High rate deposition of tin-doped indium oxide films by reactive magnetron sputtering with unipolar pulsing and plasma emission feedback systems

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Abstract

Tin-doped indium oxide (ITO) films were deposited on the unheated alkali-free glass substrates (AN100) by reactive magnetron sputtering using an indium–tin alloy target with an unipolar pulsed power source feeding 50 kHz pulses and a plasma control unit (PCU) with a feedback system of oxygen plasma emission intensity at 777 nm. In order to achieve very high deposition rates, depositions were carried out in the ‘transition region’ between the metallic and the reactive (oxide) sputter modes where the target surface was metallic and oxidized, respectively. Stable depositions were successfully carried out in the whole ‘transition region’ with an aid of PCU. The lowest resistivity as the transparent ITO films deposited on unheated alkali-free glass was $7.5 \times 10^{-4}$ $\Omega$cm with the deposition rate of 650 nm/min. The electrical and optical properties of the films could be controlled systematically in the very wide range.

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1. Introduction

Several kinds of transparent conductive oxide (TCO) films have been widely used in the field of optoelectronics, such as in transparent metallization for various kinds of flat panel displays (FPDs) or solar cells. Sn-doped In$_2$O$_3$ (ITO) is an n-type, highly degenerate, wide-gap semiconductor which, due to its relatively low resistivity and high visible transmittance compared to the other TCO materials such as SnO$_2$ or ZnO, is at present overwhelmingly used as transparent electrodes in liquid crystal displays (LCDs), plasma displays and light emitting diodes (LEDs) [1–6]. Considerable effort has been focused on depositing ITO films of significantly low resistivity in order to accommodate the increasing technological demand for larger area flat panel displays with higher image quality [7–11].

The deposition method of ITO films employed so far for commercial productions has been the dc magnetron sputtering using an oxide ceramic target because of high stability and reproducibility. This method provides the low resistivity of about $10^{-4}$ to $10^{-3}$ $\Omega$cm [7,8,11–14]. However, the deposition rate, one of the most important factors dominating the deposition cost, is not so high because of the low sputtering yield of the oxide. On the other hand, the reactive dc magnetron sputtering process using a metal or alloy target is considered to have higher potential for the large area coatings with very high deposition rates and low cost. The reactive sputtering process, however, is highly non-linear, where the deposition rate shows the ‘hysteresis’ with respect to the reactive gas flow rate [15–20]. Such a behavior originates from the oxidation state of the target surface, resulting in drastic changes in the sputtering yield. Therefore, in the ‘transition region’, the deposition rate decreases drastically with increasing oxygen gas flow rate depending on target surface conditions. Moreover, the reactive dc sputtering on the non-uniformly oxidized target surface causes the problem of abnormal discharges such as arcing during long time operations in the production. Dual magnetron sputtering (DMS) systems with mid-frequency pulsing of 50 kHz have been proposed for oxide or nitride films to reduce the arcing drastically even under high power density impression [21–23]. Two types of plasma control
units (PCU) with a feedback system of either plasma emission intensity [21,22] or discharge impedance [23] have been reported in combination with the DMS systems for the very high rate deposition controlled stably in the ‘transition region’. However, the DMS system needs two cathodes and two power supplies, which make it difficult to be reversible with a conventional single target production systems.

In this study, a reactive dc magnetron sputtering system with unipolar pulsed powering and the PCU was adopted to deposit ITO films, which is much simpler than the DMS system. The reactive sputter depositions in the ‘transition region’ were carried out in order to obtain high quality ITO films at around room temperature and at very high deposition rates. The structures and electrical properties were investigated in relation to various deposition parameters.

2. Experimental details

ITO films were deposited on unheated alkali-free glass substrates (AN100, Asahi Glass) by reactive sputtering with unipolar pulsing unit and plasma control unit (PCU, FEP: Fraunhofer Institut fur Elektronenstrahl- und Plasmatechnik). The schematic illustration of this system is shown in Fig. 1. This system consists of one magnetron cathode (RM400, FEP), specially designed hidden anodes, dc power source (pinnacle 6 kW, Advanced Energy) with mid-frequency pulse unit (UBS-C2, FEP) and PCU with feedback system of plasma emission intensity on the reactive gas flow. A planar In–Sn alloy target (Sn: 10 at.%, 130 mm×400 mm in size) was connected with the UBS-C2 which was operated in the unipolar pulse mode. The mid-frequency pulse unit possesses the approximate shape of a square wave with frequency of 50 kHz and duty cycle of 80%, which make it possible to impress very high power density without arcing at the cathode. The hidden anode was designed to be an effective anode to keep the discharge stably without any surface poisoning during the depositions. Reactive and sputtering gases were O\textsubscript{2} (purity: 99.999%) and Ar (purity: 99.999%), respectively. The reactive gas flow was precisely controlled by piezoelectric valves under the control of PCU. The plasma emission of the atomic O\textsuperscript{*} line at 777 nm was led into the optical emission detector (containing a photomultiplier and optical filter) to transform the optical intensity into the photovoltage. The PCU adjusted the piezoelectric valve to control O\textsubscript{2} flow precisely and rapidly until the photovoltage is equal to the set point value for the optical emission intensity (OEI). The set points could be chosen in the ‘transition region’ between the metallic and the reactive (oxide) sputter mode in order to achieve high deposition rate. The chamber was evacuated down to a pressure of less than 9.0×10\textsuperscript{-4} Pa. The second control loop kept the total gas pressure (P\textsubscript{tot}) constant at 0.5 Pa by adjusting the argon gas flow. The ‘pre-sputtering’ was carried out only with argon for 20 min in order to remove the oxide layer at the target surface and the ‘pre-sputtering’ was carried out with reactive gas for 10 min under the same conditions during deposition. The set points of the OEI of the O\textsuperscript{*} line at 777 nm were selected between the photovoltage of 2 and 9 V. The deposition parameters are listed in Table 1.

All the depositions were carried out with dc power of 5 kW on the unheated glass substrate which was fixed in front of the target (Fig. 1). The substrate surface temperature after the depositions was lower than 70 °C confirmed both by thermo-couple fixed at the substrate surface and by the radiation thermometer, where the both measurements indicated the same values.
In order to compare these reactive sputter depositions with conventional dc magnetron sputter depositions, ITO films were also deposited using the same sputtering equipment with an ITO ceramic target. The O2 flow during the depositions was controlled simply from 0 to 5 sccm by MFC, where total gas pressure was kept constant at 0.5 Pa by adjusting the Ar flow from 70 to 65 sccm. All the other deposition conditions were the same as that of the reactive sputtering with PCU using the In–Sn metal target.

The film thickness was measured using a surface profiler (Dektak3, Sloan Tech.). The resistivity, Hall mobility and carrier density were measured by the four-point probe method and Hall-effect measurement in the van der Pauw geometry (HL-550PC, Bio-Rad). The X-ray diffraction (XRD) was carried out by 40 kV, 20 mA Cu Kα1 radiation (XRD-6000, Shimadzu). Transmittance and reflectance were measured from 250 to 2500 nm using a spectrophotometer (UV-3100, Shimadzu).

3. Results and discussion

Fig. 2 shows the optical emission intensities (OEI) of O* at 777 nm from the glow discharge at the various O2 flow ratio

| Target material | In–Sn alloy (Sn: 10 at.%), ITO (SnO2: 10 wt%) |
|-----------------|-----------------------------------------------|
| Target size     | 400 mm × 130 mm                               |
| Sputter gas     | Ar (purity: 99.999%)                           |
| Reactive gas    | O2 (purity: 99.999%)                           |
| Base pressure   | <9.0 × 10−4 (Pa)                              |
| Total gas pressure | 0.5 (Pa)                                       |
| Sputtering power | 5000 (W)                                       |
| Substrate temperature (T) | RT                                          |
| Substrate material | Alkali-free glass (AN100, Asahi glass)       |
| Target to substrate distance | 115 (mm)                                      |
[O2/(O2+Ar)], where the O2 flow was precisely controlled by piezoelectric valves that were connected with the PCU. The typical S-shaped curve was obtained, where the three different O* emission intensity values were observed at the same oxygen flow ratio from 50 to 60%, implying that the precise control of the target surface condition in the ‘transition region’ was completely achieved. It also implies that the stable depositions in the transition region should be quite difficult when we simply control only oxygen flow ratio without the PCU. The deposition rate is plotted as a function of the OEI in Fig. 3. It is clearly observed that the deposition rate decreased monotonically with increasing OEI.

Fig. 4(a) shows transmittance from 250 to 2500 nm of ITO films deposited at the OEI set points of 2–9 V. The metallic films were deposited at the OEIs of 2–3 V, which were not transparent. The transmittance of the film deposited at the OEI of 4 V was 75–80% in the visible region and decreased gradually with increasing wavelength in the near infrared region. The films deposited at the OEIs of 5–9 V showed higher transmittance of about 80% both in visible and near infrared regions. The electrical properties of these films are shown in Fig. 5 as a function of the OEI set points. The ITO film with the lowest resistivity of 7.5 \times 10^{-4} \Omega\text{cm} were obtained at the OEI of 4 V, where the carrier density was larger than 10^{20} \text{cm}^{-3}.

With increase in the OEI, i.e. in more oxidative deposition conditions, the resistivity increased because of the monotonic decrease in carrier density, which should be caused by the extinction of oxygen vacancies or the increase in interstitial oxygen ions at the quasi-anion sites of In_{2}O_{3} bixbyite structure [24,25]. This decrease in carrier density corresponds to the optical properties in Fig. 4, where the transmittance in the near infrared region increased for the films with the smaller carrier density. This correlation have been explained in terms of the shift of plasma frequency to longer wavelength side with the decrease in carrier density based on the Drude’s theory [14,26]. Thus it could be concluded that the various ITO films with the...
very wide range in the electrical and optical properties were deposited systematically by the stable sputtering in the ‘transition region’.

The deposition rate of ITO films in the case of using the ITO target is shown in Fig. 6(a) in relation to the O₂ flow ratio. In this case the deposition rate hardly changed with the change in O₂ flow ratio because the target surface should be always oxidized. Fig. 6(b) shows the deposition rate of ITO films deposited by the reactive sputtering using the In–Sn alloy target as a function of OEI photovoltage. The deposition rate decreased gradually with the increasing OEI, which should be caused by the oxidation of the target surface and hence, decreasing sputtering yield.

XRD patterns of the ITO films in the case of using the ITO target is shown in Fig. 7(a) in relation to O₂ flow ratio. In general the crystallinity of the films is one of the important factors dominating the wet etching rate and patterning properties for the application for the flat panel displays [27,28]. The films deposited with oxygen flow from 0 to 5.0 sccm were confirmed to have polycrystalline In₂O₃ [27,28]. The films deposited in the ‘transition region’ of O₂ flow from 0 to 5.0 sccm were confirmed to have polycrystalline In₂O₃ [27,28]. The films deposited in the ‘transition region’ of O₂ flow from 0 to 5.0 sccm were confirmed to have polycrystalline In₂O₃ [27,28].

4. Conclusion

ITO films were deposited by reactive magnetron sputtering using a single In–Sn alloy target with unipolar pulsed powering of 50 kHz and the PCU with the feed back system of oxygen plasma emission intensity at 777 nm. Stable sputter depositions were successfully carried out in the whole ‘transition region’, which enabled us to obtain various ITO films with the wide range of stoichiometry variations. The lowest resistivity of the transparent ITO films deposited on unheated alkali-free glass substrate was 7.5 × 10⁻⁴ Ωcm with a high deposition rate of 650 nm/min.

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References

[1] I. Hamberg, C.G. Granqvist, Evaporated Sn-doped In₂O₃ films: basic optical properties and applications to energy-efficient windows, J. Appl. Phys. 60 (1986) 123–159.
[2] Y. Shigesato, I. Yasui, D.C. Paine, ITO thin-film transparent conductors: microstructure and processing, TMS Mont. Bull. (JOM) March (1995) 47–50.
[3] H. Odaka, S. Iwata, N. Taga, S. Ohnishi, Y. Kaneta, Y. Shigesato, Study on electronic structure and optoelectronic properties of indium oxide by first-principles calculations, Jpn. J. Appl. Phys. 36 (1997) 5551–5554.
[4] H. Odaka, Y. Shigesato, T. Murakami, S. Iwata, Electronic structure analyses of Sn-doped In₂O₃, Jpn. J. Appl. Phys. 40 (2001) 3231–3235.
[5] T. Tsutsumi, Present status of research and development in organic electroluminescent devices, Oyobuturi 66 (1997) 109–116 (in Japanese).
[6] H. Kobayashi, Y. Ishida, Y. Nakato, H. Tsubomura, Mechanism of carrier transport in highly efficient solar cells having indium tin oxide/Si junctions, J. Appl. Phys. 69 (1991) 1736–1743.
[7] S. Ishibashi, Y. Higuchi, Y. Ota, K. Nakamura, Low resistivity indium-tin oxide transparent conductive films. II. Effect of sputtering voltage on electrical property of films, J. Vac. Sci. Technol. A8 (1990) 1403–1406.
[8] Y. Shigesato, S. Takaki, T. Haranoh, Electrical and structural properties of low resistivity tin-doped indium oxide films, J. Appl. Phys. 71 (1992) 3356–3364.
[9] Y. Shigesato, D.C. Paine, Study of the effect of Sn doping on the electronic transport properties of thin film indium oxide, Appl. Phys. Lett. 62 (1993) 1266–1270.
[10] Y. Shigesato, I. Yasui, Y. Hayashi, S. Takaki, T. Oyama, M. Kamei, Effects of water partial pressure on the activated electron beam evaporation process to deposit tin-doped indium-oxide films, J. Vac. Sci. Technol. A13 (1995) 268–275.
[11] Y. Shigesato, S. Takaki, T. Haranoh, Crystallinity and electrical properties of tin-doped indium oxide films deposited by DC magnetron sputtering, Appl. Surf. Sci. 48/49 (1991) 269–275.
[12] Y. Shigesato, D.C. Paine, A microstructural study of low resistivity tin-doped indium oxide prepared by d.c. magnetron sputtering, Thin Solid Films 238 (1994) 44–50.
[13] P.K. Song, Y. Shigesato, I. Yasui, C.W. Ow-Yang, D.C. Paine, Study on crystallinity of tin-doped indium oxide films deposited by d.c. magnetron sputtering, Jpn. J. Appl. Phys. 37 (1998) 1870–1875.
[14] P.K. Song, Y. Shigesato, M. Kamei, I. Yasui, Electrical and structural properties of tin-doped indium oxide films deposited by d.c. sputtering at room temperature, Jpn. J. Appl. Phys. 38 (1999) 2921–2927.
[15] S. Berg, T. Larsson, C. Nender, H.O. Blom, Predicting thin-film stoichiometry in reactive sputtering, J. Appl. Phys. 63 (1988) 887–891.
[16] R.P. Howson, A.G. Spencer, K. Oka, R.W. Lewin, The formation and control of direct current magnetron discharges for the high-rate reactive processing of thin films, J. Vac. Sci. Technol. A7 (1989) 1230–1234.
[17] S. Sciller, U. Heisig, C. Kirndorfer, G. Beister, J. Reschke, K. Steinfelder, J. Strumpfel, Reactive d.c. high-rate sputtering as production technology, Surf. Coat. Technol. 33 (1987) 405–423.
[18] S. Berg, T. Larsson, H.O. Blom, The use of nitrogen flow as a deposition rate control in reactive sputtering, J. Vac. Sci. Technol. A4 (1986) 594–597.
[19] S. Inoue, K. Tominaga, R.P. Howson, K. Kasaka, Effects of nitrogen pressure and ion flux on the properties of direct current reactive magnetron sputtered Zr–N films, J. Vac. Sci. Technol. A13 (1995) 2808–2813.
[20] R. Danneberg, P. Greene, Reactive sputter deposition of titanium dioxide, Thin Solid Films 360 (2000) 122–127.
[21] M. Kon, P.K. Song, Y. Shigesato, P. Frach, A. Mizumaki, K. Suzuki, Al-doped ZnO films deposited by reactive magnetron sputtering in mid-frequency mode with dual cathodes, Jpn. J. Appl. Phys. 41 (2002) 814–819.
[22] S. Ohno, D. Sato, M. Kon, P.K. Song, M. Yoshikawa, K. Suzuki, P. Frach, Y. Shigesato, Plasma emission control of reactive sputtering process in mid-frequency mode with dual cathodes to deposit photocatalytic TiO₂ films, Thin Solid Films 445 (2003) 207–212.
[23] M. Kon, P.K. Song, Y. Shigesato, P. Frach, S. Ohno, Impedance control of reactive sputtering process in mid-frequency mode with dual cathodes to deposit Al-doped ZnO films, K. Suzuki, Jpn. J. Appl. Phys. 42 (2003) 263–269.
[24] N. Yamada, I. Yasui, Y. Shigesato, H. Li, Y. Ujihira, K. Nomura, Doping mechanisms of Sn in In₂O₃ powder studied using ¹¹¹Sn Mössbauer spectroscopy and X-ray diffraction, Jpn. J. Appl. Phys. 38 (1999) 2856–2862.
[25] N. Yamada, I. Yasui, Y. Shigesato, H.L. Ujihira, K. Nomura, Donor compensation and carrier-transport mechanisms in tin-doped In$_2$O$_3$ films studied by means of conversion electron $^{119}$Sn Mössbauer spectroscopy and Hall effect measurements, Jpn. J. Appl. Phys. 39 (2000) 4158–4163.

[26] Y. Ohhata, F. Shinoki, S. Yoshida, Optical properties of r.f. reactive sputtered tin-doped In$_2$O$_3$ films, Thin Solid Films 59 (1979) 255–261.

[27] C.H. Yi, Y. Shigesato, I. Yasui, S. Takaki, Microstructure of low-resistivity tin-doped indium oxide films deposited at 150–200 °C, Jpn. J. Appl. Phys. 34 (1995) L244–L247.

[28] J.E.A.M. van den Meerakker, P.C. Baarslag, W. Walrave, T.J. Vink, J.L.C. Daams, On the homogeneity of sputter-deposited ITO films Part II. Etching behaviour, Thin Solid Films 266 (1995) 152–156.