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Effects of N_2 Gas Addition to Sputtering Plasmas on Properties of Epitaxial ZnO Films
スパッタリングプラズマへの窒素ガス添加のエピキシャルZnO薄膜物性に対する効果

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Effects of N_2/Ar flow rate ratio on properties of ZnO films fabricated via nitrogen mediated crystallization (NMC) have been studied. NMC-ZnO films are deposited by RF magnetron sputtering using Ar-N_2 mixed gas. X-ray diffraction (XRD) analysis shows that the crystallinity of NMC-ZnO films is improved by addition of a small amount of N_2 to sputtering atmosphere (N_2/(Ar+N_2) flow ratio of 8%). By using the NMC-ZnO films as homo-buffer layers, ZnO films with high crystallinity are deposited by RF magnetron sputtering. The full width at half-maximum of XRD patterns for ω scan of (002) plane are 0.061°, being significantly small compared with 0.49° for the films without buffer layers. A further increase in N_2/Ar flow rate ratio deteriorates the crystallinity because excess N atoms in the films disarrange the crystal structure of ZnO. The results indicate that utilizing NMC buffer layers deposited at an adequate N_2 partial pressure is very promising to obtain epitaxial ZnO films with high crystallinity.

1. Introduction

Zinc oxide (ZnO) is one of the most fascinating oxide semiconductors with unique features. Wide direct band gap (3.3eV), high exciton binding energy (58meV), and material abundance make ZnO a promising material for optoelectronic devices. For realizing such devices, a fabrication method of high quality crystalline ZnO films are required. We have recently demonstrated a new fabrication method of ZnO films utilizing nitrogen mediated crystallization (NMC), where the crystal nuclei density can be controlled because the nitrogen atoms suppress crystallization of ZnO films. By using NMC-ZnO films as a buffer layer, ZnO:Al (AZO) films with low resistivity have been obtained [1, 2]. Furthermore, we have succeeded in epitaxial growth of ZnO films on sapphire substrate by using the NMC method [3]. Here we investigate relationship between the film properties of NMC-ZnO films and N_2 partial pressure in order to further improve the quality of ZnO films. Furthermore, the crystallinity of ZnO films fabricated on the NMC-ZnO buffer layers are described with comparison to the ZnO films fabricated by a conventional method.

2. Experimental

NMC-ZnO buffer layers were fabricated by RF magnetron sputtering. The used gasses were N_2 and Ar, where N_2/(N_2+Ar) flow rate ratio was ranged from 0 to 38%. The total pressure was 0.3 Pa. ZnO ceramic targets (2 inches in diameter; purity > 99.99%) were used. The applied RF power was 100 W and the deposition temperature was 650^{o}C. The thickness of buffer layers was 10 nm and 1 μm, which were confirmed by scanning electron microscopic images. On NMC-ZnO buffer layers, ZnO films were deposited by RF magnetron sputtering at 700^{o}C, where Ar-O_2 mixed gas was used and the total pressure was 0.67 Pa. The applied RF power was 60 W. The film thickness was 1 μm. The crystal structure was examined by X-ray diffraction (XRD) with a four-circle texture diffractometer (Bruker AXS D8 Discover).

3. Results and discussion

3.1 *Nitrogen mediated epitaxy*

Figure 1 shows FWHM of (002) rocking curves for NMC-ZnO films deposited as a parameter of N_2 partial pressure. The introduction of small amount of N_2 drastically improves the crystallinity of the films. At N_2/(N_2+Ar) of 8%, FWHM of XRD pattern decreases to a minimum value of 0.073°, being significantly small compared with 0.40° for the films fabricated without N_2. A further increase in N_2/Ar flow rate ratio deteriorates the crystallinity. as a result, FWHM increases to 3.9° at $N_2/(N_2+Ar)$ of 38%. In the case of high $N_2/(N_2+Ar)$ flow rate ratio ($N_2/(N_2+Ar) > 8\%$), the crystalline qualities are deteriorated since excess N atoms in the films disarrange the crystal structure of ZnO. While in the case of low $N_2/(N_2+Ar)$ flow rate ratio ($N_2/(N_2+Ar) < 8\%$), the amount of nitrogen adatoms on the film surface during deposition is too small to suppress crystallization of ZnO films, leading to high and randomly oriented crystallization. Thus we have obtained high quality epitaxial ZnO films with small fluctuation of the crystal orientation under the optimum nitrogen concentration (8% in the gas mixture).

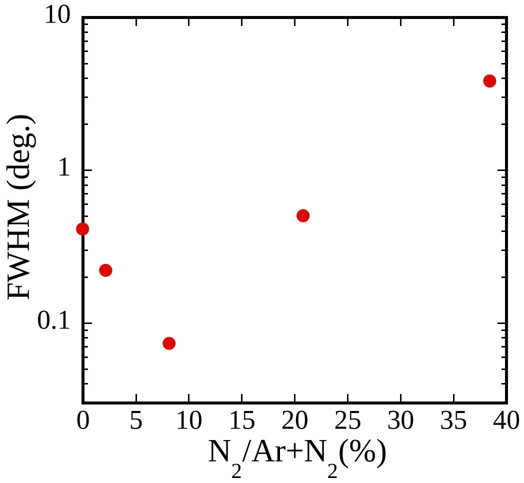

Fig. 1. FWHM of (002) rocking curves of ZnO films on NMC-ZnO buffer layers. The buffer layers were deposited as a parameter of $N_2/(N_2+Ar)$ flow rate ratio.

3.2 *Epitaxial ZnO films on NMC-ZnO buffer layers*

Figure 2 shows (002) rocking curves of ZnO films on NMC-ZnO buffer layers deposited at $N_2/(N_2+Ar)$ of 8%. For comparison, the rocking curve of ZnO films without buffer layers is also shown in Fig. 2. There are significant differences in the intensity and the FWHM of the diffracted peak between with and without buffer layers. The FWHM of ZnO films on buffer layers is 0.061^{o} which is much smaller than that of ZnO films without buffer layers (0.49^{o}). The results indicate that utilizing NMC buffer layers deposited at adequate N_2 partial pressure is very promising to obtain epitaxial ZnO films with high crystallinity.

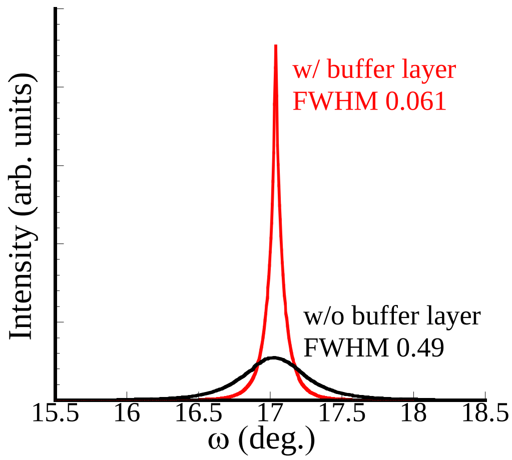

Fig. 2. XRD (002) rocking curves of ZnO films on NMC-ZnO buffer layers. FWHM of ZnO films without buffer layers is also shown.

4. Conclusions

We report here the effects of N_2 partial pressure on properties of ZnO films fabricated via NMC. We have shown that the N_2 partial pressure strongly influences the crystalline qualities of NMC-ZnO films on sapphire (001) plane. The film qualities have been drastically improved by using $N_2/(N_2+Ar)$ of 8%. By using the NMC-ZnO films as homo-buffer layers, ZnO films with high crystallinity are fabricated. FWHM of XRD patterns for (002) rocking curves for ZnO films with buffer layers is 0.061^{o}, being significantly small compared with 0.49^{o} for the films without buffer layers. From these results, we conclude that utilizing NMC buffer layers at adequate N_2 partial pressure is very promising to obtain epitaxial ZnO films with high crystallinity.

References

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