

ELECTRICAL CONDUCTIVE AND GAS SENSITIVE TRANSPARENT TIN OXIDE THIN FILMS PREPARED BY ATMOSPHERIC PRESSURE PECVD

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Abstract

In this contribution, the deposition of tin oxide thin films and the resulting layer properties are investigated. An atmospheric pressure PECVD process using a non-thermal plasma jet was applied, creating the coatings on silicon and glass slides. For a highly reactive oxygen atmosphere, the plasma process was driven with air as working gas. The precursor substance tetra-n-butyltin was provided as an aerosol towards the active plasma zone and is further converted to form the ~100 nm thin layers. Structural, electrical and gas sensing properties were determined of the undoped SnO_x layers, deposited at substrate temperatures between 20°C and 500°C.

With increasing substrate temperature a decrease in film thickness and roughness of the films could be observed. In general, the films consists of a dense part near the substrate surface and a more porous structure on top. At 300 °C the lowest electrical resistivity with about $7.2 \times 10^{-2} \Omega \cdot \text{cm}$ occurs in 4-point probe measurements. Experiments for the gas sensing characteristics revealed an electrical response to different atmospheres (water vapour, aqueous ammonia solution) already at elevated measuring temperatures of 150°C. Ammonia concentrations until 25 % were tested. The thin films are showing distinct properties in gas selectivity between the changing atmospheres, gas sensitivity during ammonia interaction as well as recurring reversibility after a surface recovery step with pressurized air. So, tin oxide coatings created by atmospheric pressure PECVD are showing already in its undoped state and without further layer post-treatments high application potential.

Keywords: Atmospheric pressure PECVD, plasma jet, tin oxide, transparent conductive oxide (TCO), gas sensor

1. INTRODUCTION

Semiconductors, including SnO₂, TiO₂, ZnO, WO₃ and ZnS have been intensively investigated for diverse applications [1]. Tin oxide in form of polycrystalline SnO₂ and amorphous SnO_x and their various material properties are of high interest. Transparent highly conducting oxides are used as electrodes for electronic devices such as flat displays [2], solar cells [3] or gas sensors [4]. Moreover, such films can be deposited and applied in form of undoped, In-, F-, or Sb-doped SnO₂ on a wide variety of substrates. Often used methods to create thin tin oxide films include physical vapor deposition (PVD) such as sputtering [5], chemical vapor deposition (CVD) [6], spray pyrolysis [7] and sol-gel technology [8]. Most PVD methods require high vacuum and will be performed in batch-processes but can be performed advantageously at low temperatures. The energy to pyrolyse tin precursors in CVD or spray pyrolysis methods is mostly provided by high substrate temperatures (> 500 °C). Hence, these methods are often inappropriate to deposit films on more temperature-sensitive materials. Beneficial is the possibility to treat larger substrate areas under atmospheric pressure conditions (in-line ability). In this study an atmospheric pressure plasma jet (APPJ) working with pressurized air as process gas was used. Film properties were characterized in dependence of the applied substrate temperature (20 °C - 500 °C) during film deposition. An additional heat post-treatment was not implemented.

2. MATERIALS AND METHODS

2.1. Film deposition

Films were deposited on monocrystalline Si wafer pieces (Si-Mat Silicon Materials) and soda lime glass slides (VWR International), latter coated with a 20 nm thick silicon dioxide film (deposited by Pyrosil® procedure). These silicon dioxide films were created to prevent Na⁺-diffusion during substrate heating into the SnO_x films. The tin-organic precursor tetra-butyl-tin(IV) (TBT) was used as starting substance for film deposition and was purchased from Sigma Aldrich in 98 % purity. This precursor was further diluted with isopropanol to a concentration of 50 % (v/v). Experimental setup, the atmospheric pressure plasma jet and detailed information on the film deposition process are described in previous publications [9]. Shortly: An APPJ based on the Plasma MEF (Tigres GmbH) technology was used. This jet system was driven with pressurized air as working gas and creates an electrically potential-free cold plasma (DC pulsed discharge). The nozzle of this plasma source was modified to spray liquids or liquid dispersed particulate materials into the active plasma discharge. TBT and the TBT/isopropanol mixture is liquid at room temperature, the corresponding flow rates were kept constant at 50 µl/min. Substrates were placed on a hot plate (temperature: 20 °C to 500 °C) fixed on a x-y-table. This x-y-positioning system performed a meandering movement of the samples relatively to the plasma nozzle exit with a velocity of 100 mm/s. 30 successive runs were performed to create thin SnO_x films.

2.2. Characterization

Films were extensively examined and results are presented in literature [9]. Supplementary results will be presented in the following sections with focus on gas sensing properties. The morphology of the deposited tin films were characterized by scanning electron microscopy (SEM) with a Supra 55 VP (Carl Zeiss NTS GmbH) using the in-lens detector and an operating voltage of 5 kV. Applying 4-point probe measurements using the Sheet Resistivity Meter SD-600 (Nagy Instruments) the sheet resistance was measured. To demonstrate the response of the deposited SnO_x to oxidizing and reducing gases a custom-made test system was used (see Figure 1).

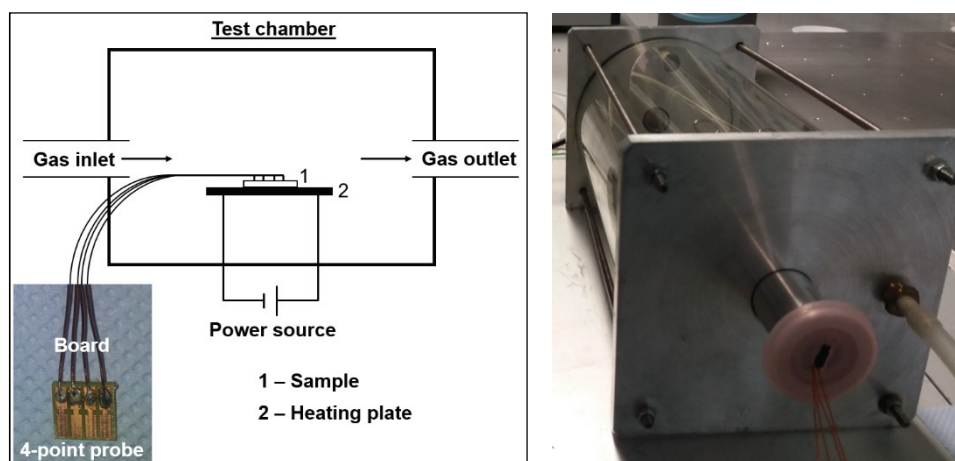


Figure 1 Setup investigating the gas sensing properties: scheme (left) and the build test chamber (right)

This setup is composed of a sealable glass cylinder (length = 250 mm, inner diameter = 130 mm) with a gas inlet and a gas outlet. Furthermore, a hot plate was used and placed inside the chamber. The samples (coated glass slides) were mounted on top of this hot plate and during the experiments the sample temperatures were controlled between 20 °C and 150 °C. In order to measure sheet resistance during the gas interaction four copper wires were mechanically fixed to the sample. Outside of the chamber the opposite parts of the wires were soldered to a board containing four copper stripes. 4-point probe measurements were conducted on top of these copper stripes every 30 s during the test procedure. During the experiment ammonia was used as

test gas. Therefore 10 ml aqueous ammonia solutions with different ammonia concentrations (1.56 %, 3.12 %, 6.25 %, 12.5 %, 25.0 %) were filled in a bubbling system and heated up to 50 °C by use of a water bath. Pressurized air (flow rate 1.5 l/min) was used as carrier gas and directed through this bubbling system in order to transport gaseous ammonia into the test chamber. After each test run the sample surfaces were recovered using pressurized air (flow rate = 30 l/min) for 20 min.

3. RESULTS

3.1. Morphology

Films deposited at optimized working conditions appear homogeneously on Si and glass substrates and clear interference pattern can be observed. To demonstrate this, **Figure 2** presents a coated stainless steel substrate. Furthermore, the related cross-sectional SEM investigation (SnO_x on Si) is also shown in this figure. SEM investigations reveal that created films compose of a thin and dense layer close to the substrate and a more porous layer with an aligned columnar structure on top of it. A change from dense film growth to columnar film growth mechanism led to the formation of this structure. Such an effect is well-known in CVD processes: The formation of a thermal barrier film on a thermally conductive substrate could be a reason for this, whereby such thermal barrier lead to a modification in the heat flux toward the substrate [10].

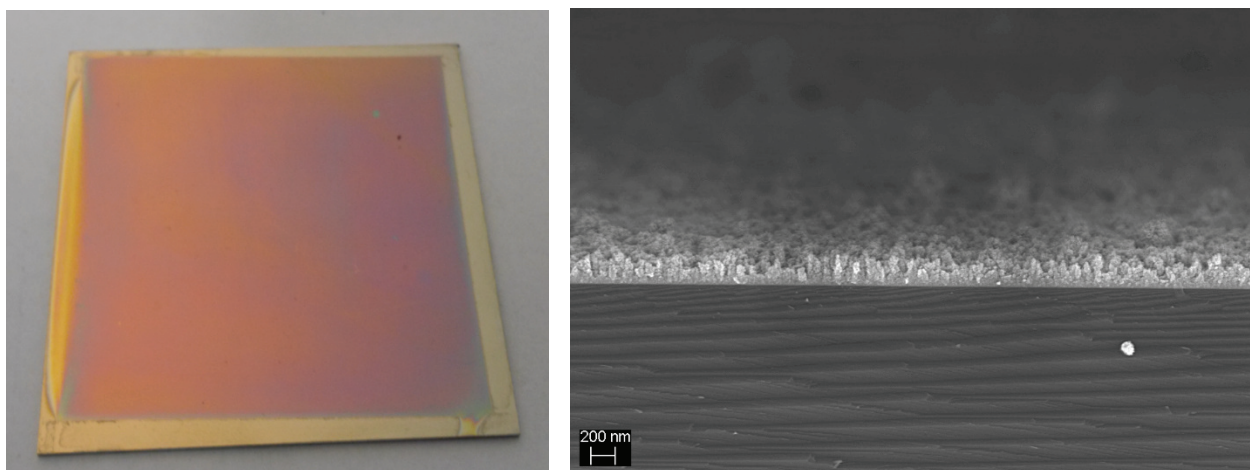


Figure 2 Stainless steel (size: 5 cm × 5 cm) coated with SnO_x (left) and cross-sectional SEM image of SnO_x coated silicon wafer (right); both at substrate temperature 300 °C

3.2. Electrical properties

Figure 3 presents the calculated resistivities of SnO_x thin films deposited on glass. By 4-point probe measurement no electrical conductivity could be determined (conductivity too low) for films deposited at substrate temperatures lower than 250 °C. Films produced at 300 °C substrate temperature show the lowest sheet resistivity ($\sim 0.07 \Omega\cdot\text{cm}$) and therewith the highest electrical conductivity. With increasing the substrate temperature to 400 °C the sheet resistivity increases to $\sim 0.25 \Omega\cdot\text{cm}$ and a further increase to 500 °C leads to $\sim 0.5 \Omega\cdot\text{cm}$ sheet resistivity. A commonly used method to create SnO_x is spray pyrolysis. In literature reported values for the resistivity of undoped films ranges from $\sim 0.008 \Omega\cdot\text{cm}$ to $0.7 \Omega\cdot\text{cm}$ [11, 12]. To obtain these low resistivities elevated substrate temperatures between 450 °C and 500 °C were necessary. Lowest resistivities obtained in our work were at substrate temperatures of 300 °C. Therewith a significant reduction of substrate temperatures down to 300 °C was possible and resistivities of SnO_x films comparable to films deposited by spray pyrolysis using > 450 °C could be achieved. One reason for this improvement could be the creation of a reactive and oxygen-rich environment in the plasma and hence, a promotion of oxidation processes and the reduction of organic residuals within the films.

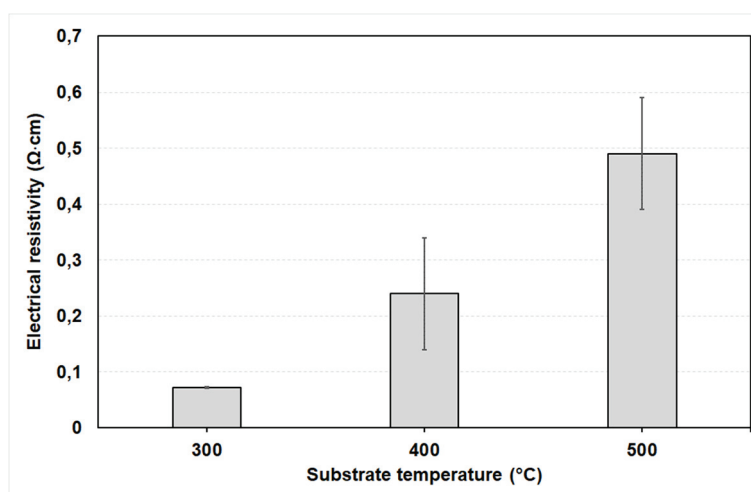


Figure 3 Electrical resistivity of plasma deposited SnO_x thin films on glass as a function of substrate temperature

3.3. Gas sensing

The presented results in this chapter were obtained for films deposited using 400 °C substrate temperature. During the gas sensing measurements the films temperature was kept at 150 °C. Tests were also conducted at lower measuring temperatures, however, first changes of the sheet resistance during surface/ammonia-interaction was monitored at 150 °C. These findings are in good accordance to literature data: surface temperatures of 200 °C were often necessary for SnO₂ films [13]. **Figure 4** shows the relative sheet resistance ($R_{\text{ammonia}}/R_{\text{air}} \times 100$ (%)) in dependence of time at different ammonia solution concentrations.

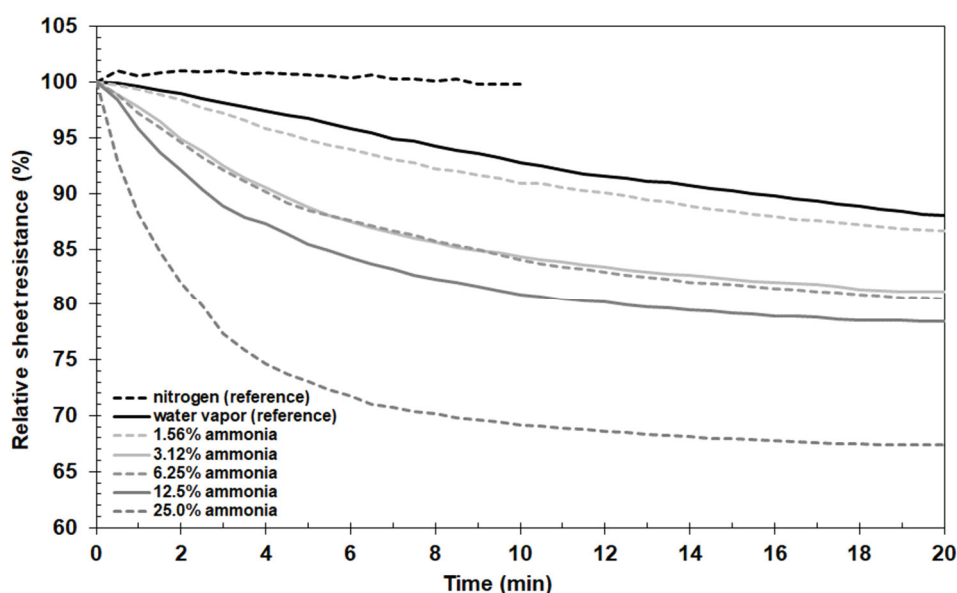


Figure 4 Electrical response of SnO_x films ($T_{\text{Sub}} = 400$ °C) to different atmospheres: Relative sheet resistance vs. time at ammonia-containing atmospheres and references [9].

The solvent (pure deionized water) and nitrogen as an inert gas medium were used as references and fed into the test chamber. The water vapor itself causes a reduction of the sheet resistance and a relative sheet resistance of ~88 % was achieved following 20 min treatment. In comparison to water vapor, nitrogen did not influence the sheet resistance. By introducing ammonia into the test chamber the relative sheet resistance decrease stronger and values of approximately 86 %, 81 %, 80 %, 78 % and 67 % were achieved using 1.56 %, 3.12 %, 6.25 %, 12.5 % and 25.0 % ammonia solution concentrations, respectively.

3.12 %, 6.25 %, 12.5 % and 25.0 % ammonia concentration, respectively. Therewith a clear decrease of relative sheet resistance with increasing ammonia concentration was observed. Hence, films show distinctive gas sensitivity and selectivity. This behavior is typical for SnO₂ gas sensors and described in literature [13,14].

Furthermore, measurements could be repeated several times consecutively with similar results (see **Figure 5**). Following an ammonia test step, the chamber was purged by air and a recovery of the sheet resistance was observed. Thus, one test cycle consists of one ammonia exposure step and one air-purging step. By applying this routine, several cycles were conducted consecutively. The sheet resistance at the start (before introducing ammonia) and the end of each cycle (saturation of sheet resistance and start of air-purging) were comparable among several test cycles.

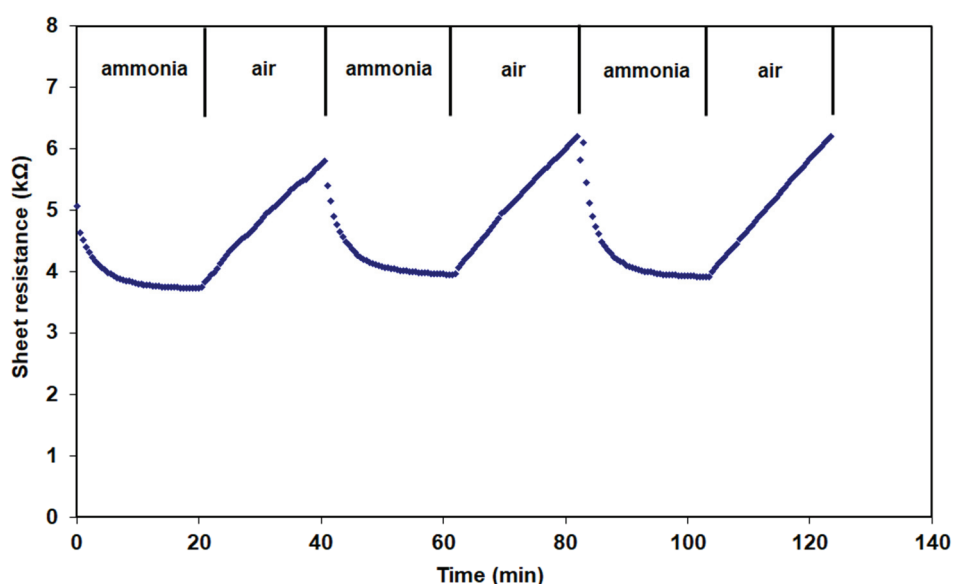


Figure 5 Reversibility of SnO_x films ($T_{\text{Sub}} = 400\text{ }^{\circ}\text{C}$): Sheet resistance vs. time for recurring changing atmospheres; ammonia (25.0 %) and pressurized air.

4. CONCLUSION

By using a modified APPJ system, nanostructured SnO_x thin films were successfully deposited in one single operation step. TBT was introduced in form of an aerosol into the reactive plasma, chemically converted and transported to the substrate where film formation took place. Good electrical conductivity was achieved using substrate temperatures between 250 °C and 500 °C. The deposition procedure itself can be described as a combination of plasma assisted CVD and spray pyrolysis. However, compared to spray pyrolysis, lowest sheet resistivity could be achieved at lower substrate temperatures. Hence, this technology could be a more suitable method also for temperature sensitive materials. First experiments clearly indicate the gas (ammonia) sensing properties of the deposited films. So, tin oxide coatings created by atmospheric pressure PECVD using the APPJ technology are showing already in its undoped state and without further layer post-treatments high application potential.

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