



Thin film characterization of zinc tin oxide deposited by thermal atomic layer deposition



Marja N. Mullings^a, Carl Hägglund^a, Jukka T. Tanskanen^a, Yesheng Yee^b, Scott Geyer^a, Stacey F. Bent^{a,*}

^a Department of Chemical Engineering, Stanford University, Stanford, CA 94305, USA

^b Department of Electrical Engineering, Stanford University, Stanford, CA 94305, USA

ARTICLE INFO

Article history:

Received 1 August 2013

Received in revised form 23 January 2014

Accepted 24 January 2014

Available online 31 January 2014

Keywords:

Zinc tin oxide

Atomic layer deposition

Thin film

Transparent conductive oxide

ABSTRACT

Zinc tin oxide (ZTO) thin films are of interest for many applications, including transparent conducting oxides and buffer layers in thin film solar cells. In this work, the ability of atomic layer deposition (ALD) to control both thickness and composition of the ternary material is explored and the resulting film properties are characterized. ZTO was deposited at 150 °C by alternating growth of tin oxide (SnO_x) and zinc oxide (ZnO) using tetrakis(dimethylamido)tin and diethyl zinc as metal precursors and water as the oxygen source. The growth behavior of ZTO was systematically examined as a function of the relative fraction of SnO_x to ZnO ALD cycles and their bilayer period. Variable angle spectroscopic ellipsometry (VASE) showed that the ZTO growth rate was strongly reduced as compared to the growth rates of the binaries, especially at low bilayer periods and low tin cycle fractions. Inductively-coupled plasma optical emission spectroscopy showed that the composition, together with other properties of ZTO films, was not simply proportional to the binary ALD cycle fractions utilized in the deposition. Structurally, the deposited films were shown by X-ray diffraction to be amorphous for tin content exceeding 10%, for which only smooth features were observed by scanning electron microscopy. Optically, VASE revealed a minimum refractive index in the visible range for intermediate compositions and a maximum for the pure SnO_x phase. Conversely, the ZTO bandgap was maximized for intermediate metal compositions near ~50%, and converged to the direct ZnO bandgap of 3.3 eV for compositions with decreasing amounts of Sn in the films. Linear extrapolations gave a range of 2.9 to 4.0 eV for SnO_x bandgap depending on the bandgap type (indirect or direct).

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Transparent conducting oxides (TCOs) are wide bandgap (≥ 3 eV), transmissive to visible light ($\geq 80\%$), and highly conductive ($\geq 10^3$ S cm⁻¹) metal oxides with many applications in consumer electronics and in photovoltaics [1–4]. The oxides of indium, tin, and zinc are the most commercially-important TCOs [4,5]. These binary TCOs are typically doped with an impurity to improve stability at high temperatures [6]. Within the indium/tin/zinc oxide family, indium tin oxide (ITO) remains the industry-standard for high-end TCOs because of its high conductivity ($\geq 10^4$ S cm⁻¹) [7–9]. However, the scarcity of indium, with an abundance in the earth's upper crust of about 0.05 ppm [10], coupled with the increasing demand in consumer electronic and photovoltaic markets has led to rising costs [11], which motivates the need to find alternative TCO materials.

Impurity-doped or alloyed zinc oxides are interesting candidates for this purpose, where mixtures with aluminum (AZO) or gallium (GZO) are well known examples [1,12–14]. While AZO and GZO exhibit attractive properties as inexpensive indium-free alternatives, other options such as zinc tin oxide (ZTO) are also being studied as an inexpensive

indium-free TCO [1,11,15–23]. Notably, the upper crustal abundances of Zn and Sn are around 70 and 5.5 ppm [24], these values being significantly higher than the 0.05 ppm abundance of indium. In addition to its use as a TCO and buffer layer in high efficiency solar cells [25], ZTO has been used in thin-film transistors [26–28] and it has potential in varistor applications as well [29,30]. Despite its promise, a review of the literature suggests little agreement among various structural, optical, and electrical properties of ZTO, motivating a more detailed characterization of this material.

In general, there is an agreement that ZTO forms two crystal structures. The metastable ZnSnO₃ phase, known as zinc metastannate, has two polymorphs — a face-centered perovskite [31] and an ilmenite [32] structure. The other structure, Zn₂SnO₄, is known as zinc orthostannate and has a cubic spinel structure that is stable under ambient conditions [33]. However, the correlation between composition and crystallinity is not well-understood. This lack of understanding applies to many other ternary oxides as well, and it originates from the mixing of binaries with potentially different crystal structures, densities, and/or stoichiometries to produce the ternary material. The most extensively used deposition technique for ZTO has been sputtering [6,15,16,18–20,34]. During crystallization, ZTO transforms to ZnSnO₃ from 300 to 500 °C and to Zn₂SnO₄ for temperatures exceeding 600 °C. At these high temperatures, however, obtaining pure Zn₂SnO₄

* Corresponding author.

E-mail address: sbent@stanford.edu (S.F. Bent).

is difficult, as mixed phases including both forms of ZTO and SnO_2 are formed [33]. Other techniques for ZTO deposition have included sol-gel spin coating [27,28,35], chemical vapor deposition [36], and only very recently, atomic layer deposition (ALD) [25,37–40].

A lack of agreement on the ZTO crystal structure as a function of composition may explain the variation in reports on its optical properties. One study (using pulsed layer deposition) reported bandgaps for amorphous ZTO of 2.80 eV for ZnSnO_3 and 2.86 eV for Zn_2SnO_4 [41]. Young et al. found crystalline Zn_2SnO_4 to have a fundamental bandgap of 3.35 eV that was widened to 3.89 eV by a Burstein–Moss shift due to high carrier concentration [42]. For ZTO synthesized by hydrothermal methods, the optical bandgap for crystalline Zn_2SnO_4 has been reported with great variation in the range of 3.3 to 3.9 eV [43,44]. The bandgap for crystalline ZnSnO_3 has not been rigorously characterized experimentally, but one report presents a value of ~ 3.9 eV [45], which is significantly higher than the gap of 2.80 eV reported for the amorphous phase (see above).

Most previous studies using ZTO focused on device performance instead of film characterization, resulting in few comprehensive reports of material and electrical properties as a function of composition. Because ALD allows one to carefully dope or alloy material in an atomic-level controlled fashion with uniform and conformal growth [46–48], it provides an opportunity to systematically analyze ZTO properties by fine tuning the composition. In addition to ZTO, ALD has been used to deposit several other ternary metal oxides including AZO, [49–53] GZO [54,55], ITO [56], $(\text{Zn,Mg})\text{O}_x$ [57], and $(\text{Sn,Al})\text{O}_x$ [58].

In this study, we demonstrate a reproducible thermal ZTO ALD process and determine the composition, optical properties, and structural characteristics of the resulting thin films by variable angle spectroscopic ellipsometry (VASE), X-ray photoelectron spectroscopy (XPS), inductively-coupled plasma optical emission spectroscopy (ICP-OES), scanning electron microscopy (SEM), X-ray diffraction (XRD) and ultraviolet–visible spectroscopy (UV–vis). An analytical model based on analysis of the ZTO growth rates is developed for understanding the main features of the ZTO growth characteristics. Relationships between deposition parameters, namely bilayer period and relative fraction of SnO_x to ZnO ALD cycles (cycle fraction), and ZTO growth rate, composition, structure, and optical properties are established and discussed in the context of previous studies on ZTO.

2. Experimental methods

2.1. ZTO ALD process

The ALD experiments were carried out in a custom-built, viscous-flow, hot-wall reactor previously described [59]. Diethyl zinc (DEZn; Sigma-Aldrich) and tetrakis(dimethylamido)tin (TDMASn; Strem, >99% purity) were used as precursors with deionized water as the counter-reactant. Precursors were dosed from 10 cm^3 stainless steel sample vials using computer controlled air-actuated valves. The water and DEZn sample vials were kept at room temperature, while the TDMASn vial was heated to 45°C during depositions. A positive temperature gradient was maintained toward the reaction zone to prevent precursor condensation. During the ALD process, excess precursor was purged with nitrogen for half-reaction separation and reaction completion. For ZnO ALD, we express the pulse time sequences as $z_1:z_2:z_3:z_4$, where z_1 and z_3 correspond to the pulse lengths of DEZn and water, respectively, and z_2 and z_4 correspond to N_2 purge times following these doses. A typical ZnO ALD pulse time sequence was 1:15:1:30 s. The purge times of $z_2 = 15$ s and $z_4 = 30$ s were chosen based on the return of the precursor concentrations to their baseline values as monitored by in situ mass spectrometry, as well as previously-found saturation in this range for the ZnO system [50,60]. For SnO_x ALD, we similarly express the ALD sequences as $t_1:t_2:t_3:t_4$, where t_1 and t_3 correspond to the pulse lengths of TDMASn and water, respectively, and t_2 and t_4 correspond to N_2 purge times following these doses. A typical timing sequence

was 1:30:2:30 s which corresponded to saturated ALD of SnO_x as previously described [59].

Designing a reproducible ZTO ALD process first required optimization of the binary ZnO and SnO_x ALD processes in our reactor. It is convenient that there is overlap in the ALD temperature windows for these binary metal oxide processes. It was reported previously that within the ZnO ALD temperature window, a maximum growth rate of about $\sim 2.0\text{ \AA/cycle}$ occurs at 150°C [61], which is close to the optimized growth rate of 1.85 \AA/cycle for our reactor. The ALD of SnO_x , reported elsewhere [59], results in SnO_x growth rate of about 0.70 \AA/cycle at 150°C . For the optimized SnO_x ALD system, the as-deposited film is amorphous, whereas as-deposited ZnO grown by ALD from DEZn and water at 150°C has a crystalline hexagonal wurtzite structure [62].

The ALD super cycle is defined as the minimum sequence of SnO_x and ZnO cycles that is repeated over the course of the ZTO ALD process. A corresponding super cell results from the stack of layers produced by one super cycle. To characterize the ALD system, we define t and z , the total number of SnO_x and ZnO ALD cycles in one ZTO ALD super cycle, respectively. Using these parameters, illustrated in Fig. 1, the system can be characterized by the bilayer period Λ , defined as the number of cycles in one super cycle $\Lambda = (t + z)$, and the relation for the total number of ZnO and SnO_x cycles in a ZTO ALD process, referred to as cycle fraction. If a total number of ALD super cycles S are performed, then the total number of ALD cycles in the deposition is given by $S \times \Lambda$.

Substrates for ZnO, SnO_x , and ZTO ALD were n-type Si(100) with phosphorous dopant and a resistivity of $1.0\text{--}5.0\text{ }\Omega\text{ cm}$ (WRS Materials) and fused silica quartz (ChemGlass). Substrates were pre-cleaned using a UV-ozone (PSD Benchtop UV-Ozone Cleaner) to remove organic contamination, after which the thin films were deposited onto the native Si oxide.

2.2. Characterization

A PHI VersaProbe 5000 scanning X-ray photoelectron spectrometer with Al-K α radiation was used to survey film elemental content. The C1s peak at 285.0 eV was used as a reference. After initial survey scans, adventitious carbon was removed by Ar^+ sputtering for 12 s (1 keV, $0.5\text{ }\mu\text{A}$, $1\text{ mm} \times 1\text{ mm}$ at 45° incidence from the sample). A Thermo Scientific ICAP 6300 Duo View spectrometer was used to perform inductively-coupled plasma optical emission spectroscopy (ICP-OES) on ZTO deposited on Si(100). For these measurements, films were dissolved in aqua regia (3:1 concentrated $\text{HCl}:\text{HNO}_3$) and sonicated for at least 6 h before characterization. X-ray diffraction (XRD)

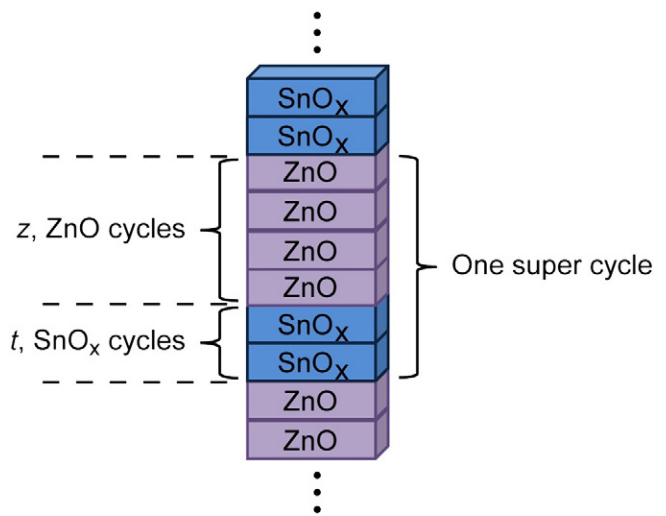


Fig. 1. Schematic of ZTO super cycle formalism visualized as a lamellar stack of ALD cycles of constituent binary oxides. One super cycle includes a certain number of SnO_x cycles, t , and ZnO cycles, z , resulting in a bilayer period $\Lambda = (t + z)$.

Download English Version:

<https://daneshyari.com/en/article/8035163>

Download Persian Version:

<https://daneshyari.com/article/8035163>

[Daneshyari.com](https://daneshyari.com)