

## ZnO Film Fabrication by Reactive Shielded Vacuum Arc Deposition

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Zinc oxide (ZnO) thin films were prepared on borosilicate glass substrates by reactive shielded cathodic arc deposition. The macrodroplet shield plate was placed 100 mm from the cathode in order to prevent the macrodroplets from adhering to the film, and the substrate was placed 100 mm from the shield plate. The arc was operated at DC 30 A and the process pressure was varied from 0.1 to 5.0 Pa. No bias voltage was applied to the substrate. The substrate temperature was below 75°C. The arc voltage, erosion rate of the cathode, and film deposition rate were measured as process characteristics. The crystalline state, transmittance, refractive index, and electrical resistivity of the films were analyzed. The maximum deposition rate (40 nm/min) was obtained at 1.0 Pa. The films exhibited a hexagonal wurtzite polycrystalline structure and were highly oriented to the *c*-axis, perpendicular to the substrate. Well-crystallized and highly transparent films were obtained in the pressure range of 0.5 to 3.0 Pa. However, the lowest resistivity ( $10^{-3} \Omega \text{ cm}$ ) was obtained at 0.1 Pa, and this resistivity increased with the process pressure. The refractive index at 600 nm varied from 1.8 to 1.9.

Keywords: zinc oxide film, reactive shielded cathodic arc deposition, process characteristics, film properties

### 1. INTRODUCTION

Zinc oxide (ZnO) exhibits outstanding potential properties, such as optical transparency in ultraviolet and visual regions, low electrical resistivity, good piezoelectric, photoelectric, and electrooptic properties, and a wide optical band gap (typically, 3.3 eV). Therefore, much attention has been paid to ZnO thin film and its application to surface acoustic wave (SAW) devices, ultrasonic transducer arrays, chemisorption gas sensors, mass-loading sensors, transparent electrodes used in solar cells, optical wave guides, and others [1, 2]. To date, ZnO thin film has been produced by a variety of techniques, such as spray pyrolysis [3-5], chemical bath deposition [6], chemical vapor deposition (CVD) [7-9], various sputtering techniques [2, 10-12], laser deposition [1], and cathodic arc deposition [13].

The cathodic vacuum arc deposition process is one of the ion plating methods and exhibits a high deposition rate, excellent adhesion, ease of system scale-up, and does not require a crucible. However, the major disadvantage of the process is the emission of macrodroplets from the cathode spot and their adhesion to the films under preparation. This problem can be overcome by employing the shielded method [14]. The authors have successfully prepared various metal-nitride and oxide thin films using a shielded cathodic vacuum arc [13, 15-17]. In the present study, ZnO films were prepared by this method as a function of process pressure. The process characteristics of arc voltage, erosion rate of cathode target, deposition rate, and substrate temperature

were measured. The film properties of crystalline state, optical properties and electrical resistivity were investigated.

### 2. EXPERIMENTAL DETAILS

A schematic diagram of a reactive shielded vacuum arc deposition apparatus is shown in Fig. 1. A Zn cathode of 64 mm diameter was placed in a cylindrical chamber (SUS304, 600 mm in length, 400 mm in diameter), which was an anode and grounded. The substrate holder table (SUS304, 150 mm in diameter) was placed 200 mm away from the cathode surface, and the shield plate (SUS304, 64 mm in diameter, 1 mm thick)

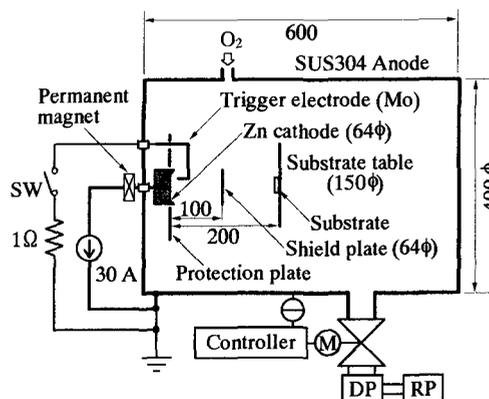


Fig. 1. Reactive shielded cathodic vacuum arc deposition apparatus (M: motor, DP: diffusion pump, RP: rotary pump).

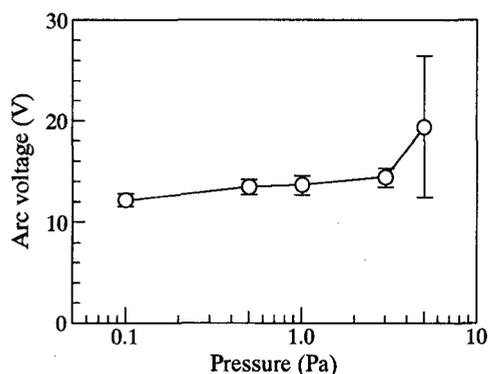


Fig. 2. Arc voltage for Zn cathode in  $O_2$  gas flow as a function of pressure (arc current: 30 A,  $O_2$  gas flow: 35 sccm).

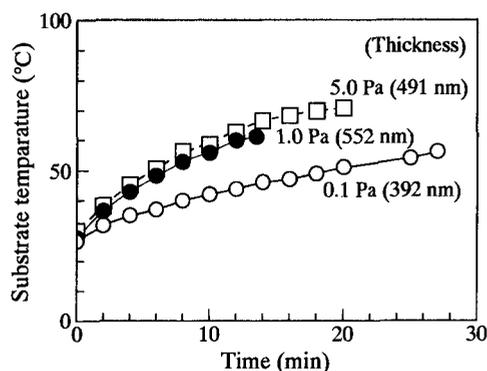


Fig. 4. Time variation of substrate temperature (arc current: 30 A,  $O_2$  gas flow: 35 sccm).

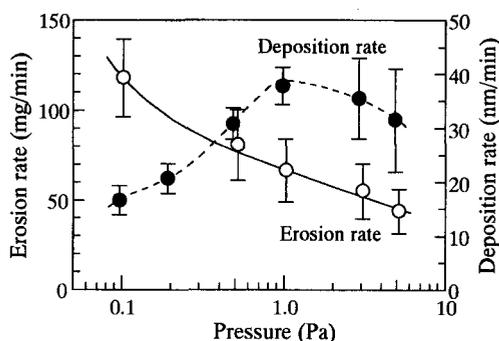


Fig. 3. Erosion rate of Zn cathode and deposition rate of the film (arc current: 30 A,  $O_2$  gas flow: 35 sccm).

was located between the cathode and the shield plate in order to prevent macrodroplets from traveling to the substrate. The shield plate was electrically floated. A permanent magnet was placed behind the cathode in order to drive the cathode spot on the cathode surface and reduce the generation of macrodroplets [18]. The radial component of magnetic flux density at the edge of the cathode surface was approximately 5.5 mT.

The chamber was evacuated once to less than 0.005 Pa and then oxygen ( $O_2$ ) gas of 35 sccm, regulated with a mass flow controller, was introduced into the chamber. The chamber pressure was kept constant at a certain value using an automatic conductance valve and pressure monitor. The arc was ignited by a mechanical triggering system with a molybdenum (Mo) trigger electrode, and powered by DC power supply in constant current mode. The films were prepared with an arc current of 30 A on borosilicate glasses (26 mm  $\times$  38 mm, 1 mm thick) as a function of process pressure (0.1 to 5.0 Pa). The substrate was floated and not heated. No bias was applied to the substrate.

### 3. RESULTS AND DISCUSSION

#### 3.1 Process characteristics

Fig. 2 shows the arc voltage as a function of process pressure. As the pressure increased, the arc voltage increased slightly and rose abruptly with a large fluctuation at 5.0 Pa. This rise was caused by the footpoint appearance on the anode surface [19].

The erosion rate of the Zn cathode was obtained from the weight difference before and after the process divided by the deposition time. The deposition rate of the film was obtained from the film thickness, which was derived from transmittance spectra as described later. The results are shown in Fig. 3. The erosion rate of the cathode decreased as the pressure increased. The gradient of the characteristics was sharper than those for titanium (Ti) and aluminum (Al) cathodes in nitrogen gas ( $N_2$ ) [20]. On the other hand, the film thickness increased with the pressure until 1.0 Pa. The highest deposition rate of approximately 40 nm/min was obtained at 1.0 Pa. When the pressure was above 1.0 Pa, the deposition rate tended to decrease and varied widely.

The temperature of the substrate was measured using a thermocouple. The result is shown in Fig. 4. The temperature gradually increased from room temperature during the deposition process. However, the temperature was found to be quite low for 500-nm-thick film preparation.

#### 3.2 Film properties

The crystalline states of the films were investigated using an X-ray diffraction analyzer (Rigaku, RINT-2500, X-ray source: Cu  $K_\alpha$ ). The X-ray patterns of the films (approximately 500 nm thick) are shown in Fig. 5. The patterns were consistent with a hexagonal wurtzite polycrystalline structure. The diffraction peaks detected were 002, 101, 103, 112 and 004. The appearance of the strongest ZnO 002 peak indicates that the *c*-axis of hex-

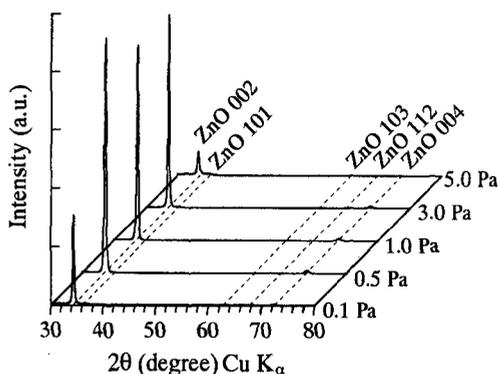


Fig. 5. X-ray diffraction patterns of films on glass substrates (film thickness: approximately 500 nm).

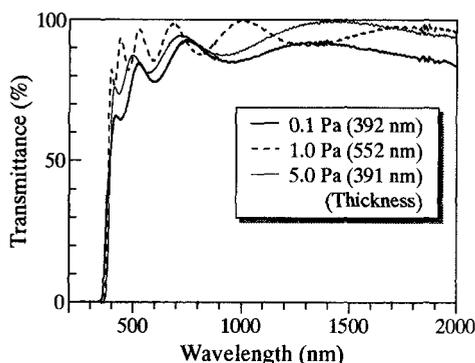


Fig. 6. Transmittance spectra of the films, referring to the substrate transmittance as a background level.

agonal ZnO was strongly oriented perpendicular to the substrate surface. With regard to process pressure, the highly crystallized film was obtained in the range of 0.5 to 3.0 Pa.

The transmittance spectra of the films were measured in the wavelength range of 300 nm to 2,000 nm using a double-beam spectrometer (Hitachi, 330), referring to the substrate transmittance as a background level. The result is shown in Fig. 6. The transmittance of the film prepared at 0.1 Pa was the lowest and this was consistent with the fact that the film was light brown in color. The films prepared at 0.5 to 3.0 Pa were highly transparent in the ultraviolet to near infrared region, as is the result at 1.0 Pa shown in Fig. 6. The transmittances of the films prepared at pressures above 3.0 Pa decreased somewhat.

Fig. 7 shows the refractive indices as a function of wavelength obtained from the transmittance spectra by means of Swanpoel's method [21]. The refractive index tended to be higher when the film was prepared at a lower pressure. At the wavelength of 600 nm, the value of the refractive index varied from approximately 1.8 to

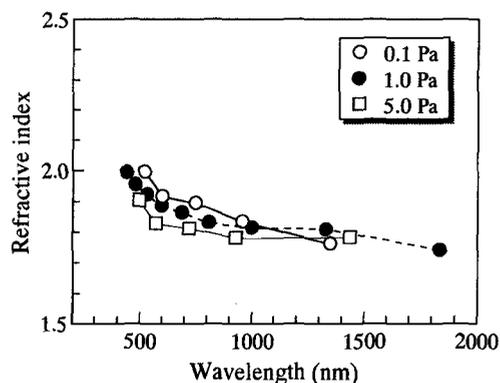


Fig. 7. Refractive indices of ZnO films, calculated from the transmittance spectra.

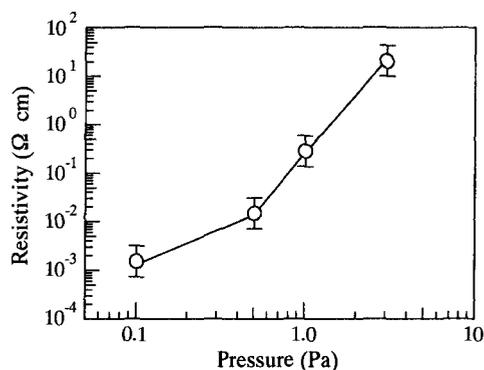


Fig. 8. Resistivities of the ZnO films prepared on glass substrates by a shielded vacuum arc deposition process.

1.9.

The resistivities of the films were measured using a four-point probe conductivity tester. The result is shown in Fig. 8. The resistivity was found to increase markedly with process pressure. At the pressure of 0.1 Pa, the resistivity was approximately  $10^{-3} \Omega \text{ cm}$ , which was very low. However, at 1.0 Pa, the resistivity was  $0.3 \Omega \text{ cm}$ . The lower resistivities of ZnO films are considered to be realized by the lack of O in the films. Therefore, the present result is interpreted as follows. At lower pressures, the amount of Zn in the film is much more than that of O, so the film resistivity is low. On the other hand, at higher process pressures, too much O is taken into the film, so the resistivity is high.

#### 4. CONCLUSIONS

ZnO thin films were prepared by reactive shielded vacuum arc deposition as a function of process pressure. The maximum deposition rate (40 nm/min) was obtained at 1.0 Pa. All films exhibited a hexagonal wurtzite structure and were highly oriented to the *c*-axis, perpendicular to the substrate. Well-crystallized and highly

transparent films were obtained at 0.5 to 3.0 Pa. However, the lowest resistivity ( $10^{-3} \Omega \text{ cm}$ ) was obtained at 0.1 Pa, and the resistivity increased with the process pressure. The refractive index at 600 nm varied from 1.8 to 1.9.

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