Crystallinity control of sputtered ZnO films by utilizing buffer layers fabricated via nitrogen mediated crystallization

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ABSTRACT

High quality ZnO:Al (AZO) films have been obtained by utilizing buffer layers fabricated via nitrogen mediated crystallization (NMC), where sputtering method is employed for preparation of both buffer layers and AZO films. Introduction of small amount of N_2 ($N_2/(Ar+N_2)$ = 16%) to the sputtering atmosphere of NMC-ZnO buffer layers drastically improves the crystallinity of buffer layers and thus AZO films. The most remarkable effect of the buffer layers is a significant reduction in the resistivity at high base pressure of background gases. The resistivity of conventional AZO films increases from 2.0 mΩ•cm to 70.0 mΩ•cm with increasing the base pressure from 3×10^{-5} Pa to 1×10^{-3} Pa, while the resistivity of AZO films with NMC buffer layers increases from 0.5 mΩ•cm to 2.0 mΩ•cm, where the thickness of AZO film is 88 nm. Furthermore, AZO films with a sheet resistance of 10 Ω/□ and an optical transmittance higher than 80% in a wide wavelength range of 400–1100 nm have been obtained.

Keywords: zinc oxide, transparent conducting oxide, nitrogen mediated crystallization, magnetron sputtering, buffer layer

1. INTRODUCTION

Oxide semiconductors have attracted much attention because of their advantages such as high transparency and wide-ranging conductivity [1, 2]. ZnO is one of the most fascinating oxide with a wide application range. The low electrical resistivity, the high transparency to visible lights, and the material abundance make ZnO a great potential alternative to indium-doped tin oxide (ITO) for transparent conductive oxide (TCO). The resistivity of ZnO-based TCO, however, is higher than that of ITO especially at high base pressure of background gases [3-5]. Since the crystallinity of ZnO films strongly affects both the carrier density and the mobility, fabrication methods of high crystalline ZnO films have been required.

Many efforts have been devoted so far to improve the crystallinity of ZnO films. Introduction of the buffer layers is one of the promising methods to obtain high quality films. Nakamura et al. have studied the effects of low temperature (LT) ZnO homo-buffer layers on the qualities of ZnO films, which were deposited by PLD on c-plane sapphire substrate[6]. In the same way, high quality epitaxial ZnO layers have been obtained at reducing growth temperature by using ultra violet assisted deposition techniques[7].

Recently, we have developed a novel fabrication method of ZnO buffer layers crystallized via nitrogen-atom mediation (NMC) [8-11], which enable us to make high-quality ZnO films, especially when a sputtering method is employed for film preparation. In the case of a conventional sputtering, ZnO is immediately crystallized once it is deposited on a substrate even at room temperature because of its low crystallization temperature. Furthermore, a lot of high energetic species incoming to the substrate enhance high-density and randomly-orientated nucleation at initial stage of deposition, which causes the reduction in grain size and the large crystal mosaics. On the other hand, in the case of NMC method, the nucleation density can be reduced since the adsorbed nitrogen atoms on the growth surface disturb the crystallization of ZnO, as a result, ZnO films with well-aligned crystal orientation and large grain size are obtained.

In this paper, we study the effects of NMC buffer layers on the properties of ZnO:Al (AZO) films, which are discussed with comparison to those of ZnO films fabricated without NMC layers. Furthermore, we report the dependence of electrical properties of AZO films with NMC buffer layers on the base pressure during AZO film deposition.

2. EXPERIMENT

NMC buffer layers were deposited on quartz glass substrates by radio-frequency (RF) magnetron sputtering at 300°C. The used targets were ZnO (2 inches in diameter; purities > 99.99 %) and the applied RF powers were 100 W. Ar-N_2 mixed gas was used and the total pressure was 0.3 Pa. The flow rates of Ar and N_2 were 4.5-24.5 sccm and 0.0-20.0 sccm, respectively. According to X-ray diffraction (XRD) analysis, as-deposited ZnON films were confirmed to have ZnO crystal grains. In this experiment, the thickness of NMC buffer layers was 5 nm.

AZO films were deposited on NMC buffer layers by RF magnetron sputtering with AZO targets (2wt.% Al_2O_3). The used gas was Ar and the total pressure was 0.3 Pa, where the base pressure was varied from 3×10^{-5} Pa to 1×10^{-3} Pa. The substrate temperature was kept at 200°C and no post annealing of AZO was performed. For a comparison, AZO films deposited directly on quartz glass substrates were fabricated under the same deposition conditions as AZO films mentioned above. The crystal structures of the films were examined by XRD and the optical transmittance spectra were measured with UV-Visible spectrophotometer. The electrical properties of AZO films were evaluated by 4 point probe measurements and hall-effect measurements.

3. RESULTS AND DISCUSSION

XRD measurement reveals that all AZO films show a strong peak at 34.4° that corresponds to the (002) plane of ZnO wurtzite structure, indicating that the films are strongly orientated along the c-axis. Here, the film thickness of AZO and NMC buffer layer are 100 nm and 5 nm, respectively. Both the crystal orientation and the grain size of the NMC buffer layers, however, highly depend on the N_2/Ar flow rate ratio. Introduction of small amount of N_2 (N_2/Ar = 4/20.5 sccm) drastically improves the crystallinity of the buffer layers. FWHM of XRD patterns for 2θ-ω and ω scan of (002) plane are 0.25° and 2.6°, being significantly small compared with 0.92° and 3.5° for the buffer layers fabricated without N_2. On the other hand, 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. As a result, AZO films with high crystallinity have been successfully fabricated by utilizing the NMC-buffer layers deposited at N_2/Ar = 4/20.5 sccm. The crystal grain size of 100-nm-thick AZO films on the NMC-buffer layers is 60 nm, which is about 5 times larger than that of conventional AZO films. From these results, we conclude that utilizing NMC buffer layer fabricated at adequate Ar/N_2 flow rate ratio is very promising to obtain well-orientated AZO films with high crystallinity.

The effects of the NMC buffer layers on the electrical properties of AZO films have been also investigated by measuring the resistivity, hall mobility and carrier density of the films. Figure 2 shows the resistivity of 88-nm-thick AZO films prepared on 5-nm-thick buffer layers, which is plotted against the base pressure during AZO film deposition. The deposition rates of AZO films were 21.0 nm/min and 26.5/min, which were controlled by changing the RF power. For all base pressures, the resistivity of AZO films with NMC-ZnO buffer layer is lower than the films prepared

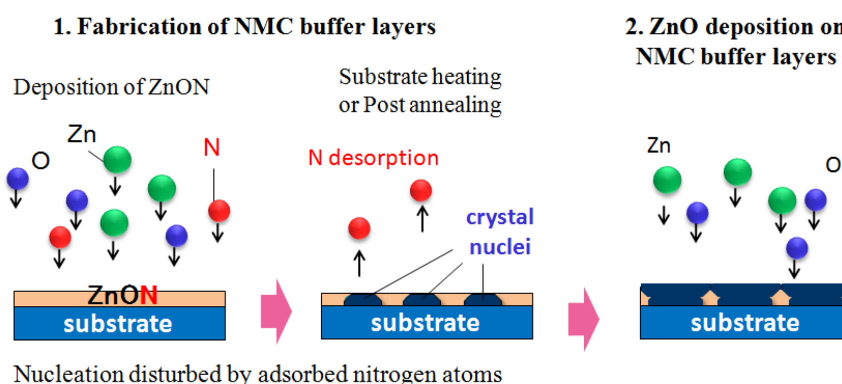

Figure 1. Flow chart of our fabrication method utilizing buffer layers prepared by NMC method.

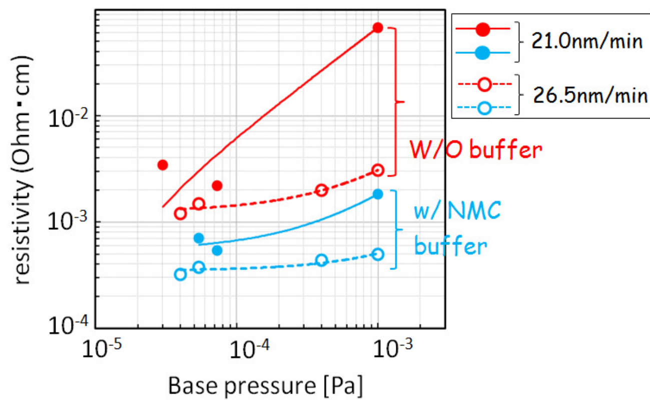

Figure 2. Resistivity of AZO films prepared on NMC buffer layers with a thickness of 5 nm as a function of base pressure during AZO deposition. The deposition rates of AZO films were 21.0 nm/min and 26.5 nm/min, which were controlled by changing the RF power.

by conventional sputtering without NMC layer. It was found from the hall-effect measurement that the decrease in the resistivity by using buffer layer is attributed to increase in both the carrier mobility and the carrier density of the films. The most remarkable effect of NMC-ZnO buffer layers is a significant reduction in the resistivity at high base pressure. As shown in Fig. 2, the resistivity of AZO films fabricated by conventional sputtering increases substantially with increasing the base pressure, while the resistivity of AZO films with NMC buffer layers does not change much. In the case of conventional sputtering, the excessive nucleation with various orientations is induced by high energy of impingement of the sputtered species and/or the fragments from plasma at the initial stage of the deposition. As a result, the AZO films have small grain size and low degree of c-axis orientation. Furthermore, it has been reported that the residual water vapor in background gases deteriorates the crystallinity of transparent-conducting-oxide films, leading to a decrease in the grain size, which is caused by the absorption of H_2O molecules at the growing film surface[5,13]. This decrease in the grain size results in low carrier mobility of AZO films. The residual water also induces the decrease in the oxygen vacancies that generate electron carriers via water oxidation of AZO films[5]. These are the reasons why the resistivity is high and increases much with increasing the base pressure in the case of conventional sputtering. On the other hand, in the case of NMC method, the excessive nucleation can be suppressed and the films with high crystallinity are grown from the early stage of deposition. As a result, the crystallinity of AZO films deposited on the NMC buffer layers is high independent of the base pressure and thus low resistivity is observed even at high base pressure. Since the dopant-activation efficiency depends on the degree of c-axis orientation in AZO films, the significant improvement of resistivity at high base pressure can be also accompanied by an enhancement in the orientation degree of the AZO films by using the NMC-ZnO buffer layers[14]. As a result, highly conducting AZO films with a small thickness, that is, high transparency, have been obtained. Figure 5 shows the optical transmittance AZO films with a sheet resistance of 10 Ω/☐. Here, the film thickness of AZO films with and without NMC-ZnO buffer layers is 400 nm and 1000 nm, respectively. We observed that the films with NMC-ZnO buffer layers has high transmittance (>80%) in a wide wavelength range of 400–1100 nm.

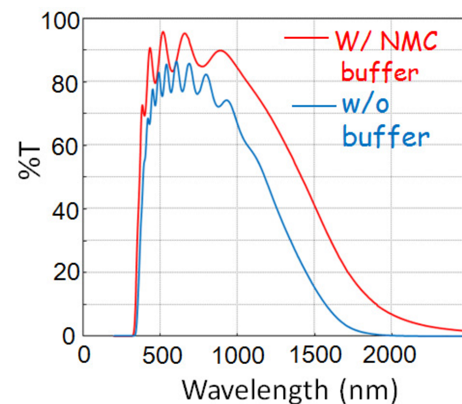

Figure 3. Optical transmittance of AZO film with a sheet resistance of 10 Ω/☐. The film thickness of AZO films with and without NMC-ZnO buffer layers is 400 nm and 1000 nm, respectively.

4. CONCLUSIONS

Effects of NMC-ZnO buffer layers on the properties of AZO films have been studied, where sputtering method is employed for preparation of both buffer layers and AZO films. As a result, high quality AZO films have been obtained by utilizing NMC buffer layers. The crystal grain size of AZO films with NMC-buffer layers is about 3 times larger than that of conventional films, which is considered to be due to the low nuclei density of NMC-buffer layers. The most remarkable effect of NMC-ZnO buffer layers is a significant reduction in the resistivity at high base pressure. The resistivity of conventional AZO films increases from 2.0 mΩ•cm to 70.0 mΩ•cm with increasing the base pressure from 3×10^{-5} Pa to 1×10^{-3}

Pa, while the resistivity of AZO films with NMC buffer layers increases from 0.5 mΩ•cm to 2.0 mΩ•cm, where the thickness of AZO film is 88 nm. Furthermore, AZO films with a sheet resistance of 10 Ω/□ and an optical transmittance higher than 80% in a wide wavelength range of 400–1100 nm have been obtained. From these results, we conclude that our method described here is full of promise for fabrication of ZnO-based transparent conducting films.

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