# Single source precursors for piezoelectric and optical coatings

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The field of chemical vapor deposition (CVD) has grown very rapidly in the last thirty years and applications of this versatile fabrication process are now used in many industrial products, such as semiconductors, optoelectronics and optics [1]. In comparison to thermal evaporation, sputtering and other physical vapor deposition (PVD) approaches, CVD offers excellent conformity to cover deep recesses, holes, and other difficult three-dimensional geometries [2]. In addition to thin film applications, where an ultra thin deposit is desired, CVD is also applicable for thick coatings due to its high deposition rate [3]. Another advantage is that CVD does not normally require ultrahigh vacuum unlike to state of the art PVD methods [4].

Beside these unique process advantages however, CVD has also some disadvantages, such as the need of high deposition temperatures, generally above 600 °C [5]. Development of metal-organic molecular precursors partially solved this problem and opened up new possibilities to deposit crystalline thin films at much lower temperatures [6]. As the material of interest becomes increasingly complex, the choice of the precursor also becomes more difficult. In the deposition of such multi-component complex materials, the common approach is to use several different precursors simultaneously [7]. On the other hand, the different volatilities of the precursors and undesired side reactions between decomposed chemical species affect the purity, composition, homogeneity and microstructure of the resulting materials [8]. In order to overcome these difficulties, the *single source precursor (SSP)* approach has been developed [9]. This is based on a molecular design which, instead of using several precursors, contains all desired elements in one molecule.

In the last years we have researched a number of SSPs for the synthesis of different nanocrystalline and composite materials. Recently, we have shown the synthesis of $Al/Al_2O_3$ and $Ga/Ga_2O_3$ nanocomposite structures with precisely controlled composition and microstructure [10]. The control of the composition, purity and homogeneity is especially critical for synthesis of electronic and optical materials. Thus, we present the use of the SSP concept for the synthesis of ferroelectric and optical coatings. First the synthesis of PZT coatings with a precise stoichiometry (between lead, zirconate and titanate) is presented. Dielectric properties of deposited PZT coatings (dielectric constant $\varepsilon_r$ and dielectric loss $\delta$) were measured with a precision LCR Meter. The remnant polarization ($P_r$) was also determined. The effectiveness of the SSP method is also shown by presenting transparent ITO layers with controlled dopant concentration. The ITO layers were characterized with the X-ray diffraction method. Electrical resistivity of the deposited layers is also presented.

## Experimental

*Synthesis and characterization of PZT coatings*

The combination of two bimetallic alkoxide compounds, $(C_2H_5)_3Pb[O\text{-}C(CH_3)_3]_5Ti$ and $(C_2H_5)_3Pb[O\text{-}C(CH_3)_3]_5Zr$ a lead titanate and a lead zirconate source with identical properties and complete miscibility resulted in a new mixed single source PZT precursor which evaporates at a temperature of 25 °C and a pressure of 0.13 mbar. The composition of the precursor is adjusted to Pb:Zr:Ti = 2:1:1.

The precursor was deposited at temperatures around 400 °C on (100) Pt/Ti/$SiO_2$/Si substrates using a vertical cold-wall CVD chamber. Following the deposition, the coatings were annealed at 650 °C. After sputtering the top electrode with diameters from 100 µm to 400 µm, the planar PZT-films were structured by wet chemical etching using lithographical techniques.

The crystallization behaviour of the PZT films was analyzed by X-Ray diffraction (XRD, Bruker (AXS D8 Advance)). Surface microstructures of the films were observed using a FEI (Quanta 400 ESEM FEG) field emission scanning electron microscope (SEM).

The dielectric properties of the films (dielectric constant $\varepsilon_r$ and dielectric loss δ) were measured with a precision LCR Meter (Agilent 4284A). To display the ferroelectric hysteresis loop, a classical Sawyer-Tower circuit [11] was used (A modified PUND setup, as described by Veith et al. [12] was employed for the determination of the remnant polarization $P_r$.).

*Synthesis and characterization of ITO coatings*

For the synthesis of the precursor, an organometallic indium compound $[(CH_3)_2In\text{-}O\text{-}C(CH_3)_3]$ is chemically bonded to an organometallic tin-compound $Sn[OC(CH_3)_3]_2$. Through intra- and intermolecular interactions, a quasi-SSP system can be formed, the source material for ITO-coatings. The ratio of In to Sn was adjusted to 9 to 1 to give a doping concentration of 10 % of tin in ITO.

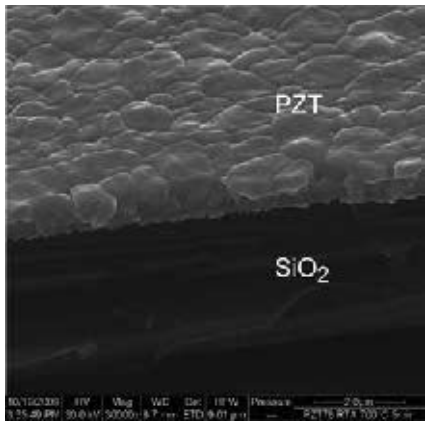


Figure 1: SEM-Image of the deposited PZT-film on a Pt/Ti/$SiO_2$/Si-substrate.

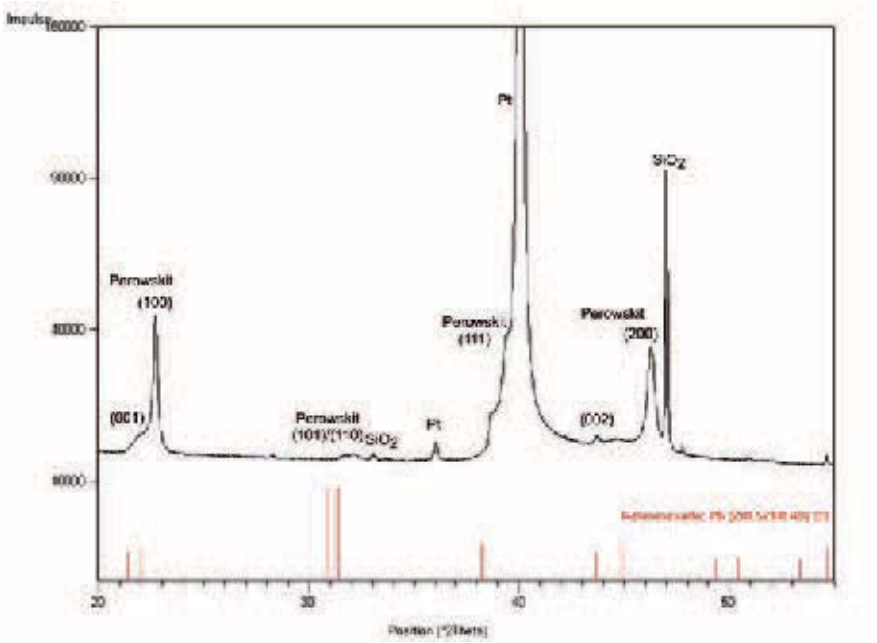


Figure 2: XRD-pattern of a deposited PZT film. The film shows a (100)-orientation.

A cold-wall-CVD-apparatus was used to deposit the ITO-films. 1g of the precursor was placed in a reservoir-container and connected to the CVD-reaction chamber. Glass substrates (borosilicate, 2 mm thick) of 15x15 mm in size were cut and placed onto the graphite substrate holder. Both the wall of the reaction chamber and the precursor reservoir were heated to 80 °C. The substrate was heated to 500 °C by a HF-generator. After reaching the desired temperature, the precursor-valve was opened for five minutes to enable deposition of the film from gaseous materials.

The composition and morphology were analysed by X-ray diffraction, using Cu $K_\alpha$ radiation. Layer thickness was measured by ellipsometry. Post-treatment in reducing atmosphere was performed for 30 minutes at 300 °C in forming gas (95 %$N_2$, 5 %$H_2$). Measurements of electrical resistivity have been performed with a four point probe technique (Hewlett-Packard 34401-A). SEM-images were taken by a JEOL JSM-7000 F scanning electron microscope.

## Results

*PZT coatings*

After the CVD-process, the deposited films were thermally annealed at 650 °C to obtain the desired perovskite-phase. The SEM-images show a smooth 1 µm thick film-surface with a grain-size of about 500 nm (Figure 1). In XRD-measurements, a pure (100)-oriented perovskite-phase on the Pt/Ti/$SiO_2$/Si-substrate is observed (Figure 2).

The dielectric constant $\varepsilon_r$ and dielectric loss $\delta$ of the PZT-films were measured to be 412 and 0.025. The hysteresis loop (Figure 3) shows a remnant polarization of 25 µC/cm² and a coercive field of 30 V/µm.

*ITO Coatings*

The deposited films appear transparent and show a crystalline cubic tin-doped indiumoxide phase in the SEM-image (Figure 4) and in the diffractogram (Figure 5) with a crystallite size of approx. 100 nm. No other crystalline phases could be observed.

The thickness of the ITO-layer is 23 nm. The as-prepared transparent samples show a sheet resistance of 1640 kΩ/sq. After post-treatment in reducing atmosphere, the value has slightly decreased to 1542 kΩ/sq, corresponding to a specific electrical resistivity of 3.55 x $10^{-3}$ Ωcm. This increase in electrical conductivity can be explained by the creation of oxygen vacancies in the oxide lattice during reduction treatment.

## Discussion

The synthesis of a quasi-SSP is a key issue in the simplification of state-of-the-art CVD processes. PZT-films with the desired perovskite phase were deposited using only one source instead of three (lead, zirconate and titanate). The film properties ($E_c$ = 30 V/µm, $P_r$ = 25 µC/cm²) exceed those of sol-gel-PZT-coatings [13]. The properties are comparable with PZT-films, produced by sputtering-techniques [14]. In comparison to sputtered films

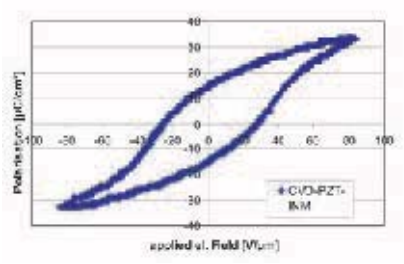


Figure 3: Hysteresis-loop of the deposited PZT-film.

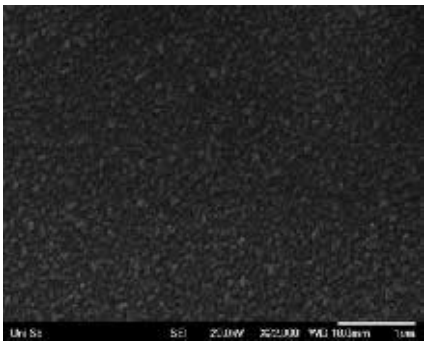

Figure 4: SEM image of the transparent ITO coating.

our layers show a better coverage on complex geometries.

CVD of a new SSP was shown for synthesis of ultra thin films of ITO. After five minutes deposition, a 23 nm thick, crystalline layer of tin-doped indiumoxide has grown on the glass substrate. The electrical resistivity after post-annealing in reducing atmosphere is 3.55 x $10^{-3}$ Ωcm. Further enhancement of the layer growth might be achieved when oxygen is added to a carrier gas.

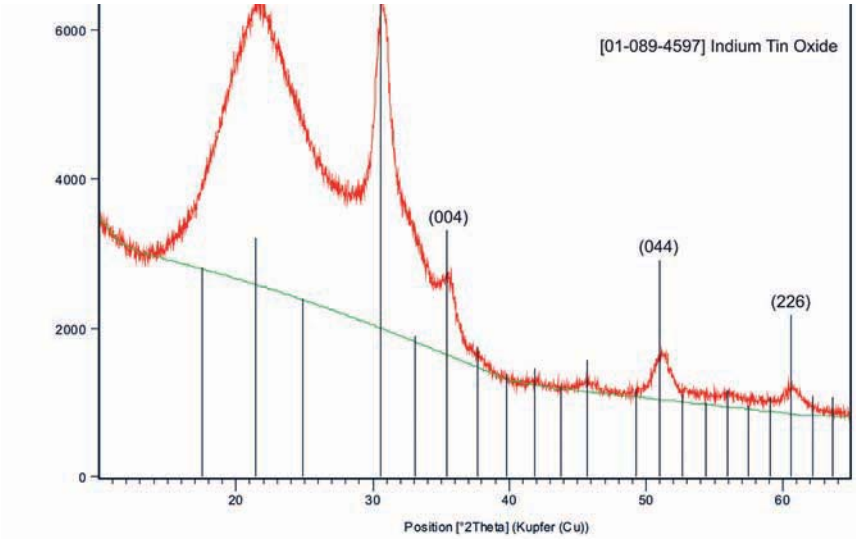


Figure 5: XRD-Pattern of the ITO-coating on glass substrate. Reference lines according to Indium Tin Oxide (PDF-Nr. 01-089-4597).

## Conclusion

Single-Source-Precursors have been used to produce high performance coatings of PZT and ITO using the CVD-process. PZT-coatings from a single source combining Pb, Zr and Ti in one metal-organic precursor system show excellent properties. ITO-CVD-coatings from a SSP-system exhibit high transmission in visible range and good electrical conductivity. The ITO-layer consists of densely packed, cubic ITO-crystals.

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