Carbon-dioxide as annealing atmosphere to retain the electrical properties of indium-tin oxide

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Abstract:

In practical applications of indium-tin-oxide (ITO) annealing at temperatures ~400 °C without degrading its electrical and optical properties is an important challenge. In the present work, commercial Indium-tin oxide (ITO) coated on glass was subjected to post-annealing treatment in the range of 200-400 °C at different annealing atmospheres; oxygen, nitrogen and carbon-dioxide. The annealed samples were characterized by X-ray diffraction, UV-visible spectroscopy and Hall measurements to evaluate the structural, optical and electrical properties. Both oxygen and nitrogen treated samples degrades the structural, optical and conducting properties of ITO, while carbon-dioxide atmosphere inhibits the degradation of ITO at 400 °C. The obtained results suggest that carbon-dioxide can be well utilized as annealing ambient to retain opto-electronic, structural and electrical properties of ITO and thereby improve the efficiency of ITO based solar cells.

Key words: Indium-tin oxide, thermal stability, annealing atmospheres, carbon-dioxide.

Introduction:

Indium tin oxide (ITO) is a transparent conducting oxide (TCO) that is widely used in device applications such as flat-panel displays, flexible electronics, thin film photovoltaics, smart glass windows, etc. [1-4] and often device fabrication involves thermal and chemical treatments. General requirements for TCOs are low electrical resistivity and high transparency in visible spectral region. Although ITO films show high transparency and electrical conductivity at room temperature, the electrical property often degrades when ITO films are exposed to oxidizing atmospheres (Air or oxygen-O_2) at temperatures higher than 300 °C [5]. The increase of resistivity is attributed to the decrease of oxygen vacancies or compensating oxygen interstitials in the ITO film. Nevertheless, annealing in inert nitrogen (N_2) atmospheres improve the electrical conductivity due to formation of donor-like oxygen vacancies [6]. Importantly, in ITO enriched with oxygen vacancies, the conduction band is pinned to the Fermi level affecting the work function [7]. As another extensively used TCO, Fluorine doped tin oxide (FTO) has higher thermal stability. However, ITO has higher transparency than FTO at a specified sheet resistivity [3]. Chen et.al demonstrated the thermal stability of ITO by employing a two-step O_2/N_2 annealing process of the dye-sensitized solar cell (DSSC) photo anodes and solar cell efficiency was found to vary with sheet resistivity of ITO [8]. For DSSC devices, it is an important challenge to anneal ITO at temperatures higher than 300 °C without degradation of its electrical and optical properties. The benefits of a solution can benefit other type of devices using TCO. In this work, CO_2 inert atmosphere was proposed as an alternative annealing atmosphere to hinder the thermal degradation of ITO.

Experimental method:

Commercial ITO (Hoya, Japan) coated on glass with 170 nm film thickness was used in the present work. The ITO films were annealed at 200, 300 and 400 °C for 1 hour in CO_2 atmosphere. For comparison and to demonstrate the thermal degradation, ITO films were also annealed in O_2 and N_2 atmospheres. The structural properties were investigated by X-ray diffraction studies (Rigaku, Ultima III Max). The transmittance of the post-annealed ITO film was investigated by UV-Vis-NIR spectroscopy in the spectral range 290 -2500 nm (Shimadzu SolidSpec-3700 DUV) and UV-Visible spectroscopy in the spectral range 200-850 nm (Jasco V650). Both transmittance measurements were performed with integrating sphere and 1nm spectral resolution. The sheet resistivity was measured using conventional four probe-setup (with keithley meter). Closed-cycle refrigerator–variable temperature insert (CCR–VTI) system for resistivity analysis was used to measure the resistivity of the as-received and annealed ITO films from 20 – 300 K. The carrier concentration and Hall mobility of the films at room temperature was measured using a magnetic field strength of 10 kGauss (Lakeshore 7604).

Results and Discussion:

Figure 1 shows the XRD spectra of as-received and ITO films annealed in O_2, N_2 and CO_2 atmosphere at 400 °C. The as-received ITO film has preferential (222) orientation along with a small fraction of $In_3Sn_4O_{12}$ phase. All ITO films exhibit body-centered cubic crystal structure (space group 206, I –a 3) with lattice parameter of a = 10.1517 Å against a = 10.1195 Å for undoped indium oxide (In_2O_3). Substitution of Sn^{4+} ions on In-sublattice (In^{3+} ions) would increase the lattice parameter and electron concentration [9]. The solubility of tin in indium

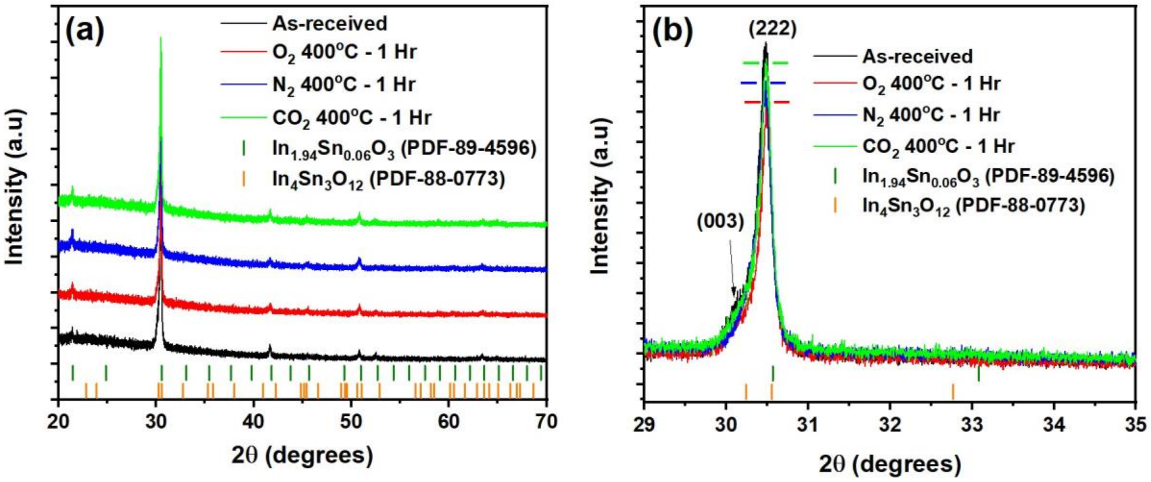

Fig. 1: XRD spectra of (a) as-received and 400 °C annealed ITO films in O_2, N_2 and CO_2 atmospheres along with PDF data for 6 at.% Sn doped In_2O_3 (a = 10.1234 Å) and $In_4Sn_3O_{12}$ phase and (b) expanded view demonstrating $In_4Sn_3O_{12}$ phase along with intensity variation for annealed samples. Note: dashed line is only for eye guidance (for peak intensity).

oxide is 6 at. % and $In_4Sn_3O_{12}$ rhombohedral phase precipitates at higher concentrations of tin [10]. Importantly, decrease in the intensity of the XRD characteristics peaks (represented by dashed lines in fig. 1(b) for (222) orientation) suggest degradation of the film quality, which occurs for 400 °C annealing in O_2 and N_2 atmospheres compared to as-received ITO films. Annealing in CO_2 atmosphere has very small influence on the crystalline quality compared to as-received film. It should be noted that the fraction of the $In_3Sn_4O_{12}$ phase varies depending on the annealing atmosphere. However, no apparent change in lattice parameter was observed for the annealed ITO films.

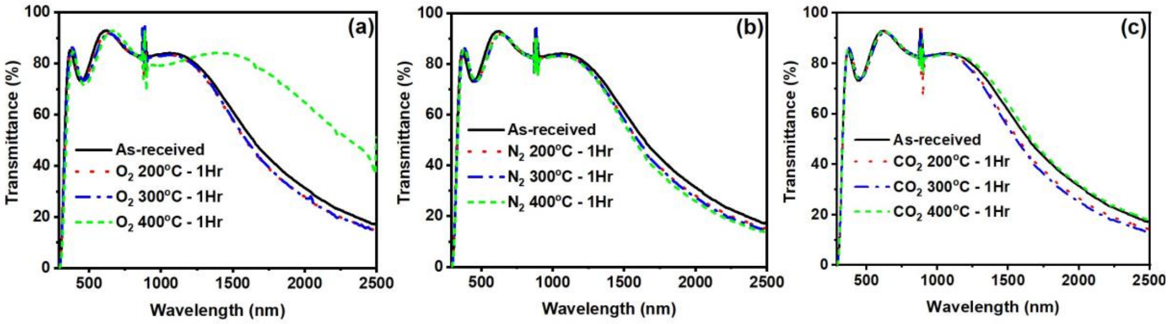

Fig. 2: UV-Vis-NIR spectra of ITO films annealed in (a) O_2, (b) N_2 and (c) CO_2 atmospheres in the range of 200 -400 °C for 1hr.

Figure 2 shows the transmittance spectra of the ITO films annealed in different atmospheres along with the as-received ITO film. All the films exhibit similar transmittance in the UV-Vis region. In addition, a decrease in transmittance in the NIR spectral region (1000 -2500 nm) is observed for all samples, and may be attributed to the free carrier absorption. Annealing at 400 °C in O_2 atmosphere increases the transmittance in NIR region, due to suppression of excess

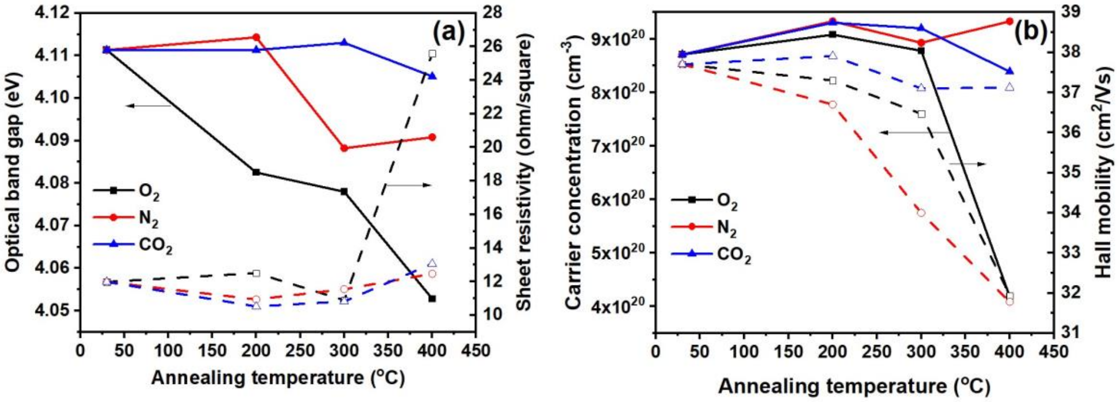

Fig. 3: Optical and electrical properties of ITO films annealed in O_2, N_2 and CO_2 atmospheres (a) Annealing temperature vs optical band gap and sheet resistivity (b) Annealing temperature vs carrier concentration and Hall mobility

oxygen vacancies, while a nominal decrease is observed in N_2 atmosphere. However, the transmittance characteristics are retained for ITO films annealed in CO_2 atmosphere at 400 °C.

Figure 3 shows the optical band gap extracted from Tauc-plot [11] for annealed ITO films. It is observed that increasing the annealing temperature the optical band gap of the ITO films decreases for N_2 and O_2 atmosphere. A minor change is noticed for the CO_2 case. Moreover, annealing in O_2 atmosphere at 400 °C increase the sheet-resistivity of the films, in agreement with the observation made in transmittance spectra (reduction of oxygen vacancies), also supported by decrease in carrier concentration in fig. 3(b). However, annealing at 400 °C in N_2 atmosphere shows increase in carrier concentration (excess generation of oxygen vacancy V_O) as observed in fig. 3(b). This is attributed to the degradation of crystalline quality observed in XRD analysis along with decrease in Hall mobility observed in fig 3(b). Annealing in CO_2 atmosphere has retained the electrical properties of the ITO films even at 400 °C.

Temperature dependent resistivity of the films is shown in fig. 4 for annealed ITO at 400 °C; suggests that all the ITO films exhibit degenerate characteristics with metal-like temperature dependence. Chokawa et al.[12] investigated the influence of carbon-monoxide (CO) and CO_2

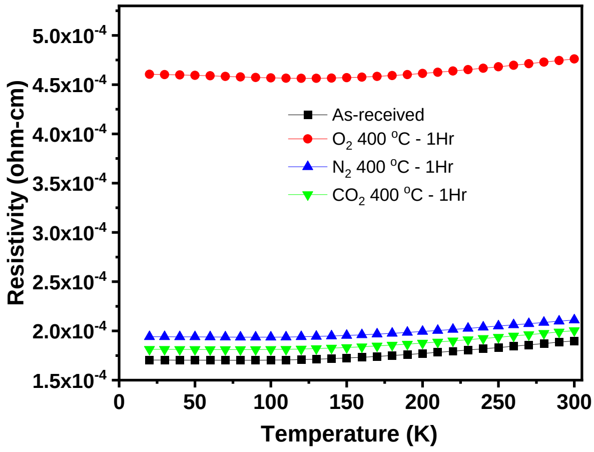

Fig. 4: Temperature dependent resistivity of ITO films annealed at 400 °C in O_2, N_2 and CO_2 atmospheres.

atmospheres on the stoichiometry of the SiO_2 near the SiC/SiO_2 interface. Post- annealing in CO atmosphere induced defects degrading the breakdown field of SiO_2 layer. On the other hand, CO_2 atmosphere reduced the oxygen vacancy defects in SiO_2 as the partial pressure of the CO_2 molecules is larger than that of the CO molecules. Similar effect was observed in the present work, where CO_2 atmosphere suppressed the formation of excess V_O and its inert characteristics decreased the incorporation of excess oxygen atoms in ITO films. Based on these observations, we propose that formation of excess V_O defects may be suppressed by increasing the partial pressure of the CO_2 molecules at temperatures higher than 400 °C for DSSC solar cell applications.

Conclusions:

ITO films were annealed in CO_2 inert atmosphere and the influence on the electrical and optical properties was investigated. It was found that CO_2 atmosphere retained the structural, electrical and optical properties. Similar annealing conditions in O_2 atmosphere decreased the conductivity due to recombination of excess oxygen interstitials, while N_2 atmosphere increased the oxygen vacancy concentration. Importantly, degradation of crystalline quality was observed in XRD analysis for O_2 and N_2 atmospheres at 400 °C. The present work suggests that thermal stability of ITO can be retained at high temperatures in CO_2 atmosphere and with its characteristic high transmittance, high efficient ITO based solar cells could be realized.

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References:

1. H. Kim, C. M. Gilmore, A. Piqué, J. S. Horwitz, H. Mattoussi, H. Murata, Z. H. Kafafi, and D. B. Chrisey, J. Appl. Phys., 86 (1999) 6451; https://doi.org/10.1063/1.371708
2. T. Margalith, O. Buchinsky, D. A. Cohen, A. C. Abare, M. Hansen, S. P. DenBaars, and L. A. Coldren, Appl. Phys. Lett., 74 (1999) 3930; https://doi.org/10.1063/1.124227
3. M. Zhang, B. Wilkinson, Y. Liao, J. Zheng, C.F.J. Lau, J. Kim, J. Bing, M.A. Green, S. Huang and A.W-Y. H-Baillie, Joule, 2 (2018) 2694 - 2705 ; https://doi.org/10.1016/j.joule.2018.08.012
4. V.A. Shakhnov, A.I. Vlasov and S.V. Tokarev, IOP Conf. Ser.: Mater. Sci. Eng., 151 (2016) 012005; https://doi.org/10.1088/1757-899X/151/1/012005
5. F. Li, C. Chen, F. Tan, C. Li, G. Yue, L. Shen and W. Zhang, Nanoscale Res. Lett., 9 (2014) 579 ; https://doi.org/10.1186/1556-276X-9-579
6. C.J. Huang and W.C: Shis, J. Elec. Mater. 32 (2003) L9–L13; https://doi.org/10.1007/s11664-003-0099-x
7. I. Irfan, S. Graber, F. So, and Y. Gao, Org. Electron., 13 (2012) 2028-2034; https://doi.org/10.1016/j.orgel.2012.05.036

8. C-M. Chen, Y-C. Hsu, and S-J. Cherng, J. Alloys and Compounds, 509 (2011) 872–877; https://doi.org/10.1016/j.jallcom.2010.09.118
9. J. C. C. Fan, F. J. Bachner, and G. H. Foley, Appl. Phys. Lett. 31 (1977) 773; https://doi.org/10.1063/1.89544
10. N. Nadaud, N. Lequeux, M. Nanot, J. Jove, and T. Roisnel, J. Solid State Chem., 135 (1998) 140 -148; https://doi.org/10.1006/jssc.1997.7613
11. V. Venkatachalapathy, A. Galeckas, R. Sellappan, D. Chakarov, and A. Kuznetsov, J. Crystal Growth, 315 (2011) 301- 304; https://doi.org/10.1016/j.jcrysgro.2010.09.056
12. K. Chokawa, M. Araidai, and K. Shiraishi, J. Appl. Phys. 124 (2018) 135701; https://doi.org/10.1063/1.5041794