Thin Solid Films 520 (2012) 3751–3754

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

In-situ analyses on the reactive sputtering process to deposit Al-doped ZnO films using an Al–Zn alloy target

Naoki Tsukamoto, Nobuto Oka, Yuzo Shigesato *

Graduate School of Science and Engineering, Aoyama Gakuin University, 5-10-1 Fuchinobe Chuo-ku, Sagamihara, Kanagawa 252-5258, Japan

ARTICLE INFO

Article history:
Received 15 April 2011
Received in revised form 15 July 2011
Accepted 4 August 2011
Available online 22 August 2011

Keywords:
Reactive sputtering
Al-doped ZnO (AZO)
Transparent conducting oxide (TCO)
In-situ analyses
Energetic negative ion
Positive ion

ABSTRACT

The kinetic energies of generated ions were investigated during the reactive sputtering process to deposit Al-doped ZnO (AZO) films using an Al–Zn alloy target. The sputtering system was equipped with specially designed double feedback system to stabilise the reactive sputtering processes and analysis was performed with a quadrupole mass spectrometer combined with an energy analyser. Negative ions O^-, O_2^-, AlO^- and AlO_2^- with high kinetic energies corresponding to cathode voltage are generated at the partially oxidised target surface, after which some of the ions undergo subsequent charge exchange and/or dissociation. Positive ions O^+, Ar^+, Zn^+ and Al^+ with lower kinetic energies (around 10 eV) are generated by charge exchange of sputtered neutral O, Ar, Zn and Al atoms, respectively. As the target surface oxidises, cathode voltage decrease, the flux of high-energy negative ions increases and the electrical properties of the AZO degrade by ion bombardment as well as the AZO films that are deposited by conventional magnetron sputtering using an AZO target.

1. Introduction

Al-doped ZnO (AZO) is the most promising transparent conducting oxide (TCO) alternative to In_2O_3 based TCOs [1–4]. AZO films have been prepared by conventional magnetron sputtering using an AZO target. The reactive sputtering using an Al–Zn alloy (AZ) target is also researched to achieve higher deposition rate because higher sputter power density can be applied on the alloy target having higher thermal conductivity [5,6].

Reactive sputtering process is highly nonlinear, where cathode voltage exhibits hysteresis with respect to reactive gas flow rate [5–11]. Cathode voltage is influenced by the secondary electron yield of the cathode surface and changes as the target surface changes from metal (metal mode) to compound (compound mode) via an intermediate state involving a mixture of metal and compound (transition region). Reactive gas is consumed by absorption at surfaces of the target, chamber and substrate and is also output as exhaust from the vacuum pump [8–11]. Therefore, the graph shape of cathode voltage as a function of reactive gas flow rate is influenced not only by the target material but also by the nature of the sputtering equipment, such as the surface area of the chamber and the exhaust gas flow rate.

The electrical properties of AZO films are known to depend on stoichiometry and crystallinity, which are determined by the conditions of conventional magnetron sputtering [5,6,12–14]. For example, we previously reported that the bombardment of negative oxygen ions (O^-) with kinetic energies corresponding to the cathode voltage significantly affects the crystallinity and hence the electrical properties of AZO films [15,16].

In this study, we examined the behaviour of ions generated during reactive sputtering including the transition region using an AZ target by performing *in-situ* analyses on their mass spectra and energy distributions. We also discussed the mechanisms by which the energetic ions are generated and the influence of the ion bombardment on the films.

2. Experimental details

Fig. 1 shows a schematic illustration of our system used for *in-situ* analyses on reactive sputtering using an Al–Zn alloy target (Al: 3.6 at%, Φ 3 inch). To stabilise the reactive sputtering process in the transition region, the system was equipped with the specially designed double feedback system based on analogue proportional-integral-derivative (PID) controllers (SIM960, Stanford Research System). The signal of the cathode voltage from the dc power supply and the set-point of the cathode voltage were input to the first PID controller; its output signal controlled O_2 flow rate. Another feedback system kept the total gas pressure constant at 0.3 Pa by controlling Ar flow rate for corresponding to shift of O_2 partial pressure. The signal of pressure from the vacuum gauge and the set-point of pressure were input to second PID controller; its output signal controlled Ar flow rate. Sputtering power was maintained at 100 W and the magnetic field was 0.1 T. Exhaust gas flow rate was varied by controlling a valve in front of turbo-molecular pump in order to show different graph shapes of the cathode voltage as a

* Corresponding author.
E-mail address: yuzo@chem.aoyama.ac.jp (Y. Shigesato).

0040-6090/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2011.08.031

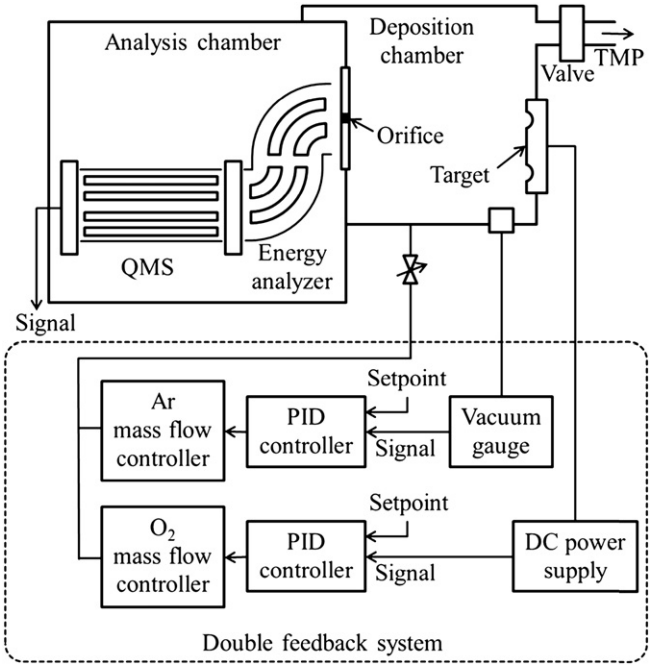

Fig. 1. Schematic illustration of the system used for *in-situ* analysis on the reactive sputtering process. The system includes a quadrupole mass spectrometer combined with an electrostatic energy analyser and a double feedback system to stabilise the reactive sputtering processes in the transition region.

function of O_2 flow rate relative to the characteristics of various sputtering equipments.

O_2 partial pressure during reactive sputtering was calculated as follows. First, the total gas pressure was maintained at 0.3 Pa without discharge, where Ar flow rate was 20, 10, 5, 2.5 or 1.25 sccm. The exhaust gas flow rate can be defined as each Ar flow rate at this moment. Second, O_2 gas was introduced and the feedback system maintained the total gas pressure of 0.3 Pa by controlling the Ar flow rate. The O_2 partial pressure during the reactive sputtering was estimated by $[0.3(GFR_{ex} - GRF_{Ar})/GFR_{ex}]$, where GFR_{ex} and GFR_{Ar} respectively mean the exhaust gas and Ar flow rates.

The energy distributions of the energetic ions were analysed using a quadrupole mass spectrometer (QMS) combined with an electrostatic energy analyser (AQA-360 ANELVA). The head of the energy analyzer was mounted 60 mm away from the target through an orifice (Φ1 mm) facing the erosion area on the target. Gas pressure in the analysis chamber was maintained at 0.05 Pa. The energy resolution of the energy analyser is 2–3 eV. Only ions impinging on the orifice at normal incidence could enter the analyser.

The carrier concentration, Hall mobility and resistivity of AZO films on fused silica substrates (sample size 10×10 mm^2) were analysed by the four-point probe method and Hall-effect measurement in van der Pauw geometry (HL5500PC, Bio-Rad).

3. Results and discussion

Fig. 2(a) shows plots of cathode voltages as a function of O_2 flow rate for a range of exhaust gas flow rates (1.25–20 sccm). Cathode voltage decreases because of the oxidation of the metallic target surface which has the larger secondary electron emission coefficient and hence decreases the plasma impedance. The shape of the cathode voltage vs. O_2 flow rate relationship changes from linear to S-shape with decreasing exhaust gas flow rate [8–11]. Fig. 2(b) shows plots of cathode voltage as a function of O_2 partial pressure for the same range of exhaust gas flow rates. The relationship between voltage and O_2 partial pressure is essentially the same for all the exhaust gas flow rates, indicating that the feedback systems could successfully control the reactive sputtering process.

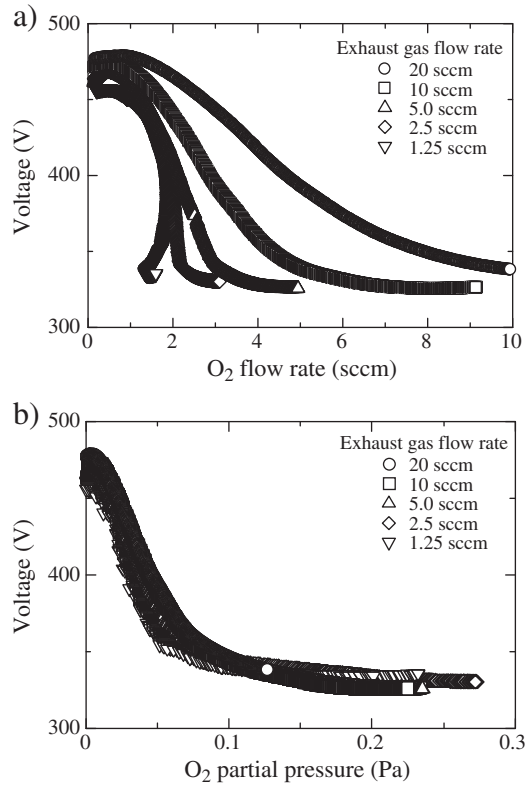

Fig. 2. Plots of cathode voltage as a function of (a) O_2 flow rate and (b) O_2 partial pressure. Exhaust gas flow rates are 1.25, 2.5, 5, 10 and 20 sccm.

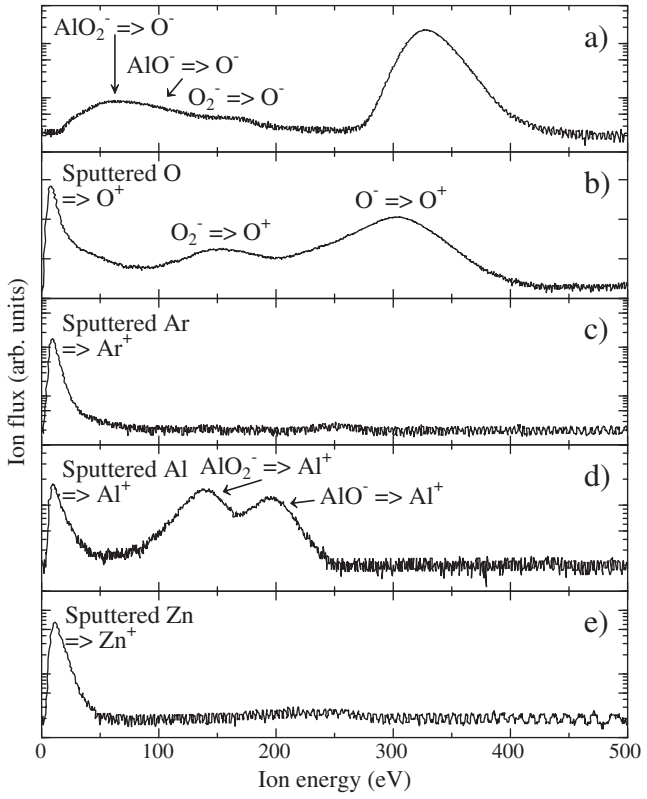

Fig. 3. Energy distributions of various ions: (a) O^-, (b) O^+, (c) Ar^+, (d) Al^+ and (e) Zn^+.