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P-type conductivity in hydrogenated radio frequency sputtered tin oxide thin films

M.F. Al-Kuhaili*, M.B. Mekki

Physics Department, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

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ABSTRACT

P-type oxide semiconductors are being intensively investigated for their potential use in optoelectronic and microelectronic applications, such as active electronics and transparent transistors. In this work, the p-type conductivity of tin oxide thin films was examined. The films were deposited using radio frequency magnetron sputtering in an atmosphere containing a mixture of hydrogen and argon. The structural, chemical, optical, and electrical properties of the films were analyzed as the hydrogen-to-argon concentration was varied from 0% to 20%. The films were polycrystalline except those deposited under the highest hydrogen concentration which became amorphous. Chemical analysis of the films revealed a substantial concentration of oxygen vacancies. Optically, the films were transparent and their band gaps decreased as the hydrogen concentration increased. The pure tin oxide films had n-type conductivity, which was attributed to oxygen vacancies. However, the conductivity was converted to p-type as the hydrogen concentration increased. This was attributed to the formation of hydrogen shallow acceptor states, which was supported by the observation of a red-shift of the band gap. The optimum hydrogen concentration for p-type conductivity was found to be 10%. The p-type character of the films was demonstrated by fabricating a hetero p-n junction based on SnO_2/Si, which exhibited the expected non-linear diode rectification behavior.

1. Introduction

Tin oxide (SnO_2) is a II–VI semiconductor that possesses a wide direct band gap (3.6–3.8 eV), large exciton binding energy (130 meV), high transparency in the ultraviolet and visible ranges, and high infrared reflectance [1–11]. It is also characterized by thermal and chemical stability, as well as mechanical hardness [1–11]. From a processing standpoint, SnO_2 is inexpensive, abundant, and non-toxic [1–11]. Undoped SnO_2 is an n-type semiconductor with a low electrical resistivity, which is attributed to intrinsic defects (such as oxygen vacancies) [5,12]. In contrast, tin monoxide (SnO) is a p-type semiconductor with conductivity that is attributed to tin vacancies [12]. SnO_2 thin films have been widely used for gas sensing, photodetection, varistors, and photocatalysis [3–6,8–11,13,14]. However, the most important application for SnO_2 thin films is their use as transparent conducting oxide (TCO) coatings, which are characterized by their optical transparency ($\geq$80% in the visible range) and low electrical resistivity ($\approx 10^{-4}\,\Omega\,\mathrm{cm}$). Thus, TCO coatings combine electric current collection and light harvesting [15]. These coatings have been used as transparent electrodes in flat–panel display devices, light–emitting diodes, solar cells, low-emissivity windows, lithium ion batteries, and thin–film transistors (TFTs) [1,5,7,15,16].

TCO-based materials currently in use are mostly of the n-type, and, thus, have been utilized primarily as transparent metals [16]. Nevertheless, micro- and opto–electronic applications necessitate the synthesis of p-type TCOs. Consequently, if the n- and p-type TCOs can be joined to form p-n junctions, active transparent electronics could be developed [7,9], allowing the fabrication of transparent TFTs [18]. Compared to n-type oxides, only a few oxides exhibit p-type conduction [18]. This has been an obstacle to forming oxide p-n junctions [8]. Two main problems hinder the development of p-type oxides: (i) their intrinsically low electrical conductivity, and (ii) low hole mobility [17]. The latter challenge is attributed to the low transport paths of holes, which are composed mainly of localized oxygen 2*p* orbitals in the conduction band [7]. This results in a large effective mass of the holes and, hence, limited mobility [12].

Recently, extensive research has been devoted to develop p-type

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* Corresponding author.
E-mail address: kuhaili@kfupm.edu.sa (M.F. Al-Kuhaili).

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SnO_2 thin films. This was driven by several factors: (i) the wide band gap of SnO_2, which is optimum for TCOs; (ii) the lack of TCO-compatible p-type SnO_2; (iii) the need for junction-based transparent electronics; and (iv) the fact that SnO_2 is a more suitable candidate for p-type TCOs because of its weaker ionization [16]. Two methods have been developed to synthesize p-type SnO_2-based thin films. In the first method, SnO_2 was doped with various elements or compounds. Representative dopants are listed in Table 1. The resistivity, mobility, and hole concentration varied over a wide range of values even when the same dopant was deposited using a different technique. Notably, p-type doping was achieved only with substrate heating and/or post-deposition thermal annealing, which are both high-temperature processes. The obtained resistivities were higher than those required for TCO applications. Nevertheless, several hetero- [10,24,31] or homo- [13,14,16,30,32] p-n junctions were fabricated based on p-type SnO_2 layers. In contrast, the second method involved controlling the growth conditions of SnO_2 to produce p-type SnO thin films [33–35].

The current research investigated the p-type conductivity of *in-situ* hydrogenated SnO_2 thin films. A similar study was reported by Hsu et al. [34,35], who sputtered SnO_2 or Sn/SnO_2 targets in an Ar/H_2 atmosphere and obtained p-type SnO thin films after annealing in a vacuum at 200–400 °C. In contrast, the films in our study were deposited by radio-frequency (RF) sputtering on unheated substrates. This technique offers several advantages: (i) a low growth temperature, (ii) no need for post-deposition annealing, (iii) a simple methodology that did not require doped targets or co-sputtering, and (iv) a relatively low RF power.

2. Materials and methods

Tin oxide thin films were deposited onto unheated single-crystal-sapphire and molybdenum substrates using RF magnetron sputtering. Thin film deposition was carried out in an Oerlikon Univex 350 sputtering system. A 3-inch-diameter SnO_2 target of 99.99% purity was used, and the source-to-substrate distance was 10 cm. First, the system was evacuated to a base pressure of 5×10^{-6} mbar. Next, sputtering was initiated using an RF sputtering power of 80 W applied to the sputtering gas, which was composed of a mixture of argon and hydrogen. The argon flow rate was 10 sccm (standard cubic cm per min), and the H_2/Ar ratio was 5%, 10%, 15%, or 20%. The target was pre-sputtered for 5 min before a shutter was opened, allowing the sputtered species to be deposited onto the substrates. For better film uniformity, the substrates were rotated during deposition at a speed of 8 rpm. Sputtering was carried out for 3 h.

Structural properties were analyzed by x-ray diffraction (XRD) performed using a Bruker D2 Phaser diffractometer that employed a Cu K_α source ($\lambda_\alpha = 1.54$ Å) operating at 30 kV at a 2θ scanning step size of 0.01°. The surface morphology of the films was examined using tapping mode atomic force microscopy (AFM; Bruker Innova). The scan area was $2 \times 2\,\mu m^2$, and the scan rate was 0.8 Hz. The chemical properties of the films were investigated using x-ray photoelectron spectroscopy (XPS) performed in a Thermo Scientific Escalab 250Xi spectrometer equipped with a monochromatic Al K_α x-ray source with an instrumental energy resolution of 0.5 eV. The films deposited on molybdenum substrates were used for XPS analysis so that the charging of non-conducting samples could be reduced. The transmittance spectra of the films were measured over a wavelength (λ) range of 300–1500 nm using a JASCO V-570 double-beam spectrophotometer. The thickness (d) of each film was determined optically from the interference extrema in the transmittance spectra (Fig. 4, Table 2).

Table 1
Previously reported research on p-type doped SnO_2 thin films.

Dopant	Deposition Method[a]	T_s(°C)	Annealing		ρ(Ω.cm)	μ(cm^2/V.s)	N(cm^{-3})	Ref.
			T_a (°C)	ambient				
Al	RFS	50	300–550	N_2	2.0×10^0	1.9	1.7×10^{18}	[7]
Al	DCS/RFS	200	400–650	Air	$8.1 \times 10^{-1} - 5.7 \times 10^0$	0.6–3.6	$1.6 \times 10^{17}–7.2 \times 10^{18}$	[19]
Al	SP	300	–	–	4.9×10^{-2}	7.6	1.7×10^{19}	[20]
B	sol-gel	–	400–750	Air	$3.4 \times 10^{-3} - 8.2 \times 10^{-3}$	2.5–7.8	$9.7 \times 10^{19}–7.4 \times 10^{20}$	[21]
Co	SP	480	–	–	$3.7 \times 10^1–1.5 \times 10^2$	–	$4.1 \times 10^{14}–9.3 \times 10^{15}$	[22]
Fe	SP	500	–	–	$6.3 \times 10^1–3.4 \times 10^3$	–	$1.8 \times 10^{15}–1.2 \times 10^{16}$	[23]
Ga	RFS	150–750	–	–	$2.8 \times 10^{-3} - 3.3 \times 10^0$	0.24–230	$2.0 \times 10^{17}–9.5 \times 10^{18}$	[16]
Ga	sol-gel	–	520	O_2	$7.1 \times 10^{-1} - 5.2 \times 10^0$	6.3–8.4	1.0×10^{18}	[24]
Ga	RFS	–	400–700	O_2	1.2×10^0	–	2.6×10^{19}	[8]
Ga	DCS	–	450–750	Air	4.9×10^1	0.015	1.0×10^{19}	[25]
GaN	EB	50	450–500	N_2	$3.7 \times 10^0–1.2 \times 10^2$	0.12–2.3	$1.4 \times 10^{15}–4.4 \times 10^{18}$	[13]
Gd	RFS	–	700	O_2	$1.0 \times 10^2–8.3 \times 10^3$	0.44–0.52	$1.7 \times 10^{16}–1.2 \times 10^{18}$	[26]
In	DCS	25–500	550–600	Air	$6.8 \times 10^{-1} - 1.4 \times 10^2$	2.9–8.1	$1.6 \times 10^{16}–1.1 \times 10^{18}$	[10]
In	dip coating	–	400–600	Air	$2.0 \times 10^1–6.6 \times 10^4$	1.6–16	$5.7 \times 10^{12}–1.9 \times 10^{17}$	[27]
Li	SP	480	–	–	$1.6 \times 10^{-1} - 1.1 \times 10^2$	–	$9.3 \times 10^{13}–1.1 \times 10^{18}$	[28]
Mg	EB	200	300	Air	$2.2 \times 10^{-2} - 3.2 \times 10^{-2}$	2.3–10	8.2×10^{18}	[6]
Mn	sol-gel	–	500	Air	$3.6 \times 10^2–3.8 \times 10^3$	4.2–6.1	$1.9 \times 10^{14}–6.7 \times 10^{14}$	[29]
N	DCS	–	400–800	O_2	$5.4 \times 10^{-1} - 1.2 \times 10^1$	1.6–8.1	$6.2 \times 10^{17}–2.1 \times 10^{19}$	[4]
N	RFS	–	350–500	O_2	$1.4 \times 10^{-1} - 1.2 \times 10^1$	0.6–3.6	$9.1 \times 10^{17}–1.9 \times 10^{19}$	[11]
NdF_3	sol-gel	–	475	Air	$8.2 \times 10^{-3} - 3.9 \times 10^{-2}$	4.1–9.7	$3.9 \times 10^{19}–9.0 \times 10^{19}$	[17]
Sb	PLD	500–800	500	Air	$8.7 \times 10^{-1} - 5.4 \times 10^0$	0.69–3.8	$3.0 \times 10^{17}–1.0 \times 10^{19}$	[14]
Sb	RFS	200	550–800	Air	$1.7 \times 10^{-1} - 1.5 \times 10^1$	0.65–31	$1.5 \times 10^{16}–5.8 \times 10^{19}$	[30]
Zn	DCS/RFS	200	300–600	Air	$7.4 \times 10^0–3.2 \times 10^2$	0.56–35	$1.2 \times 10^{16}–2.4 \times 10^{17}$	[5]
Zn	SP	340	–	–	$7.3 \times 10^0–1.2 \times 10^1$	1.0–25	$<1.0 \times 10^{18}$	[9]
Zn	DCS	25–500	550–600	Air	$4.9 \times 10^{-1} - 4.8 \times 10^0$	1.5–3.0	$8.7 \times 10^{17}–4.3 \times 10^{18}$	[31]

T_s: substrate temperature; T_a: annealing temperature; ρ: electrical resistivity; μ: hole mobility; N: hole concentration.

[a] **DCS**: direct current sputtering; **EB**: electron beam evaporation; **PLD**: pulsed laser deposition; **RFS**: radio frequency sputtering; **SP**: spray pyrolysis.

The p-type nature of the films was examined by two methods. First, Hall effect measurements were conducted on the samples deposited on sapphire substrates using the four-probe geometry (van der Pauw configuration) carried out using an Ecopia HMS 3000 system. The setup was used to measure the Hall voltage whose sign determines the conductivity type of the sample. Second, current-