Research Article

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

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We have explored the effective approach to fabricate GZO/ZnO films that can make the pyramidal surface structures of GZO films for effective light scattering by employing a low temperature ZnO buffer layer prior to high temperature GZO film growth. The GZO thin films exhibit the typical preferred growth orientations along the (002) crystallographic direction at deposition temperature of 400°C and SEM showed that column-like granule structure with planar surface was formed. In contrast, GZO films with a pyramidal texture surface were successfully developed by the control of (110) preferred orientation. We found that the light diffuse transmittance of the film with a GZO (800 nm)/ZnO (766 nm) exhibited 13% increase at 420 nm wavelength due to the formed large grain size of the pyramidal texture surface. Thus, the obtained GZO films deposited over ZnO buffer layer have high potential for use as front TCO layers in Si-based thin film solar cells. These results could develop the potential way to fabricate TCO based ZnO thin film using MOCVD or sputtering techniques by depositing a low temperature ZnO layer to serve as a template for high temperature GZO film growth. The GZO films exhibited satisfactory optoelectric properties.

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 μ m). 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 SnO₂ 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 $\sim 3.95 \text{ kcal mol}^{-1}$. Moreover, the growth rate is also proportional to the surface density of the unit structure (N_s), meaning that the

FIGURE 1: X-ray diffraction patterns of GZO film as a function of deposition temperature.

FIGURE 2: Arrhenius plot of the film growth rate of GZO film against the reciprocal of the absolute temperature.

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.

Crystal plane	(110)	(100)	(002)
Surface atomic density (N_s) (atom/cm ²)	0.22×10^{16}	0.12×10^{16}	0.11×10^{16}
Crystal plane structure

FIGURE 3: Structural properties of ZnO films at various thicknesses. The deposition temperature was 146°C.

2.2. Effect of ZnO Buffer Layer Thicknesses on the Orientation of GZO Films. Figure 3 illustrates the evolution XRD patterns for the first step growth of ZnO layers at various film thicknesses. At a low growth temperatures of 146°C, the films thicker than 212 nm exhibited two diffraction peaks at a value of 2θ of 31.8 and 56.8°, corresponding to the (100) and (110) plane of hexagonal ZnO. When the film thickness is less than 212 nm, no diffraction peaks were observed due to the amorphous nature. Generally for low growth temperature of ZnO by LPCVD at about 150°C, the preferred orientation of ZnO films is (110) plane, which is evident when the film thickness is larger than ~200 nm. This result is understandable because the film growth at this temperature is controlled by surface reaction, by which the crystalline plane with the highest surface atomic density (N_s) is formed favorably. As a result, the (110) plane would be preferred for hexagonal ZnO because it has the highest surface atomic density compared with (100) and (002) plane as shown in Table 1.

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.

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.

Obviously, the orientation of GZO film growth was preferred to (100) and (110) plane in which (110) is the

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°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°C.

main crystal plane, as shown in Figure 6. This result implies that the orientation of GZO film growth might not have been influenced by deposition temperature. The intensity of (100) peak was increased slightly with increasing deposition temperature. From the change of (100) intensity ratio, we

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°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.

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 .

$\sim 11.24 \text{ kcal mol}^{-1}$, which is higher than that observed for film growth ($3.9 \text{ kcal mol}^{-1}$). 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

TABLE 2: Summary of the electrical properties of GZO films prepared at 400°C on various ZnO buffer layer thickness.

Samples	Resistivity (Ω cm)	Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Bulk concentration (cm^{-3})
GZO (800 nm)/ZnO (30 nm)	5.3×10^{-4}	16.25	7.3×10^{20}
GZO (800 nm)/ZnO (212 nm)	5.5×10^{-4}	16.10	7.1×10^{20}
GZO (800 nm)/ZnO (422 nm)	5.7×10^{-4}	16.30	6.8×10^{20}
GZO (800 nm)/ZnO (652 nm)	5.8×10^{-4}	16.35	6.7×10^{20}
GZO (800 nm)/ZnO (766 nm)	5.9×10^{-4}	16.45	6.5×10^{20}

FIGURE 9: Optical properties of GZO film with thickness ~800 nm on different ZnO buffer layer thicknesses. The deposition temperature of GZO film was 400°C.

with pyramidal texture surface, confirming that the highly textured morphology of the GZO films is preserved well after two-step growth. The surface morphology of the GZO (800 nm)/ZnO (766 nm) film shows the largest pyramidal grain size, indicating that the grain size of GZO layer strongly depends on the grain size of ZnO buffer layer.

The optical properties illustrate the transmittance and light trapping efficiency of the bilayer GZO (800 nm)/ZnO films. As shown in Figure 9, the average optical transmittances were over 80% at the wavelength from 400 to 800 nm. However, the transmittance of the films decreased slightly in the long-wavelength range above 1000 nm because of the absorption of free carriers in the ZnO films caused by gallium doping. As shown and indicated by Figures 8-9, the light scattering properties had a good relationship with the surface morphologies. The thicker the ZnO buffer layer, the higher the diffuse transmittance that was obtained due to the increasing of surface texture grain size. This suggests that the facile way to improve the light scattering capability of GZO layers is to increase the ZnO buffer layer thickness. However, one has to consider also the transparency of the GZO layer, which may be drastically reduced for too thick layers [18]. As

a result, the light diffuse transmittance of the film with a GZO (800 nm)/ZnO (766 nm) exhibited 13% increase at 420 nm wavelength due to the larger grain size of the pyramidal texture surface.

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 $10^{-4} \Omega$ 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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References

- [1] A. Shah, P. Torres, R. Tscharnner, N. Wyrsh, and H. Keppner, "Photovoltaic technology: the case for thin-film solar cells," *Science*, vol. 285, no. 5428, pp. 692–698, 1999.
- [2] H. Sai, H. Jia, and M. Kondo, "Impact of front and rear texture of thin-film microcrystalline silicon solar cells on their light trapping properties," *Journal of Applied Physics*, vol. 108, no. 4, Article ID 044505, 2010.
- [3] M. Berginski, J. Hüpkes, M. Schulte et al., "The effect of front ZnO:Al surface texture and optical transparency on efficient light trapping in silicon thin-film solar cells," *Journal of Applied Physics*, vol. 101, no. 7, Article ID 074903, 2007.
- [4] O. Isabella, J. Krč, and M. Zeman, "Modulated surface textures for enhanced light trapping in thin-film silicon solar cells," *Applied Physics Letters*, vol. 97, no. 10, Article ID 101106, 2010.
- [5] V. E. Ferry, M. A. Verschuuren, M. C. V. Lare, R. E. I. Schropp, H. A. Atwater, and A. Polman, "Optimized spatial correlations for broadband light trapping nanopatterns in high efficiency ultrathin film a-Si:H solar cells," *Nano Letters*, vol. 11, no. 10, pp. 4239–4245, 2011.
- [6] G. Yue, L. Sivec, J. M. Owens, B. Yan, J. Yang, and S. Guha, "Optimization of back reflector for high efficiency hydrogenated nanocrystalline silicon solar cells," *Applied Physics Letters*, vol. 95, no. 26, Article ID 263501, 2009.
- [7] S. Calnan, J. Hüpkes, B. Rech, H. Siekmann, and A. N. Tiwari, "High deposition rate aluminium-doped zinc oxide films with highly efficient light trapping for silicon thin film solar cells," *Thin Solid Films*, vol. 516, no. 6, pp. 1242–1248, 2008.
- [8] H. Zhu, J. Hüpkes, E. Bunte, J. Owen, and S. M. Huang, "Novel etching method on high rate ZnO:Al thin films reactively sputtered from dual tube metallic targets for silicon-based solar cells," *Solar Energy Materials and Solar Cells*, vol. 95, no. 3, pp. 964–968, 2011.
- [9] H. L. Ma, D. H. Zhang, S. Z. Win, S. Y. Li, and Y. P. Chen, "Electrical and optical properties of F-doped textured SnO₂ films deposited by APCVD," *Solar Energy Materials and Solar Cells*, vol. 40, no. 4, pp. 371–380, 1996.
- [10] N. Amin, T. Isaka, A. Yamada, and M. Konagai, "Highly efficient 1 μ m thick CdTe solar cells with textured TCOs," *Solar Energy Materials and Solar Cells*, vol. 67, no. 1–4, pp. 195–201, 2001.
- [11] S. Fay, S. Dubail, U. Kroll, J. Meier, Y. Ziegler, and A. Shah, "Light-trapping enhancement for thin-film silicon solar cells by roughness improvement of the ZnO front TCO," in *Proceedings of the 16th European Photovoltaic Solar Energy Conference and Exhibition (EU PVSEC '00)*, p. 361, Glasgow, Scotland, 2000.
- [12] T. Oyama, M. Kambe, N. Taneda, and K. Masumo, "Requirements for TCO substrate in si-based thin film solar cells -toward tandem," in *Proceedings of the Light Management in Photovoltaic Devices-Theory and Practice*, vol. 1101 of *MRS Proceedings*, Materials Research Society, 2008.
- [13] M. Kambe, K. Masumo, N. Taneda, T. Oyama, and K. Sato, "Improvement of light-trapping effect on microcrystalline silicon thin film solar cells fabricated on high haze transparent conducting oxides films," in *Proceedings of the Technical Digest/17th International Photovoltaic Science and Engineering Conference (PVSEC '07)*, p. 1161, Fukuoka, Japan, December 2007.
- [14] N. Giang Nguyen, V. T. Thanh Ho, and L.-S. Hong, "Low-resistivity, high-transmittance Ga:ZnO films prepared through metalorganic chemical vapor deposition using an inexpensive solution of diethylzinc in n-hexane as the Zn precursor," *Applied Physics Letters*, vol. 102, no. 18, Article ID 181912, 2013.
- [15] K. Nishioka, N. Mizutani, and H. Komiyama, "A model for predicting preferential orientation of chemical–vapor–deposited films," *Journal of the Electrochemical Society*, vol. 147, no. 4, pp. 1440–1442, 2000.
- [16] Y. Kajikawa, S. Noda, and H. Komiyama, "Preferred orientation of chemical vapor deposited polycrystalline silicon carbide films," *Chemical Vapor Deposition*, vol. 8, no. 3, pp. 99–104, 2002.
- [17] N. Fujimura, T. Nishihara, S. Goto, J. Xu, and T. Ito, "Control of preferred orientation for ZnO_x films: control of self-texture," *Journal of Crystal Growth*, vol. 130, no. 1–2, pp. 269–279, 1993.
- [18] S. Faÿ, J. Steinhäuser, S. Nicolay, and C. Ballif, "Polycrystalline ZnO: B grown by LPCVD as TCO for thin film silicon solar cells," *Thin Solid Films*, vol. 518, no. 11, pp. 2961–2966, 2010.