Thin Solid Films 532 (2013) 26–30

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

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

Halide doping effects on transparent conducting oxides formed by aerosol assisted chemical vapour deposition

Nuruzzaman Noor, Ivan P. Parkin *

Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK

ARTICLE INFO

Available online 20 November 2012

Keywords:
Transparent conducting oxide
Chemical vapour deposition
Fluorine-doped tin oxide
Thin film
Tin oxide
Halide exchange
Aerosol

ABSTRACT

We report on the effect of halide doping on the Aerosol-assisted Chemical Vapour Deposition of tin oxide. Specifically, the importance of precursor interactions is highlighted. A halide exchange reaction involving part substitution of the tin precursor is believed to occur in the solvent; the complex acting as a marker for improved films with improved transparent-conducting properties. Precursor mixtures of butyltin trichloride and potassium halide (X = F, Cl, Br, I) in propan-2-ol were deposited at a substrate temperature of 450 °C using air carrier gas. Hall Effect results indicate that fluorine gave the best performing n-type transparent conducting thin films that exhibited high optical transparency (>80% at 550 nm) and resistivity values of 4.9×10^{-4} Ω.cm, with charge carrier density and carrier mobility values of 8.85×10^{20} cm^{-3} and 15 cm^3/V.s respectively. Such parameters yield high figures of merit.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Transparent conducting oxides (TCOs) are a class of multifunctional material which demonstrate both electrical conductivity and optical transparency over visible light wavelengths. This is made possible due to their intrinsic semiconducting nature and wide bandgap (>3.2 eV) respectively [1,2]. The coincidence of two highly useful physical properties means that such materials find use in diverse roles such as flat panel displays and solar cell applications [2–4].

Tin oxide (SnO_2) based TCOs are increasingly used due to their impressive TCO properties and their relative inexpense as compared to the traditional alternative; Indium-Tin-Oxide (ITO) [5]. The high performance properties are due to the ability to dope the SnO_2 framework, enhancing the intrinsic n-type semiconducting properties by an order of magnitude or more [1].

The best SnO_2 dopant to date has been fluorine (FTO). It introduces an extra charge carrier into the system per dopant ion; its effectiveness attributed to the ease with which it substitutes for oxygen within the SnO_2 framework. Doping with fluorine also introduces donor levels localised to the conduction band, so improving the n-type electrical properties [1,3]. Since the integrity of the bandgap is largely preserved, optical transparency properties are also maintained which allows the concurrence of two normally conflicting physical phenomena.

Aerosol-assisted Chemical Vapour Deposition (AACVD) is a widely used thin film preparation. The technique involves the transport of precursors within a vapourised solvent over a heated substrate, whereby the precursors effect thin film formation [6–8]. Doped-SnO_2 formation in AACVD requires the presence of tin, oxygen and dopant sources, delivered either together within the same solution or from separate solutions. It has been found that the choice of precursor components and reactions prior to deposition have a marked effect on the resultant TCO properties [9]. FTO and other doped-SnO_2 materials have also been deposited using atmospheric-pressure CVD (APCVD), spray pyrolysis, sol–gel dip coating and sputtering [5,10–12].

The aim of this paper is thus to investigate the effects of halide dopants on the TCO properties of SnO_2. Furthermore, the effects of these dopants on the general precursor chemistry will also be investigated. The results reinforce the position of fluorine as the best dopant and yield insight into the interaction between precursor components prior to thin film deposition; namely that of a halide exchange reaction.

2. Experimental details

All chemicals were used as bought; butyltintrichloride (95%; Sigma-Aldrich), potassium fluoride (98%; Aldrich), potassium chloride (99.5%; Analar), potassium bromide (99+ %; Aldrich), potassium iodide (99.8%; Analar), and propan-2-ol (Merck). Filtered compressed air was obtained through a house line. Deposition was carried out on 3.2 mm thick plain soda–lime silica float glass with a 50 nm thick SiO_2 barrier layer, as supplied by Pilkington NSG. All substrates were pre-washed with soaped water, propan-2-ol and acetone then dried in air prior to loading into the reactor.

2.1. Synthesis

The single-source AACVD FTO precursor was made by mixing butyltin trichloride (MBTC; 0.2 mol dm^{-3}), potassium halide (KX;

* Corresponding author. Tel.: +44 20 7679 4669; fax: 44 20 7679 7463.
E-mail address: i.p.parkin@ucl.ac.uk (I.P. Parkin).

0040-6090/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tsf.2012.10.110

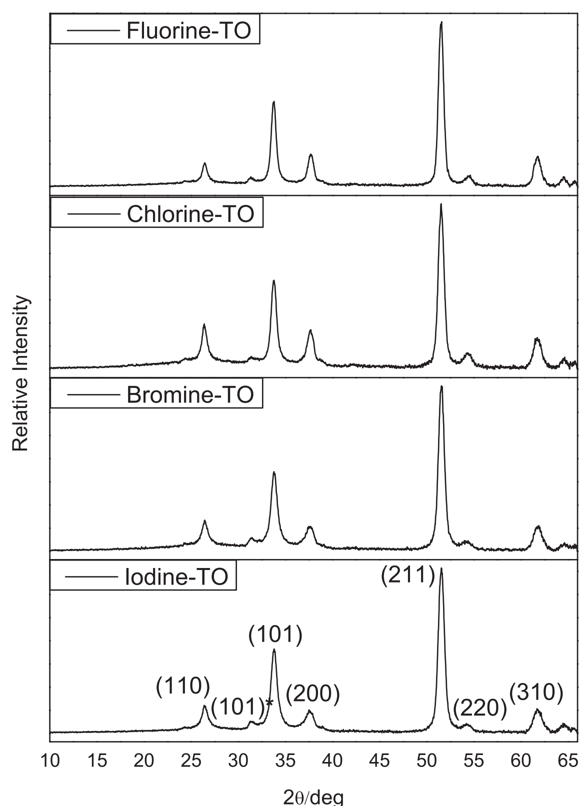

Fig. 1. XRD comparison of halide-doped SnO_2 films. SnO_2 Miller indices have been highlighted as well as the anomalous SnO peak.

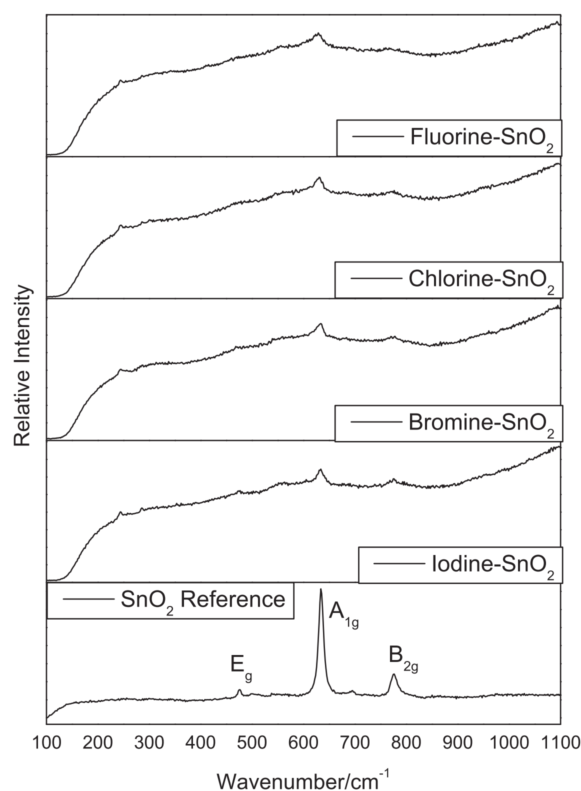

Fig. 2. Raman spectra of halide-doped SnO_2 films.

where X = F, Cl, Br or I) (6 wt.%-X) and propan-2-ol. The mixture was stirred for 12 h then filtered prior to deposition to remove the precipitate. The AACVD was carried out in a flat-bed, cold-walled tubular reactor, as described elsewhere [6,13]. A thermocouple controlled carbon block heater maintained substrate temperatures. Depositions were carried out on Pilkington silica-coated barrier glass in order to prevent the leaching of ions from the glass into the thin film. A second piece of float glass was suspended 8 mm above the substrate, silica-side down in order to ensure a laminar flow of the gas/aerosol. Films were deposited at 450 °C with substrates heated to the desired temperature before deposition and cooled in air ambient in the reactor after deposition. AACVD was carried out using the pneumatic aerosol generation method employing a TSI Model 3076 Constant Output Atomiser utilising filtered, compressed air carrier gas operating at constant 200 kPa pressure. Deposition times were kept constant at 30 min.

2.2. Analysis

X-ray diffraction (XRD) measurements were made on a Bruker GADDS D8 diffractometer in a glancing angle configuration using a Cu-Kα X-ray source. Readings were taken over a 2θ range of 10–66°. Diffraction patterns were analysed for crystallinity, orientation, phase purity and crystallite size against a corundum (Al_2O_3) standard. Powder XRD (PXRD) measurements of precipitates were made on a Bruker D4 flat plate powder x-ray diffractometer using a Cu-Kα X-ray source over the 15–70° 2 θ range. Raman spectroscopy measurements were carried out on a Renishaw 1000 invia UV–visible spectrometer under ambient conditions. A 514.5 nm laser source was used to probe the film over the 100–1100 cm^{-1} wavenumber range. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6301F Field Emission SEM at a 5 keV accelerating voltage. Samples were coated with gold prior to deposition. Images were examined to determine the surface morphology and grain growth characteristics. Room temperature Transmittance–Reflectance (T–R) profiles were taken using a Perkin Elmer Fourier Transform Lambda 950 UV–visible spectrophotometer over a 250–3000 nm wavelength range against an air background. Film thickness measurements were carried out on a Filmetrics F20 analyser in against an as-supplied FTO reference. Room temperature Hall Effect measurements were carried out on an Ecopia HMS-3000 in the Van der Pauw configuration. Measurements were taken using a 0.58 T permanent magnet and a current of 0.1 μA. Tests were carried out on samples cut to squares measuring ≈1 × 1 cm. Silver paint (Agar Scientific) was used to form ohmic contacts, the integrity of which was tested prior to measurement. The Hall Effect method was used to find the resistivity, charge carrier mobility and charge carrier density.

Table 1
Electrical conductivity and optical properties of halide-doped tin oxide films produced by AACVD.

System	d/nm	N/cm^{-3}	μ/$cm^3.V^{-1}.s^{-1}$	ρ/Ω.cm	$R_{sheet}/\Omega.^{-1}$	$T_{400-700}$/%	T_{550}/%	E_{opt}/eV	E_U/meV	Text. Coeff. (Pref. Orn)	Cryst. Size/nm	F.o.M./Ω^{-1}
F-TO	698	8.85×10^{20}	15.0	4.9×10^{-4}	7.0	78	81	3.99	195	2.79 (211)	8	1.0
Cl-TO	743	3.9×10^{20}	19.8	9.3×10^{-4}	12.5	80	82	4.00	189	1.99 (211)	12	0.7
Br-TO	722	3.74×10^{20}	21.0	9.8×10^{-4}	13.6	79	80	3.98	192	2.47 (211)	11	0.6
I-TO	931	4.4×10^{20}	16.4	9.0×10^{-4}	9.7	81	83	3.90	193	2.51 (211)	12	1.1

Download English Version:

https://daneshyari.com/en/article/8036982

Download Persian Version:

https://daneshyari.com/article/8036982

Daneshyari.com