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Effect of sublayer surface treatments on ZnO transparent conductive oxides using dc magnetron sputtering

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ABSTRACT

Novel sublayer surface treatments were investigated to improve the conductivity of aluminum-doped zinc oxide (ZnO:Al) fabricated by using dc magnetron sputtering on a glass substrate. Introducing artificial minute flaws on the surface of glass substrates enhanced the crystallinity of ZnO:Al films and decreased the resistivity accompanying the increase of electron mobility. Combination of the surface treatment and sputter beam control, *i.e.*, interruption of high-energy oxygen with shadow masks, further reduced the resistivity of the film to 3.7×10^{-4} Ω cm (thickness 70 nm).

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1. Introduction

Indium tin oxide (ITO) is a typical transparent conductive oxide (TCO) in widespread use as a transparent electrode for optoelectronic thin film devices, such as liquid crystal displays (LCDs) or solar cells [1]. Because ITO contains a rare metal, indium (In), the limited reserves and economic demand for these devices have caused the price to increase significantly. Zinc oxide (ZnO) is a most promising candidate for indium-free alternative TCOs. Many kinds of dopants were studied, of which aluminum (Al) and gallium (Ga) were the best at improving the electric conductivity [2]. Excellent low resistivity (8.54×10^{-5} Ω cm) was obtained in aluminum-doped ZnO (ZnO:Al) by using pulsed laser deposition (PLD) [3].

Another requirement for the alternative TCOs is their mass productivity (large-area deposition, stable and high throughput, or cost-performance), so dc magnetron sputtering (dc-MSP) with oxide targets is adopted to fabricate ITO in flat panel displays (FPDs). Fig. 1 shows an example of resistivity dependence on film thickness of ZnO:Al (3%) vs. ITO fabricated by dc-MSP on a glass substrate. ITO indicates low and flat resistivity dependence (1 to 2×10^{-4} Ω cm) in the 50 to 300 nm thickness range required for LCD application. However, ZnO:Al shows larger and reciprocal resistivity dependence on thickness, and the lowest limit of infinitely extrapolated resistivity is 3.86×10^{-4} Ω cm. To attain low resistivity, especially for ZnO thinner than 100 nm, crystal orientation of ZnO needs to be controlled, and the number of defects in thin films needs to be reduced due to the lower symmetry of ZnO in the crystal structure (wurtzite, hexagonal) compared with ITO (bixbyite, cubic).

In this paper, we introduce the results of a study on the effect of sublayer surface treatments on the resistivity of ZnO:Al fabricated by dc-MSP.

2. Experimentals

ZnO thin films were fabricated by dc-MSP. The apparatus (Hitachi, KR-104) was in-line, load-locked, and had the following features: sputtering gas was pure Ar, base pressure 2×10^{-6} Torr, sputter pressure 5×10^{-3} Torr, and dc power 320 W. The sputtering target (5 × 15 in.) was ZnO doped with Al_2O_3 (Al content: 3.4 at.% in the films) and the distance between target and substrate was 70 mm. The substrates were non-alkali glasses (Asahi Glass, AN-100) and non-doped ZnO single crystals (Tokyo Denpa, Zn-/O-face polished). The substrates loaded on a holder moved horizontally upon the target with constant speed (typically 25–50 mm/min) and the temperature was kept at 215 °C during sputtering. In the case of sputter beam control investigation, shadow masks having a specific shape of hole to avoid the bombardment damage of film by high-energy oxygen [4], were equipped between the substrate and the target. To obtain the same order of thickness as no shadow mask case, the substrates moved repeatedly with the same speed.

Several kinds of cleaning techniques of glass substrates were preliminarily studied: detergent (Teepol®) cleaning, pure water flow, ultrasonic cleaning in pure water or acetone, immersion in 1% hydrofluoric acid (HF), and UV/ozone exposure. After the preliminary study, all of these methods except immersion in HF were adopted as a cleaning procedure.

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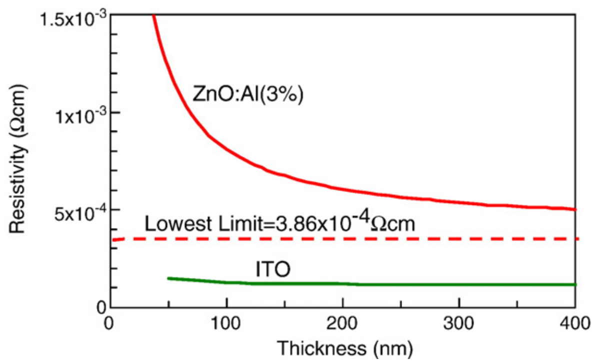

Fig. 1. Resistivity dependence on film thickness of ZnO:Al (3%) vs. ITO fabricated by dc-MSP on glass substrates. Dashed line shows the infinitely extrapolated resistivity of ZnO:Al.

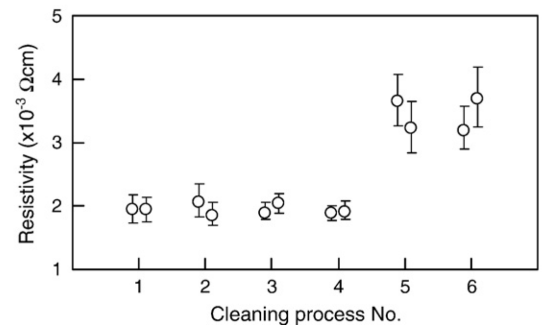

Fig. 2. Resistivity of ZnO:Al (thickness = 30 nm) on glass substrate for the cleaning procedures.

An abrasive glass substrate finishing method was used to introduce artificial minute flaws on the glass surface, which had been hand rubbed uniaxially by using an abrasive sheet (Sankyo Rika Co., type DCCS, average abrasive particle size aap = 10 ~ 46 μm) or cotton sheet soaked in abrasive slurry (Japan Microcoating Co., diamond slurry, aap = 10, 30 nm; Trustwell Co., diamond and alumina slurry, aap = 50, 300 nm; Wako Chemicals Co., α-titania, aap = 50 nm). After rubbing, the substrates were passed through the cleaning procedure again.

A ZnO single crystal was cleaned with the procedure (dipping into 0.01% HCl and pure water flow) before sputtering.

The structural and electrical properties of ZnO:Al films were analyzed by several methods: atomic force microscopy (AFM), X-ray diffraction (XRD), scanning electron microscope (SEM), four-point probe resistivity measurement, and van der Pauw method.

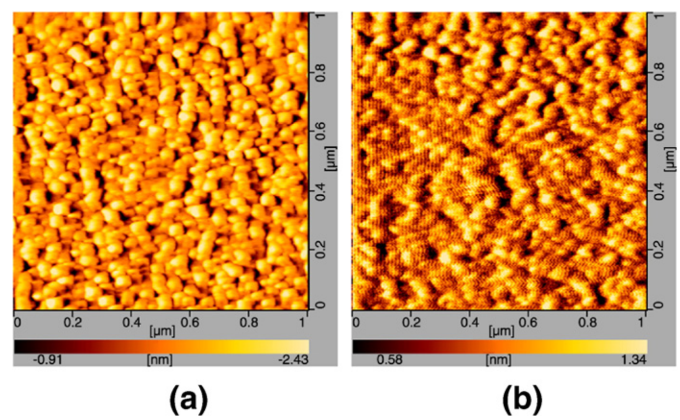

Fig. 3. AFM deflection images for ZnO:Al on (a) glass and (b) ZnO single crystal.

3. Results and discussions

3.1. Surface cleanings

First, the effect of cleanliness of the glass surface on the resistivity of ZnO:Al sputtering films was verified. Table 1 shows the list of surface cleaning preliminary procedures, which had six potential cleaning steps, from detergent cleaning to UV/ozone exposure. The cleaning procedures (1 to 6) were combinations of these steps. (In the list, "Y" means that cleaning step was included, and "N" means it was not.)

Fig. 2 shows resistivity of ZnO:Al (thickness = 30 nm) on a glass substrate for the cleaning procedures. Most procedures indicated the same values compared with the raw substrate (no. 1). However, the use of HF immersion increased the resistivity, which was speculated to be caused by denudation of minor additives in the glass. From this preliminary study, procedure no. 4 was selected as the standard glass cleaning process.

3.2. ZnO single crystal and glass without treatment

Next, as a pseudo-homoepitaxial case, ZnO:Al was fabricated on ZnO single crystal by dc-MSP. Fig. 3 shows AFM deflection images for ZnO:Al on glass and on ZnO single crystal (1 × 1 μm area). These images appear to be almost the same, and there were many random crystal domains. The average size of ZnO domains is almost the same, however, the maximum roughness is different, *i.e.*, 12.7 nm for the former and 3.7 nm for the latter. These observations indicated that the sublayer of ZnO could not produce epitaxial or larger in-plane domains.

Table 2 shows electric properties of ZnO:Al (thickness = 70 nm) on ZnO crystal (Zn-/O-face) and simple glass (without treatment). ZnO crystal produced less than half the resistivity that glass did. The detailed analyses of carrier concentration (N_e) and mobility (μ) show the improvements in these parameters. Therefore, ZnO crystal offered a lower limit of resistivity for ZnO:Al prepared by dc-MSP.

3.3. Abrasive finishing treatment

In the next step, we studied the possibility of enhancing the conductivity of ZnO:Al on glass by means of abrasive finishing

Table 1
Surface cleaning preliminary study on glass substrate.

Cleaning procedure no.	1	2	3	4	5	6
Detergent	N	Y	Y	Y	N	N
Pure water, flow	N	Y	Y	Y	N	N
Pure water, ultrasonic	N	Y	Y	Y	N	N
Acetone, ultrasonic	N	N	Y	Y	N	N
Dilute HF, immersion	N	N	N	N	Y	Y
UV/ozone exposure	N	N	N	Y	N	Y

In the list, "Y" means that cleaning step was included, and "N" means it was not.

Table 2
Electric properties of ZnO:Al (thickness = 70 nm) on several sublayers: resistivity (ρ), carrier concentration (N_e) and mobility (μ).

Sublayer	ρ ($\times 10^{-4}$ Ω cm)	N_e ($\times 10^{20}$ cm^{-3})	μ (cm^2/Vs)
ZnO crystal			
Zn-face	3.9	6.3	27
O-face	3.5	8.5	34
Glass			
Abrasive finishing	5.8 – 6.6	4.9 – 6.6	17 – 20
Shadow masking	6.1	5.9	17
Combination	3.7 – 4.9	6.3 – 7.2	20 – 24
Without treatment	10	4.7	11

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