar in all four cases. Annealing enhanced the crystalline quality; the FWHMs were sharpened and the peak shift was eliminated. At the same time, (100), (101), (102) and (110) diffraction peaks for ZnO appeared from the S1 and S2 samples, which do not appear from ZnO on Si wafer. Further, the interesting point is that the FWHM of the (002) peaks after annealing was narrower compared with ZnO on Si wafer. And the S2 sample that has a rougher surface indicated a narrower (002) peak than the S1 sample. The ZnO film with high crystalline quality can be formed on porous silicon formed especially in an ethanol-less electrolyte.

References


