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Growth of O- and Zn-polar ZnO films by DC magnetron sputtering

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Abstract O- and Zn-polar ZnO films were grown by DC magnetron sputtering. Growth of high-quality, single-crystal ZnO thin films were confirmed by XRD and pole figure analysis. O-polar ZnO was grown on an Al_2O_3 substrate, which was confirmed by a slow growth rate (378 nm/hr), a fast etching rate (59 nm/min), and by the hillocks on the surface after etching. Zn-polar ZnO was grown on a GaN/Al_2O_3 substrate, which was confirmed by a fast growth rate (550 nm/hr), a slow etching rate (28 nm/min), and by pits on the surface after etching. Results from the present study show that it is possible to use DC-sputtering to grow ZnO film with the same polarity as other epitaxial growth methods.

Key words ZnO, DC magnetron sputtering, Polarity

1. Introduction

ZnO has always been regarded as a potential candidate for GaN growth [1] since it has a lattice parameter and a crystal structure that is similar to that of GaN. Therefore, the growth of GaN on a ZnO template has attracted special interest, because it could provide an easy way to separate GaN from the substrates. Various studies have examined the growth of GaN on a ZnO/Al_2O_3 template using hydride vapor phase epitaxy (HVPE) [2, 3] and molecular beam epitaxy (MBE) [4]. To make this technique commercially viable, a high-quality ZnO layer that can be produced using a less-expensive method is needed. It is worth noting that the growth of high-quality ZnO on a Al_2O_3 substrate is not a simple process. Therefore, the sputtering of single crystalline ZnO thin film [5] has attracted special interest. Many groups have reported the successful growth of single-crystalline ZnO by high-temperature sputtering; even a light emitting diode (LED) has been produced based on sputtered ZnO thin films [5, 6]. However, a high-quality sputtered ZnO layer will not satisfy all requirements. In a previous experiment [7], this group found that under highly volatile circumstances, such as those encountered during hydride vapor phase epitaxy (HVPE), a Zn-polar ZnO surface is essential for its stability during the growth of high-quality GaN on ZnO. However, the production of Zn-polar ZnO thin film by sputtering has not been investigated. In the present study, the growth of single-crystalline Zn-polar and O-polar ZnO films by DC magnetron sputtering was investigated, along with the crystal quality and polarity of sputtered ZnO films grown at a high-growth temperature in a high-vacuum sputtering chamber.

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2. Experimental

ZnO thin films were sputtered on Al_2O_3 (0001) substrates and Ga-polar GaN templates by DC magnetron sputtering. The substrates were degreased, but no other pre-treatment, including chemical etching, was performed. The background pressure of the sputter was as low as $< 1 \times 10^{-10}$ torr. The growth temperature was 900°C, the plasma power was 50 W, and the gas flow rate was 11 sccm ($Ar : O_2 = 10 : 1$). The sputtering condition of the ZnO film was optimized in terms of the surface morphology and growth rate of the ZnO film. High-resolution X-ray diffraction (HRXRD) measurement was used to evaluate the crystallinity of the ZnO film. In the present study, (002) and (101) omega scans and a (101) pole figure scan all were measured. The polarity of the ZnO films was estimated and determined by evaluating the growth rate, etching rate, and surface morphology of each film. Chemical etching was performed using a diluted HCl solution (0.3 Vol. %), and the thickness and surface morphologies of the samples were measured by profiler and atomic force microscopy, respectively.

3. Results and Discussion

Figure 1 shows the change in growth rate and crystal quality as a function of the growth temperature. In the present study, to determine the conditions for growth, plasma power and growth temperature were optimized. The influence of plasma power has been investigated by Cebulla et al. [8], who showed that a higher ion-to-neutral ratio j_i/j_n of the growing film strongly influences the structural and electrical properties of ZnO films. Also, Kim et al. reported that the full width at half maximum (FWHM) of the XRD rocking curve for a ZnO thin film was optimized when the film was deposited at 550^{o}C with plasma powers of 80 W. They reported that the best-quality sample showed the narrowest rocking curve for FWHM, 0.16^o (576 arcsec), indicating a highly *c*-axis-oriented columnar structure. Also, as plasma power was either decreased the value for FWHM was increased 0.30~0.44^o, indicating an increase in mosaicity. A degradation in crystallinity could be explained in terms of the migration length of sputtered atoms on the substrate surface being closely related to plasma power, which aptly explains why plasma power is so important for the achievement of a high-quality thin film. Therefore, plasma power was varied from 50 to 200 W. In the present study, the ZnO film revealed the highest quality at the lowest plasma power within the experimental range 50 W.

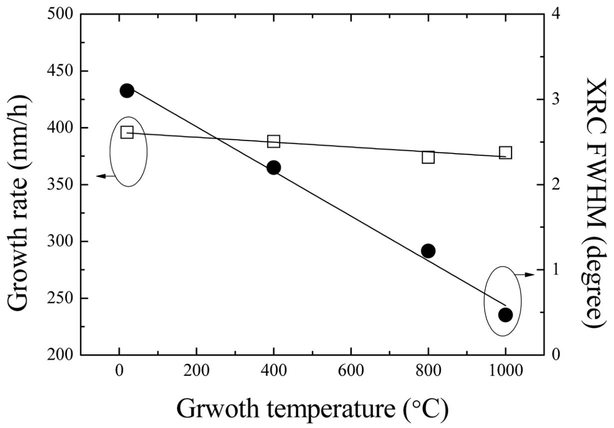

Fig. 1. Growth rate and FWHM of XRC variation of the sputtered films in a function of growth temperature. For all samples, growth temperature was 900^{o}C, and Ar : O_2 ratio was 10 : 1.

Further investigation into the sputtering of ZnO was performed. Fig. 1 shows the varied growth rates and the changes in x-ray rocking curve for FWHM as a function of growth temperature. As Fig. 1 shows, when the temperature was changed from room temperature to 1,000^{o}C, the growth rate decreased slightly from 395 to 360 nm/hr, while the FWHM value was narrowed remarkably. It shows that an energetic than kinetic growth process determines the crystal quality of a sputtered thin film.

Figure 2 shows the XRC of ZnO (002) and (101) grown on c-Al_2O_3 substrates. The plasma power was 50W, growth temperature was 900^{o}C, and the Ar/O_2 ratio was 10. The sample thickness was 586 nm. The FWHMs of (002) and (101) rocking curves were 432 and 2232 arcsecs, respectively. These results are comparable to the previous results [9], which show that sputtered ZnO has a strong c-axis-aligned columnar structure.

Figure 3 shows the (101) diffraction plane pole figure of the sample described in Fig. 2. It shows that the sample clearly has a 6-fold symmetry, which means that the films have a single crystalline phase [9, 15]. Note that, in

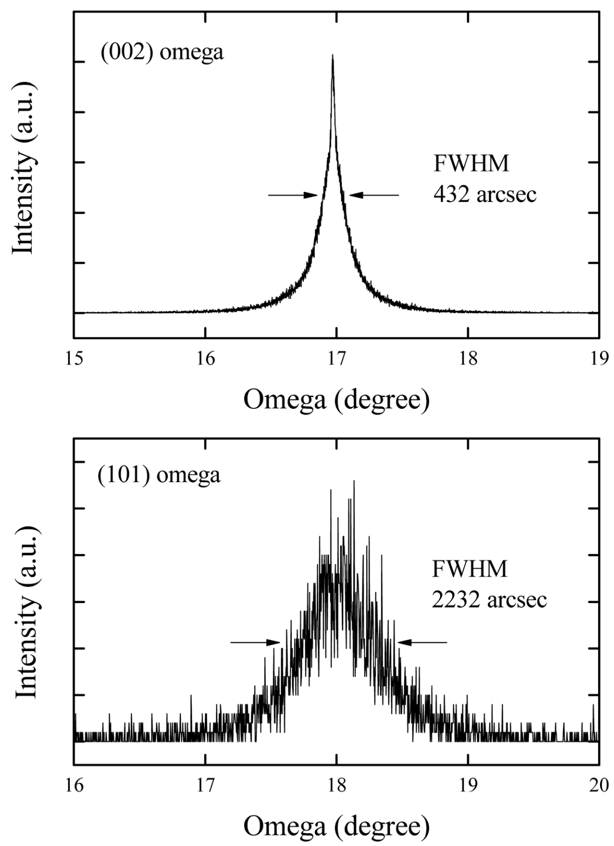

Fig. 2. (0002) and (10-11) X-ray rocking curve results of sputtered ZnO on c-Al_2O_3. The FWHM of (0002) reflection was as narrow as 432 arcsec.

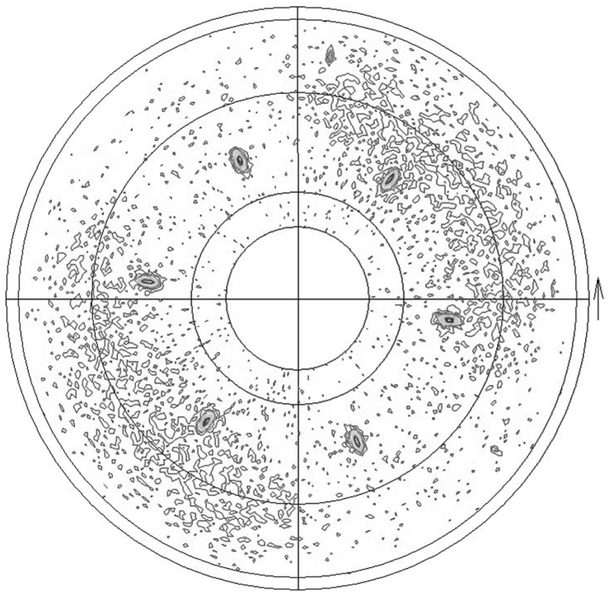

Fig. 3. X-ray pole figure pattern recorded from the (10-11) reflection. 6-fold symmetry indicates that the ZnO film has single crystalline phase.

the present experiment, only when the growth temperature was higher than 800°C was a clear 6-fold symmetry observed. However, when the growth temperature was lower than 800°C, a 6-fold symmetry was not observed except other growth parameters. This fact implies that the crystal quality of sputtered films is determined energetically.

The growth of Zn- and O-polar ZnO films was attempted using the described growth conditions. First, Al_2O_3 and GaN/Al_2O_3 substrates were used for the growth of O-polar and Zn-polar ZnO, respectively. Generally, ZnO grown on an Al_2O_3 substrate shows O-polar, while ZnO grown on a GaN template follows the polarity of GaN. A 2 μm-thick MOCVD GaN template was expected to support the growth of Zn-polar ZnO because it has Ga polarity.

Figure 4 shows AFM images of ZnO films grown on Al_2O_3 and GaN/Al_2O_3 substrates. Figure 4(a) and (c) show the surface morphologies of as-grown ZnO films on Al_2O_3 (Fig. 4(a)) and on a GaN template (Fig. 4(c)). Those two samples were simultaneously grown on the

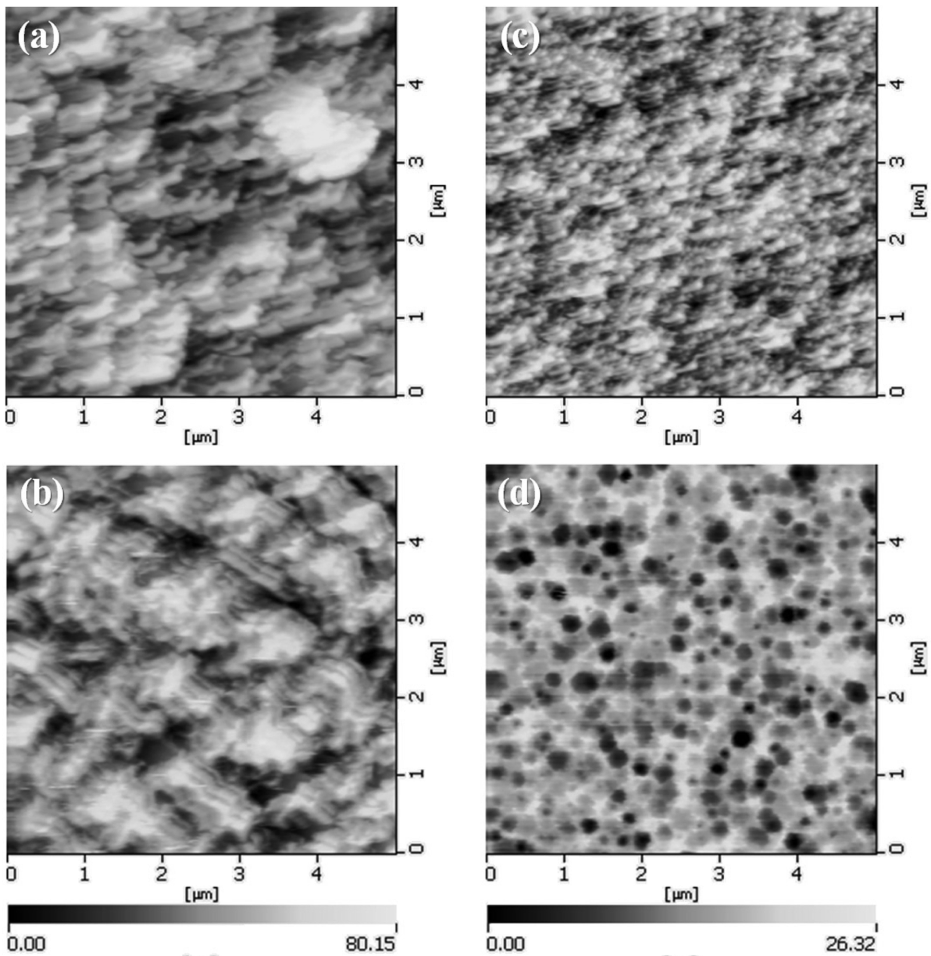

Fig. 4. AFM images of as-deposited and etched ZnO films. (a) as deposited ZnO/Al_2O_3, (b) etched ZnO/Al_2O_3, (c) as-deposited $ZnO/GaN/Al_2O_3$, and (d) etched $ZnO/GaN/Al_2O_3$.

same sample holder. Although the AFM results indicate a difference in grain size, presumably due to the difference in the lattice mismatch between the film and the substrate, a considerable morphological change was not observed. However, the growth rate for ZnO/Al_2O_3 was 378 nm/hr, while that for ZnO/GaN was as fast as 550 nm/hr. Furthermore, attempts were made to etch those samples to evaluate the etching rate. The etching rate for each sample was 28 nm/min for a ZnO/GaN sample and 59 nm/min for a ZnO/Al_2O_3 sample. Also, the etched surfaces differed significantly. The etched surfaces for the ZnO/Al_2O_3 and ZnO/GaN samples revealed hillocks (Fig. 4(b)) and pits (Fig. 4(d)), respectively. Previous studies, O-polar ZnO films have shown mainly a slow growth rate and a fast etching rate [10-14], while Zn-polar ZnO films were just the opposite and included pits [13, 14]. Consequently, the polarity of ZnO grown on either Al_2O_3 or GaN was either O-polar or Zn-polar, respectively.

4. Summary and Conclusion

Sputtering conditions for single-crystal-phase ZnO film was investigated. Under optimum growth conditions, the (002) and (101) FWHM of sputtered ZnO films were 432 and 2232 arcsec, respectively. Also, the (101) pole figure scan clearly showed 6-fold symmetry, which indicates that ZnO has a single-crystal phase. Also, O- and Zn-polar ZnO films were grown by DC magnetron sputtering using Al_2O_3 and GaN/Al_2O_3 substrates, respectively. The growth rate, the etching rate, and the surface morphology of the ZnO films indicated that the ZnO/Al_2O_3 and ZnO/GaN/Al_2O_3 films were O-polar and Zn-polar, respectively.

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