



Deposition and characterization of single magnetron deposited Fe:SnO_x coatings

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ABSTRACT

Coatings deposited by magnetron co-sputtering from a single RF magnetron with a ceramic SnO₂ target with iron inset in argon plasma were studied. The mass spectra of the process identified Sn⁺ and SnO⁺ species as the dominant species sputtered from the target, but no SnO₂⁺ species were detected. The dominant positive ions in argon plasma are Ar⁺ species. The only detected negative ions were O[−]. Sputtered neutral tin related species were not detected. Iron related species were also not detected because their concentration is below the detection limit. The concentration of iron dopant in the tin oxide coatings was controlled by the RF bias applied on the substrate holder while the discharge pressure also has some influence. The iron concentration was in the range from 0.9 at.% up to 19 at.% increasing with the substrate bias while the sheet resistivity decreases. The stoichiometry ratio of O/(Sn + Fe) in the coatings increased from 1.7 up to 2 in dependence on the substrate bias from floating bias (−5 V) up to −120 V of RF self-bias, respectively. The tin in the coatings was mainly bonded in Sn⁴⁺ state and iron was mainly in Fe²⁺ state when other tin bonding states were detected only in a small amounts. Iron bonding states in contrary to elemental compositions of the coatings were not influenced by the RF bias applied on the substrate.

The coatings showed high transparency in the visible spectral range. However, an increased metallic behavior could be detected by using a higher RF bias for the deposition. The X-ray diffraction patterns and electron microscopy pictures made on the coatings confirmed the presence of an amorphous phase.

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1. Introduction

Doped tin oxide thin film materials are highly important to state-of-the-art optical and electronic applications, especially indium tin oxides (ITO). Other SnO₂ derivatives are prominent as conductive transparent dielectric materials [1,2] or, for example, used as protection barriers in solar cell applications [3]. It has been shown previously that iron-doped SnO₂ can be used as a material for gas sensing in optical gas sensors as well as in electronic gas sensors [1,4]. To fully understand the optical gas sensing mechanism as well as to optimize these systems, it is necessary to gain insight into the properties of doped oxide materials. The properties depend on the specific conditions in the respective deposition process. Furthermore it is necessary to conduct highly reliable gas sensing experiments characterizing the critical properties like lowest detectable concentrations. The characterization of the optical properties is especially important for the optical gas sensing applications like SPREE detectors which are based on the surface plasmon resonance

effect with ellipsometric readout [4,5]. The metal oxide coatings in SPR detectors have to be prepared reproducible with thickness in range from 5 nm up to 10 nm maximum [4,5]. The effect of the thickness on the sensing properties is still not well understood.

In this paper, we present a study of spectroscopic ellipsometry and X-ray photoelectron spectroscopy (XPS) on iron-doped tin oxide layers. The goal is to characterize the layers' optical constants depending on the coating process parameters and match these findings with data on dopant concentrations and electronic states. As the maximum thickness of the Fe:SnO films necessary in SPR gas sensors is 10 nm, lower deposition rate conditions were selected [4,5]. Subsequently, low deposition rates in the range of nanometers per minutes are required.

First, radio frequency (RF) magnetron sputtering of a SnO₂ target with Fe inset was studied. The ions produced by the magnetron sputtering process were detected by mass spectrometry. Additionally, molecules from desorption processes in the vacuum chamber and external and internal leaks were detected. An off axis arrangement was used for the deposition process. This eliminates the fast neutrals reflected from targets, thus the main ion flux is related to the RF bias applied on the substrates and fully controllable.

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Although tin oxide coatings have been applied for a long time, there is not many information about the sputtering process of tin oxide targets in the RF plasma and it is important to know what the sputtered species from the target are produced. The growing coatings under the ion bombardment are commonly described by the Thornton diagram [6] or a modified scheme for metal oxides as ZnO [7]. However, the ions in the plasma discharge also re-sputter the growing coatings; therefore the total deposition rates can be significantly decreased by the ion bombardment on the coating. When composite coatings are deposited, each of the compounds has its own re-sputtering rate and thus the composition of the coatings can be modified. Especially the concentration of the dopants can be controlled by the ion bombardment. The ion bombardment can be easily controlled by the RF power applied on the substrate with growing coating to induce a self-bias on the surface.

2. Experimental setup

Fe:SnO₂ layers were deposited by RF (13.56 MHz) magnetron sputtering with high intensity NdFeB magnets powered by a Advance Energy Dressler Integro 133 power supply with built-in matching network. A target made from 99.9% SnO₂ (thickness 3 mm, diameter about 48 mm) was used and the doping was achieved by placing an iron strip (99.95% iron, 10 mm × 20 mm × 2 mm) in the center of the target which overlapped partially the erosion zone. The deposition was performed by applying a RF power of 20 W on the target in argon (99.9999%, Linde) at pressures of 0.5 Pa (gas flow at 19 sccm) and 0.2 Pa (gas flow at 7 sccm). MKS flow controllers were used and the resulting pressure was measured by a MKS Baratron capacitance manometer. The vacuum conditions during sample preparation were achieved by using as turbo molecular pump a Balzers 190 l/s with a pre-vacuum pump VARIAN Scroll. The base pressure before depositions was lower than 1×10^{-3} Pa measured by a Penning Gauge.

The Fe:SnO₂ layers were deposited on single side polished n-silicon (Si) (1 0 0) substrates (purchased from ON semiconductor) with a size of about 15 mm × 15 mm and simultaneously on glass slides with the same size. No special treatment of the substrates was performed prior to the deposition. A native SiO₂ layer was detected on the surface, as reported below. The substrates were mechanically clamped to a biasable copper table (diameter 83 mm). The RF bias on the substrates was induced by a RF generator Advance Energy Cesar with an external matching box; the RF generators were synchronized. The RF power delivered to the plasma sheath around the substrates was in the range below 2 W.

The thin films were deposited in an off-axis arrangement. The substrate was perpendicular to the target while the center of the substrate was at a distance of 70 mm from the face of the target and 40 mm from the target's axis. Both faces were vertical within the vacuum chamber as described previously [8].

The target with the iron strip attached to it was cleaned and conditioned before the deposition by sputtering it for 5 min in argon plasma at an RF power 50 W at the actual working pressure during deposition.

The sputtering process was analyzed by an energy resolved quadrupole mass spectrometer (HIDEN EQP 300). The spectrometer was mounted close to the substrate position to investigate the ion bombardment on the coating in the substrate position. Positive ions or negative ions from the plasma discharge can thus be extracted by an extraction electrode of the spectrometer and then the presence of ions depending on their energy or the m/q ratio can be detected. The HIDEN EQP is a partially pumped device with a turbo molecular pump and a rotary pump connected to the process chamber by a port with 100 μm diameter in the extraction electrode. The mass spectrometer can detect positive or negative ions. The detection of neutral particles is also possible with internal electron sources in residual gas analyses (RGA) regime. RGA regime can also be used for gas analyses and neutral sputtered particle detection.

The chemical surface composition of the coatings was studied by X-ray photoelectron spectroscopy (XPS). The XPS system (SPECS components XR50, Phoibos 100) with a base pressure below 3×10^{-7} Pa was used. An electron flood gun was not used for compensation of surface charge binding energies that were corrected to 284.5 eV for C—C bond in C 1s peak. In the measurements, an X-ray source Al (1486.6 eV) or Mg (1253.6 eV) at 12 kV and 200 W, were used. The surface composition was calculated from high resolution XPS spectra using the standard relative sensitivity factors (RSF) from CasaXPS software 2.93, 1, 14.8, and 10.8 for O 1s, C 1s, Sn 3d5/2 and Fe 2p3/2 peaks, respectively. The Shirley shape model was used for the background removal before area evaluations for composition calculations were made.

The surface topology was studied in spectrum of secondary electrons by Tescan Vega LSU electron microscope using a 20 kV electron beam.

Sheet resistivity was measured on the coatings deposited on glass. The instrument was made of ThorLabs 3D table under Jandel 4-point probe head connected to Keithley 6517B acting as a voltage source and simultaneously an ampere meter and Keithley 6514 connected as voltmeter on central pins of 4-point probe. The head and table were placed in grounded shield. The sheet resistance was evaluated with presumption of infinity thin film as $R = 4.5324 \cdot V/I \Omega/\text{sq}$. [9].

The structure of the coatings was investigated by X-ray diffraction (XRD) technique at room temperature on a PANalytical X'Pert PRO diffractometer working in Glancing Incidence X-Ray Diffraction (GI-XRD) geometry using a Cu Kα (40 kV, 40 mA) radiation and a proportional detector. The glancing angle of the X-ray source was set to 1.5°.

The transmission of the coatings was measured by a Woollam VASE ellipsometer in normal incidence transmission mode. Before each measurement the background from the microscope glass slide was taken and removed from the presented transmission data. The coatings prepared for transmission measurements had thicknesses of 40 nm with better than 20% accuracy. The ellipsometric quantities were measured using a Woollam M-2000DI ellipsometer in the spectral range of 192 nm to 1690 nm. The data were taken at multiple angles from 45° to 80° in steps of 5°. To extract the refractive index n and the extinction coefficient k , a model for the dielectric function was fitted to the data with the WVase32 software using the generalized oscillator model for all layer materials. The model of the coated samples uses the available data [10] for the substrate material Si. The dielectric function model for the SnO₂ layers with and without doping was built up as a Kramers-Kronig consistent generalized oscillator model containing several Gaussian absorption peaks. For layers with low or zero dopant concentration, two oscillators were used, for doped layers, three oscillators were necessary. For the Si substrate the optical constants from [10] were used. A 1.5 nm thick native oxide layer was inserted between the substrate layers with the optical constants taken from [10] as well. The final layer model used for the ellipsometric analysis follows the sequence: substrate – native oxide – doped SnO₂ layer. As these layers do not tend to have large surface roughness, additional features such as intermix layers were not considered here.

3. Results and discussion

3.1. Target sputtering, plasma conditions, and doped layer generation

The DC reactive magnetron sputtering of a metallic tin target [11] leads to the formation of SnO⁺ species and Sn⁺ species in plasma discharges. The occurrence of SnO₂⁺ species in low pressure plasma discharge is negligible [11] and according to other studies, the SnO₂ is formed only at higher oxygen partial pressures during the DC reactive magnetron sputtering [12].

Our study of RF magnetron sputtering with a ceramic SnO₂ target in pure argon shows similar behavior with the difference that Sn⁺ species and SnO⁺ species could be detected in the discharge, as shown in Fig. 1(a). Specifically, the identified metallic Sn species possess the masses 116 amu, 118 amu and 120 amu. These masses match the tin

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