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Structural, electrical and optical properties of SnO_x films deposited by use of atmospheric pressure plasma jet

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ABSTRACT

Structural, electrical and optical properties of undoped tin oxide thin films (SnO_x) deposited on silicon and glass slides by use of an atmospheric pressure plasma jet at substrate temperatures varying between 300 °C and 500 °C were determined. One role of the used plasma is the promotion of SnO_2 formation and reduction of organic residues from the tetra-*n*-butyltin (IV) precursor by supplying a highly reactive oxygen-containing atmosphere. Moreover, film properties were compared to SnO_x films prepared by a vacuum direct current sputtering procedure. Scanning electron microscopic investigations showed high specific surface area and porous films at 300 °C substrate temperature. With increasing this temperature a decrease in film thickness and roughness of the films could be observed. These experiments were supplemented by transmission electron microscopy and showed the formation of a dense layer close to the substrate with a more porous layer on top of it. Spectral ellipsometry further supported these results and allowed to determine the thickness of the films as well as the thickness of the dense and porous part. X-ray diffraction pattern indicated the presence of a predominantly crystalline film structure (SnO_2, cassiterite) at 500 °C substrate temperature with an average grain size of ~4 nm. Comparing to this, film deposited by vacuum sputtering method were more crystalline with average grain sizes of ~12–14 nm. Additionally, the presence of SnO_2 on the surface was demonstrated by X-ray photoelectron spectroscopy. Films with an average transmittance of > 85% and low resistivities of 7.2×10^{-2} Ωcm even at lower substrate temperatures of 300 °C could be achieved, whereby electrical film properties (conductivity) were superior to those of films prepared by sputter deposition. First attempts to show gas sensing properties were conducted and revealed a response toward ammonia gas atmospheres.

1. Introduction

Tin oxide as polycrystalline SnO_2 and amorphous SnO_x thin films have been used in a large variety of technically significant applications. This material possesses various properties of interest, e.g. a wide semiconductor band gap (3.6–3.7 eV at room temperature), chemical stability and high transparency (~85%) [1]. Especially transparent highly conducting oxide films are used as electrodes for electronic devices such as flat displays [2–4], solar cells [5,6] or gas sensors [7,8]. Other common applications are highly antireflective films [9], UV and IR filter [10] or protection layers on polymers to improve their scratch and/or chemical resistance [11]. Such films can be applied in form of undoped, In-, F-, or Sb-doped SnO_2 on a wide spectrum of substrates. Established methods to create such films include physical vapor deposition (PVD) such as sputtering [3,12], chemical vapor deposition (CVD) [5,13,14], spray pyrolysis [15] and sol-gel technology [10]. Most PVD technologies require high vacuum and will be performed in batch-processes but can in advance be performed at low substrate temperatures. Moreover, very dense films with low surface roughness can be achieved with PVD methods [16]. 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 temperature-sensitive materials. Beneficial is the possibility to treat larger substrate areas under atmospheric pressure conditions (in-line ability). High quality tin oxide films can also be achieved by sol-gel methods. To obtain crystalline films a heat treatment (> 500 °C) of substrates after film deposition is necessary. New approaches found in literature made it possible to create tin oxide films at low substrate temperatures using atmospheric pressure plasma chemical vapor deposition. Churpita and Cada et al. used a RF barrier torch

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discharge plasma jet system to create conductive indium- and tin oxide films on materials such as polymers (allydiglycol-carbonate). Sn- and In-acetylacetonat were used as precursor material and were heated up to 170 °C in order to vaporize them and to introduce these precursors into the plasma by a N_2 carrier gas flow. Helium was used as working gas to create a stable plasma discharge [17,18]. The confinements of this system are the use of expensive noble gases and special systems to vaporize the solid precursor powders. Korotkov et al. used a RF plasma source which creates a total active plasma area of 30 × 80 mm^2. The tin-organic precursors tetra-*n*-butyltin (TBT) and monobutyltin trichloride were used and injected into a stream of preheated (130 °C) nitrogen or air and this vapor mixture was directed through the active plasma [13]. In these experiments borosilicate and soda lime glasses were used as substrate materials and heated up to 80 °C during film formation procedure. Subsequently to the film deposition, the substrates were either post-annealed at 337 °C in vacuum or at 600 °C in air. After this pre-treatment tin oxide films with low sheet resistivities could be achieved. However, this approach requires an additional heat treatment following the film deposition.

Aim of this study was to overcome the disadvantages of PVD processes by the development of a deposition process working under atmospheric pressure conditions (in-line-capable). Our process uses a plasma jet system working with pressured air as process gas and no inert or noble gases were necessary. During film deposition experiments the dependence of film properties on substrate temperatures reaching from room temperature to 500 °C was investigated. Furthermore, an additional heat treatment following the film deposition was not implemented. The properties of these undoped SnO_x films are further compared to films created by a common vacuum direct current (DC) sputtering process.

2. Experimental details

2.1. Materials

Films were created on monocrystalline Si wafer pieces (100-oriented), which were cut into sizes of 20 × 20 mm^2. Furthermore, SnO_x-films were deposited on soda lime glass slides (VWR International) coated with a 20 nm thick silicon dioxide film (deposited by Pyrosil® [19] procedure) for electrical and optical investigations. These silicon dioxide films were created to prevent Na^+-diffusion during substrate heating into the SnO_x films. Previously to the film deposition experiments all substrates were ultrasonically cleaned in an isopropanol/acetone mixture (1:1 V/V) for 10 min and blown dry with pressurized air. As precursor for the SnO_x films the metal-organic substance TBT (Sigma Aldrich, 98%) was used. This precursor was further diluted to a concentration of 50% V/V in isopropanol. TBT is a liquid at room temperature and therefore no additional heating was necessary to inject it into the reactive plasmas (described below in more detail).

2.2. Atmospheric pressure plasma enhanced CVD

The experimental set-up used to create SnO_x films is shown in Fig. 1. Centerpiece of the used set-up is a commercially available atmospheric pressure plasma jet (APPJ) system based on Tigres' MEF technology (Tigres GmbH). The advantages of plasmas are well known and widely reported in literature [20–22]. Non-thermal plasma systems which operate at atmospheric pressure generate high concentrations of high-energetic electrons and species such as O^+, O_2^+, O^- or O_3. Such reactive environments can etch, activate surfaces and/or dissociate chemical bondings [20]. Especially in the field of polymer surface activation these systems can be used [23]. But also film forming procedures can be initiated with plasmas [24,25].

Our plasma jet is combined with a power supply unit and a process gas supply. The jet itself is constructed of an inner pin electrode (brass) and an outer circular nozzle electrode (stainless steel). As working gas

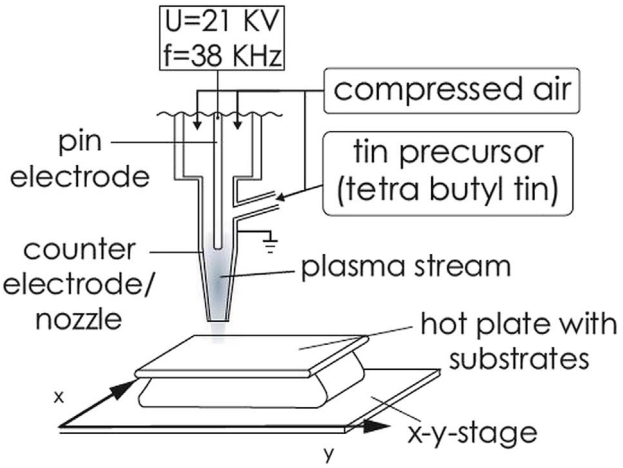

Fig. 1. Schematic illustration of the atmospheric pressure plasma jet system used (not to scale).

air, nitrogen or argon supplied at 4 to 6 bar can be used. For our experiments pressurized air was used with 6 bar working pressure. This jet system creates an electrically potential-free cold plasma (DC pulsed discharge) with an adjustable electrical power between 50 W to 500 W [25]. To create thin films the plasma system was modified. This modification is based on the use of a dosing system, build to spray liquids or liquid dispersed particulate materials through a nozzle into the active plasma discharge [26]. The liquid doses of TBT/isopropyl mixture were kept constant at 50 µl/min.

Substrates were placed on a computer-controlled moving table and were moved relatively to the plasma torch with a velocity of 100 mm/s. In order to realize areal coatings this x-y- positioning system performed a meandering movement with a line distance of 3 mm and 30 successive deposition runs were performed. Furthermore, substrates were additionally heated during the deposition procedure between 300 °C and 500 °C by use of a hot plate.

As reference materials SnO_x films deposited by a common sputtering coating process at substrate temperatures of 300 °C, 400 °C and 500 °C were produced (DC magnetron sputtering system, target: 2 in. metallic Sn, working gas: Ar ($p_{Ar} = 1.5 \times 10^{-2}$ mbar), reactive gas: O_2 ($p_{O2} = 1.3 \times 10^{-2}$ mbar), $p_{tot} = 2.8 \times 10^{-2}$ mbar, target-substrate-distance 10 cm, electrical power 50 W) and compared to the films deposited by use of the atmospheric pressure plasma jet.

2.3. Thin film characterization

Tin oxide films were examined 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 in order to analyze the thin film morphology. Additionally to morphological investigations by SEM, scanning transmission electron microscopy (STEM) was conducted on a 20S–TWIN (Tecnai) using a voltage of 200 kV and a LaB_6 cathode. Previously to the TEM investigations samples were mechanically prepared (cross section preparation) and subsequently thinned by Ar ion milling. Atomic Force Microscopy (AFM) was performed to analyze the roughness and morphological film features using a MFP3D (Asylum Research) in non-contact mode. The scanned area was 5 × 5 $µm^2$ and the scan speed was at 50 µm/s. X-ray photoelectron spectroscopy (XPS) using an AXIS ULTRA DLD (Kratos Analytical Ltd.) was carried out to determine the chemical composition of the surfaces. A compensation of charges was achieved in situ and the position of the peaks was corrected in reference to the 1 s spectroscopic state of carbon (C_{1s}) at 285.0 eV. In XPS investigations a 700 × 300 $µm^2$ spot was analyzed using a 160 eV pass energy (survey) and 40 eV pass energy (detail) and monochromatic Al K_α (1486.6 eV) source. For depth profiling monoatomic mode with