Enhanced Light Scattering by Preferred Orientation Control of Ga Doped ZnO Films Prepared through MOCVD

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1. Introduction

As a front contact for silicon based thin film solar cells, the Transparent Conductive Oxide (TCO) layers on glass should not only possess satisfactory optoelectric properties, but also exhibit light trapping capability to increase the light absorption within the active layers [1–3]. Textured surface on TCO layers is usually designed to scatter the incident light to elongate the pathway of light and subsequently increase the short circuit current density \( J_{sc} \) by 20–40% in the solar cells [4–6]. Recently, several techniques were developed for obtaining surface textures. One of the common methods was the wet-etching of sputtered Al-doped ZnO (AZO) films by using acid treatment to create crater-like structure by which the light scattering is increased. Nevertheless, this process costs highly due to the thick AZO film sputtering (~1 μm). Furthermore, complicated treatments are required to obtain textured topography, like soaking in an acid solution, lithography, and so forth, which increase the fabrication cost and accompany the risk of introducing unexpected impurities [7, 8] into the TCO layers. Moreover, atmosphere pressure chemical vapor deposition (APCVD) of F-doped SnO\(_2\) and low-pressure chemical vapor deposition (LPCVD) of B-doped ZnO, which exhibited pyramidal crystalline habits on the film surface and thus are capable of scattering the incident light, were also proposed [9–13].

In this work, we explored the methodology to increase the light diffuse transmittance through controlling the preferred orientation of polycrystalline Ga doped ZnO (GZO) films grown by the low-pressure chemical vapor deposition (LPCVD) technique using diethyl zinc (DEZn) and trimethyl gallium (TMGa) as the Zn and Ga precursors, respectively. Different from the low process temperature (~150°C) of B-doped ZnO, the GZO films exhibited satisfactory optoelectric
properties at reaction temperatures as high as 400°C. X-ray diffraction measurement indicated that major growth direction was (002) plane and secondary electron microscopy showed that column-like granule structure with planar surface was formed. By depositing a low temperature ZnO layer to serve as a template for high temperature GZO film growth, the main preferred orientation of the GZO films was manipulated to (110) plane and the film surface to the pyramid-like structure. Through this two-step growth, the light diffuse transmittance of the film with a GZO (~800 nm)/ZnO (766 nm) combination exhibited 13% increase at 420 nm wavelength due to the preservation of the pyramidal surface morphology.

2. Results and Discussion

2.1. Effect of Growth Temperature on the Crystalline Orientation of GZO Films. First of all, the GZO films were grown at various deposition temperatures to explore the effects of growth temperature and growth rate on the orientation of the GZO films. The detailed experiment was carried out as our previous work [14]. The XRD measurement was used to determine the crystalline orientation of the GZO films deposited. Figure 1 reveals the XRD patterns of the GZO films grown at various substrate temperatures. Started from (110) plane orientation at low temperatures like 300°C, the main crystalline orientation changed to (002) plane when the substrate was raised to 400°C. When further raised to 450°C, all the crystalline planes including (100), (101), (002), and (110) appeared. With increasing temperature from 300 to 350°C, the growth mode of GZO film was already in the diffusion controlled regime (Figure 2). So the surface with the highest absorption rate will dominate the film growth orientation [15, 16]. As a result, the (002)-oriented films could be obtained due to the enhancement of surface diffusion [17]. At further high temperature like 450°C, all crystal planes appeared because the surface collision rate is rate controlling; thereby all planes could appear. The intensity ratio of (002) plane for GZO film with substrate temperature 400°C increases by large amount compared to GZO film with substrate temperature 350°C due to the higher substrate temperature and the higher crystalline so that the intensity of (002) plane for GZO film with substrate temperature 400°C is higher than the GZO film with substrate temperature 350°C. Besides, the (002) plane is preferred to grow at substrate temperature 400°C than the other planes.

Figure 2 shows the Arrhenius plot of the film growth rate of GZO at various substrate temperatures. It has been demonstrated that the growth of GZO film is characterized by three regimes. For low temperature (below 250°C) the film growth rate increases exponentially with substrate temperature according to an Arrhenius behavior in which the deposition rate is controlled by an activated process such as adsorption, surface diffusion, chemical reaction, and desorption. The growth rate is thus controlled by mass transfer and reaction kinetics. The net activation energy for the ZnO thin films deposition in this region is calculated to be ~3.95 kcal mol⁻¹. Moreover, the growth rate is also proportional to the surface density of the unit structure (Nₛ), meaning that the most densely packed plane grows the fastest [14–16]. In the intermediate zone (250–350°C), the growth rate reaches its maximum and remains constant, indicating that the growth rate is diffusion limited, which leads to the fact that the crystallographic plane with the highest absorption rate grows the fastest. At higher temperatures (above 350°C), the logarithmic plot shows a negative slope. At these temperatures, the precursor solvent vaporizes away from the substrate and the precursor chemical reaction is carried out in the vapor phase. The growth mechanism is thus controlled by the surface collision. We found that the (002) preferred orientation of GZO film could be controlled by adjusting the deposition temperature and growth rate. However, the (110) preferred orientation that presents for the pyramidal-like structure could not be controlled within these conditions. According to these issues, we develop a methodology to control the (110) preferred orientation of GZO films by employing a low temperature of ZnO layer before high temperature GZO growth.
Table 1: The atomic density of some common planes for ZnO.

<table>
<thead>
<tr>
<th>Crystal plane</th>
<th>(110)</th>
<th>(100)</th>
<th>(002)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface atomic density ( (N_s) ) (atom/cm(^2))</td>
<td>(0.22 \times 10^{16})</td>
<td>(0.12 \times 10^{16})</td>
<td>(0.11 \times 10^{16})</td>
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</table>

Figure 3 demonstrates the effect of the ZnO buffer layer thickness on the natively textured surface of ZnO films prepared at 146°C. As can be seen in Figure 4, all the ZnO thin films surfaces were pyramid-like grain and the grain size was increased together with the increase of ZnO film thickness. These results clearly indicated that the surface grain size of ZnO films could be modified by adjusting the ZnO thickness. Consequently, the GZO films were grown at 400°C onto the various ZnO buffer layer thicknesses.

The crystal structure and orientation of the as-deposited GZO thin film grown on various thickness of ZnO buffer layer were investigated using XRD and the results are depicted in Figure 5. It is worthy to note that a strong (002) peak was observed for GZO film growth onto a thin ZnO buffer layer (~30 nm), indicating the GZO film is highly oriented with its crystallographic c-axis perpendicular to the substrate. This is because the thin ZnO buffer layer plays a role as a seed layer for the GZO film growth and thus there is no significant change in the orientation of GZO film. However, with the increasing in ZnO buffer layer thickness, the preferred orientation changes from the plane with minimum surface energy (002) to the plane with relatively high surface energy (110). This can be explained due to the forming of (110) structure of ZnO buffer layer served as an energy barrier and thus the (110) preferred orientation of GZO film grown on (110) plane is easier than other crystal planes. Evidently, GZO thin films used ZnO as buffer layer whose thickness is thicker than 212 nm are favorable to promote the GZO film growth along (110) preferred orientation. These results conclude that ZnO buffer layer plays an important role in the change of growth direction of GZO film. Further, we studied the effect of deposition temperature of GZO on orientation of GZO film growth by using a thick 422 nm ZnO buffer layer as a template. Figure 6(a) depicts the structure and orientation of GZO/ZnO (422 nm) films grown at different deposition temperature.

Figure 4 demonstrates the effect of the ZnO buffer layer thickness on the natively textured surface of ZnO films prepared at 146°C. As can be seen in Figure 4, all the ZnO thin films surfaces were pyramid-like grain and the grain size was increased together with the increase of ZnO film thickness. These results clearly indicated that the surface grain size of ZnO films could be modified by adjusting the ZnO thickness. Consequently, the GZO films were grown at 400°C onto the various ZnO buffer layer thicknesses.

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Figure 4: Surface morphology of ZnO films at various thicknesses: (a) 212 nm, (b) 422 nm, (c) 652 nm, and (d) 766 nm. The deposition temperature was $146^\circ C$.

Figure 5: X-ray diffraction patterns of the GZO film growth on different thickness of ZnO buffer layer. The deposition temperature of GZO film was $400^\circ C$.

Figure 6: X-ray diffraction patterns of the GZO film grown on a thick 422 nm ZnO buffer layer at different deposition temperature.

Can estimate the activation energy barrier for (100) plane through the Arrhenius plot of (100) intensity ratio at different deposition temperature.

Figure 7 shows the Arrhenius plot of (100) intensity ratio between 350 and $450^\circ C$. From the plot, the activation energy barrier $E_a = -8.314 \times \text{slope (J/mol)}$. The activation energy barrier for (100) crystal plane was estimated
Figure 7: The Arrhenius plot of intensity ratio of (100) crystal plane of the GZO film grown on a thick 422 nm ZnO buffer layer against the reciprocal of the absolute temperature.

~11.24 kcal mol\(^{-1}\), which is higher than that observed for film growth (3.9 kcal mol\(^{-1}\)). This result indicates that the (100) crystal plane could be controlled at high temperature deposition.

Figures 8(a)–8(d) reveal typical SEM images of natively textured surface GZO thin films deposited on various thickness of ZnO buffer layer. The GZO films grown on different ZnO buffer layer exhibit a well-textured morphology.

Figure 8: Surface morphology of GZO film with thickness ~800 nm on different ZnO buffer layer thicknesses: (a) 212 nm, (b) 422 nm, (c) 652 nm, and (d) 766 nm. The deposition temperature of GZO film was 400°C.
Table 2: Summary of the electrical properties of GZO films prepared at 400°C on various ZnO buffer layer thickness.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Resistivity (Ω cm)</th>
<th>Mobility (cm² V⁻¹ s⁻¹)</th>
<th>Bulk concentration (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GZO (800 nm)/ZnO (30 nm)</td>
<td>$5.3 \times 10^{-4}$</td>
<td>16.25</td>
<td>$7.3 \times 10^{20}$</td>
</tr>
<tr>
<td>GZO (800 nm)/ZnO (212 nm)</td>
<td>$5.5 \times 10^{-4}$</td>
<td>16.10</td>
<td>$7.1 \times 10^{20}$</td>
</tr>
<tr>
<td>GZO (800 nm)/ZnO (422 nm)</td>
<td>$5.7 \times 10^{-4}$</td>
<td>16.30</td>
<td>$6.8 \times 10^{20}$</td>
</tr>
<tr>
<td>GZO (800 nm)/ZnO (652 nm)</td>
<td>$5.8 \times 10^{-4}$</td>
<td>16.35</td>
<td>$6.7 \times 10^{20}$</td>
</tr>
<tr>
<td>GZO (800 nm)/ZnO (766 nm)</td>
<td>$5.9 \times 10^{-4}$</td>
<td>16.45</td>
<td>$6.5 \times 10^{20}$</td>
</tr>
</tbody>
</table>

In order to be used as front contact in thin film solar cells, electrical property of these GZO/ZnO films must be considered, as shown in Table 2. It can be revealed that the increasing of ZnO buffer layer thickness leads to slight increase in resistivity and slight reduction of carrier concentration of GZO film. Nevertheless, all the GZO films with various ZnO buffer layer thicknesses exhibit a relatively low resistivity of $10^{-3}$ Ω cm. In addition, the mobilities of GZO films are increased slightly when increasing ZnO buffer layer thicknesses due to the pyramid-like grains size being increased which was verified by SEM (Figure 8).

3. Conclusions

GZO films with a pyramidal texture surface were successfully developed by the control of (110) preferred orientation. The films exhibited satisfactory optoelectric properties. By employing the low temperature ZnO buffer layer, we improved the light diffuse transmittance of the film up to 13% at 420 nm wavelength. Thus, the obtained GZO films deposited ZnO buffer layer has high potential for use as front TCO layers in Si-based thin film solar cells. These results could develop the potential way to fabricate high haze TCO thin film using MOCVD or sputtering techniques by depositing a low temperature ZnO layer to serve as a template.

Competing Interests

The authors declare that they have no competing interests.

Authors’ Contributions

Nam Giang Nguyen and Van Thi Thanh Ho conceived and designed the experiments and then they analyzed the experimental results and wrote the paper; Long Giang Bach performed the experiments.

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