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Enhancement of the surface and structural properties of ZnO epitaxial films grown on Al_2O_3 substrates utilizing annealed ZnO buffer layers

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Abstract ZnO films were grown on Al_2O_3 (1000) substrates without and with ZnO buffer layers by using radio-frequency magnetron sputtering. Atomic force microscopy images showed that the surface roughness of the ZnO films grown on ZnO buffer layers annealed in a vacuum was decreased, indicative of an improvement in the ZnO surfaces. X-ray diffraction patterns showed that the crystallinity of the ZnO thin films was enhanced by using the annealed ZnO buffer layer in comparison with the film grown on without a buffer layer. The improvement of the surface and structural properties of the ZnO films might be attributed to the formation of the Zn-face ZnO buffers due to annealing in a vacuum. These results indicate that the surface and structural properties of ZnO films grown on Al_2O_3 substrates are improved by using ZnO buffer layers annealed in a vacuum.

Keywords ZnO epilayer · Annealed ZnO buffer layer · Surface property · Structural property · Polarity

1 Introduction

Potential applications of wide energy-gap compound semiconductors in optoelectronic devices operating in the blue spectral region have driven an extensive effort to grow high-quality ZnO thin films on Al_2O_3 (1000) substrates by using various techniques [1]. ZnO thin films have been particularly attractive because of their large exciton energy [2–4]. The large exciton energy and superior chemical stability of ZnO thin films [5, 6] have stimulated applications in many promising optoelectronic devices, such as ultraviolet laser diodes [7], light-emitting diodes [8], solar cells [9], ultraviolet photodetectors [10], and electroluminescence devices [11]. Various kinds of the growth techniques have been used to improve the quality of the ZnO films. However, since there are large lattice mismatch (18.6%), crystallographic mismatch, and thermal mismatch between the ZnO thin films and the Al_2O_3 substrates, the achievement of the high quality ZnO films is still difficult because of the delicate problems encountered in the growth process [12]. Furthermore, the physical properties of the ZnO films are significantly affected by the growth conditions [13]. Even though many works concerning the growth and the physical properties of ZnO thin films grown on Al_2O_3 (1000) substrates have been reported [14–16], since the polarity of the ZnO buffer layers significantly affect the quality of the ZnO epilayers, systematic studies of the formation and the physical properties of the ZnO epilayers utilizing ZnO buffers with a suitable polarity are necessary for achieving high-quality ZnO epilayers.

This paper reports the effect of the surface and the structural properties of ZnO films grown on Al_2O_3 substrates with and without annealed ZnO buffer layers by using the radio-frequency magnetron sputtering method. Atomic force microscopy (AFM) measurements were performed in order to characterize the surface smoothness of the ZnO layer, and X-ray diffraction (XRD) measurements were carried out to investigate the crystallinity of the ZnO thin films.

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2 Experimental details

Polycrystalline stoichiometric ZnO with a purity of 99.999% was used as a source target material and was precleaned using sublimation. Oxygen gas with a purity of 99.9999% was used as an ion source, and Ar^+ gas with a purity of 99.9999% was used as a sputtering gas. The Al_2O_3 (1000) substrates were alternately degreased in warm trichloroethylene (TCE), acetone, methanol, and acetone, etched in a solution of H_2SO_4 and HNO_3 (3:1) at 120°C for 10 min, and rinsed in de-ionized water thoroughly. As soon as the chemical process had been finished, the substrates were mounted onto a susceptor in a growth chamber. Before ZnO growth, the Al_2O_3 (1000) substrates were thermally cleaned at 850°C for 10 min. The deposition of the ZnO buffer layer, using radio-frequency magnetron sputtering, was done at a system pressure of 1.2×10^{-2} Torr and at radio-frequency powers of 150 W. Two kinds of 700-nm-ZnO films were grown on 50-nm-ZnO annealed buffer layers. The growth temperatures of the ZnO thin films and buffer layers were 800 and 550°C. After the ZnO buffer layers had been annealed at 850°C for 30 min in an oxygen atmosphere or a vacuum, the deposition of the ZnO film was performed at 800°C for 10 min at an $O_2/O_2{+}Ar$ of an 1 flow-rate ratio. The ZnO film were directly grown on Al_2O_3 (1000) substrates for comparison.

3 Results and discussion

The as-grown ZnO films had mirror-like surfaces without any indication of pinholes, which was confirmed by using Normarski optical microscopy and scanning electron microscopy measurements. Auger electron spectroscopy spectra showed that the as-grown films consisted of zinc, oxygen, and carbon at the surface and of zinc and oxygen at a 1000-Å depth. The carbon impurities at the ZnO surface might originate from contamination due to the target source materials during growth and to air pollution after growth. Auger depth profiles showed that the heterointerface between the ZnO and the Al_2O_3 was relatively abrupt and that the stoichiometry of the ZnO film was uniform. The root-mean-square average surface roughnesses of the ZnO films grown without buffer layers and with ZnO buffer layers annealed in an oxygen atmosphere and in a vacuum, as determined from the AFM measurements, were 15, 31, and 4 nm, respectively, as shown in Fig. 1. AFM images indicated that the surface morphology of the ZnO thin film grown with a buffer layer annealed in a vacuum was smoother than those of the ZnO thin films grown without a buffer layer and with a buffer layer annealed in an oxygen atmosphere. The increase in the smoothness of the ZnO thin film grown with a buffer layer annealed in a vacuum originated from an increase in the grain size in the film due to thermal treatment, indicative of the formation of a dense surface facilitated by larger grains.

Figure 2 shows the XRD patterns for the ZnO films grown on Al_2O_3 (1000) substrates (a) without a buffer layer and with buffer layers annealed in (b) an oxygen atmosphere and (c) a vacuum. The (0002) $K_{\alpha 1}$ diffraction peak around 34.41° corresponding to the ZnO (0001) films, respectively, is clearly observed. The XRD patterns for the ZnO thin films grown on the Al_2O_3 (1000) substrates without and with ZnO buffer layers indicate that all the as-grown and the annealed ZnO films have a strong *c*-axis orientation, that orientation giving the lowest surface free energy [17]. The intensity of the XRD pattern related to the ZnO (0001) film for the ZnO thin film grown with a buffer layer annealed in a vacuum is larger than those for the ZnO thin films without a buffer layer and with a buffer layer annealed in an oxygen atmosphere. The full width at half-maximum (FWHM) for the (0002) ZnO diffraction peak for the ZnO thin film grown with a buffer layer annealed in a vacuum (0.33°) is smaller than those for the ZnO thin films without a buffer layer (0.59°) and with a buffer layer annealed in an oxygen atmosphere (0.34°),

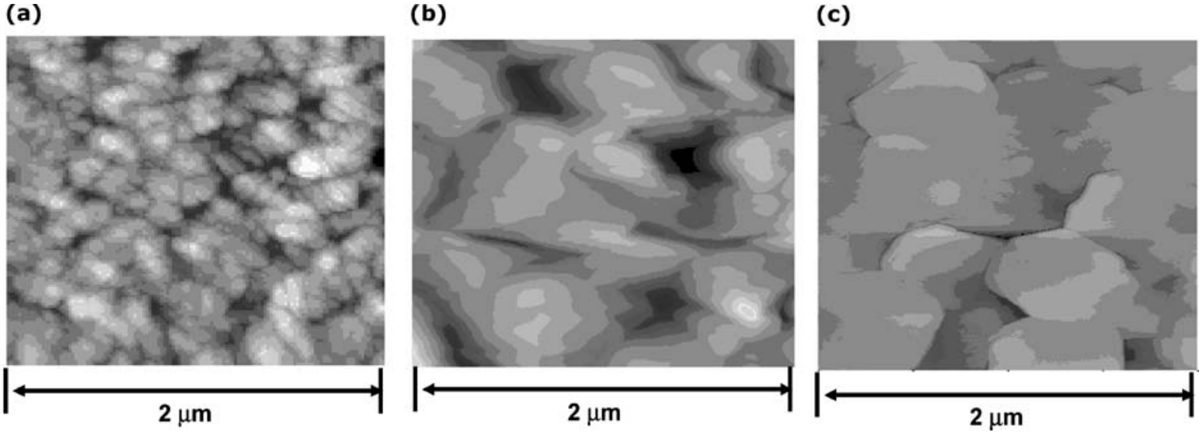

Fig. 1 Atomic force microscopy images of the ZnO films grown on Al_2O_3 (1000) substrates (a) without a buffer layer and with buffer layers annealed in (b) an oxygen atmosphere and (c) a vacuum

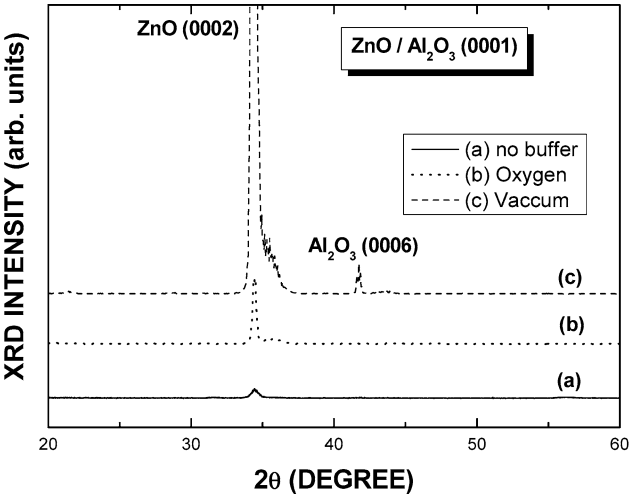

Fig. 2 X-ray diffraction patterns for the ZnO films grown on Al_2O_3 (1000) substrates (a) without a buffer layer and with buffer layers annealed in (b) an oxygen atmosphere and (c) a vacuum

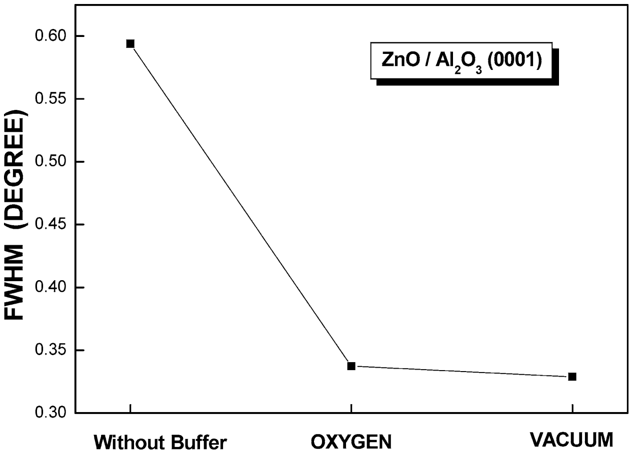

Fig. 3 Full width at half maxima of the X-ray diffraction curves for the ZnO films grown on Al_2O_3 (1000) substrates (a) without a buffer layer and with buffer layers annealed in (b) an oxygen atmosphere and (c) a vacuum

indicative of an increase in the grain size and a more preferential orientation of the (0001) hexagonal structure after thermal annealing. The XRD results indicate that the crystallinity of the ZnO film is improved by using a ZnO buffer layer annealed in a vacuum. The FWHMs of the XRD curves for the ZnO films grown on Al_2O_3 (1000) substrates (a) without a buffer layer and with buffer layers annealed in (b) an oxygen atmosphere and (c) a vacuum are shown in Fig. 3. The improvement of the surface and the structural properties of the ZnO epilayer grown on Al_2O_3 substrates utilizing ZnO buffer layers annealed in a vacuum might be attributed to the formation of the Zn-face ZnO buffers due to thermal treatment. The achievement Zn polarity of the surface in the ZnO buffer layer due to thermal annealing enhances the crystal quality of the ZnO films [18].

4 Summary and conclusions

AFM images showed that the surface roughness of the ZnO film grown on the Al_2O_3 (1000) substrate was decreased by using the ZnO buffer layer annealed in a vacuum, indicative of an improvement in the ZnO surface. XRD patterns showed that the crystallinity of the ZnO films was enhanced due to the existence of the ZnO buffer layer annealed in a vacuum. The improvement of the surface and structural properties of the ZnO films originated from attributed to the formation of the Zn-face ZnO buffers due to annealing in a vacuum. These results indicate that the surface and the crystallinity of the ZnO films grown on Al_2O_3 (1000) substrates are improved by using ZnO buffer layers annealed in a vacuum.

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