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# Influence of substrate temperature and silver-doping on the structural and optical properties of $TiO_2$ films

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ABSTRACT

Evaporation of titanium together with activated oxygen is used to grow $TiO_2$ films and simultaneously with silver to grow Ag–$TiO_2$ films (5 at.% Ag) onto sapphire substrates at three different substrate temperatures: −190, 30, and 200 °C. The obtained films were characterized by X-ray powder diffraction, Raman, X-ray photoelectron, ultraviolet–visible spectroscopy, and transmission electron microscope investigations. The properties of $TiO_2$ films varied with the substrate temperature. Amorphous, transparent $TiO_2$ films were grown at −190 °C and opaque, polycrystalline films at 200 °C, respectively. Surprisingly, at room temperature black, amorphous $TiO_2$ films are obtained which transform at 350 °C into a mixture of the anatase and brookite polymorph. In the amorphous state of the $TiO_2$ films a predefined rutile arrangement is suggested by Raman investigations, and the contraction of the lattice constant c of anatase phases (tetragonal, space group $I\,4_1/amd$) depending on the substrate temperature is experimentally observed. The silver-doped $TiO_2$ films deposited at −190 and 30 °C contain Ag-particles with 2 nm in size inside the $TiO_2$ matrix, which after annealing segregate under increasing particle sizes. The silver-doping stabilizes the anatase polymorph and yields to reduced titanium species in the films especially during deposition at 30 °C. The Ag–$TiO_2$ films deposited at −190 °C are transparent up to 350 °C. In the undoped as well as silver-doped $TiO_2$ films the rutile polymorph is directly formed at 200 °C as main phase.



## 1. Introduction

Titanium dioxide occurs in three crystalline polymorphs – rutile, anatase, and brookite – [1] beside various high pressure phases [2]. The rutile polymorph is the thermodynamically stable structure whereas anatase and brookite are metastable [3]. All structures consist of $TiO_6$-octahedra which are connected by 2 (rutile), 3 (brookite) or 4 (anatase) common edges. The brookite structure is rarely seen [4] so the main emphasis was on the investigations of rutile and anatase phase.

For metal oxides $TiO_2$ has been extensively studied for its bulk properties including defects and surface geometries [1]. Here we focused on the growth of $TiO_2$ films. In this area titanium dioxide is utilized with a progressive rate and one large application relates to optical materials. Titanium dioxide is a highly refractive material with negligible absorption in the optical regime, but in the UV, $TiO_2$ absorbs strongly [5]. This leads to use of thin films of $TiO_2$ as antireflective [6], anti-fog [7] and bandpass [8] coatings. Furthermore, $TiO_2$ films are used as catalysts [9], gas sensor [10], and dielectric materials [6]. Doped $TiO_2$ materials were studied to enhanced catalytic efficiency for the photocatalysis of water splitting [11]. Ideally for applications of $TiO_2$ thin films it would be useful to raise sensitivity to visible light and/or to eliminate the fast electrons hole recombination. Metal and nonmetal doping in $TiO_2$ have been widely investigated for extending the absorption edge of $TiO_2$ towards the visible regime [12]. In the case of metals, the noble metals, gold, and copper were mostly used and only rarely was silver investigated [13].

For these functions a large variety of methods are applied to prepare the $TiO_2$ films [14]. Films have been synthesized by chemical processes like sol–gel, dip-coating or spin coating [15], plasma spraying [16], oxidation of titanium [17] and also by vacuum processes like CVD (chemical vapor deposition) [18], sputtering [19], electric arc [20], thermal [21] and electron beam evaporation [22] as well as PLD (pulsed laser deposition) [23]. The reactive electron beam evaporation [24,25] is especially suitable method to control the structure and properties of the obtained $TiO_2$ films by the pressure and/or plasma activation of oxygen. A threshold of oxygen pressure is necessary to form stoichiometric $TiO_2$ films at a certain substrate temperature and with increasing pressure the anatase phase is preferred to the rutile phase. Furthermore, the plasma activation increases the density and the refractive index of the films [22]. For low oxygen pressures films containing various titanium suboxides can be obtained [24]. The color of the suboxides varied from yellow to dark-blue to bronze with decreasing oxygen content. In addition reduced $TiO_2$ films can be obtained by heat-treatments under oxygen, ammonia, hydrogen, nitrogen, argon [1] as well as by reduction with silicon [26]. In 2011 synthesis of black $TiO_2$ nanomaterials by a hydrogenation process was discovered [27]. The black titania is described as anatase nanoparticles encapsulated by a thin amorphous hydrogenated layer

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[28]. It has a photocatalysis with a two times higher hydrogen production rate than most semiconductor photocatalysts [29].

Until now in the literature, nearly all Ag-doped $TiO_2$ films were prepared from solution. Methods like sol–gel [30,31], dip coating [32], spin coating [33], spray coating [34], electrospinning [35], photoreduction [36], hydrothermal [37], and liquid phase deposition [38] have been used. Only in a few studies DC-sputtering [39–41], laser ablation methods [42], and electrochemically oxidation of titanium [43] were applied. Therefore the obtained samples consist of nanocomposits ($Ag/TiO_2$) or hybrid nanomaterials (core-shell [44], wires [45], and fibers [46]). The nanocomposit thin films embedded metallic Ag nanoparticles in the $TiO_2$ matrix (anatase phase) with Ag particles sizes from 5–10 nm [39] up to 150 nm [47]. For annealed films the Ag particles can also be accumulate on the surface [31]. By co-sputtering small crystalline Ag nanoparticles of 1–2 nm in an amorphous $TiO_2$ matrix can be obtained [40].

Here, the synthesis of $TiO_2$ and Ag-doped $TiO_2$ films by simultaneous deposition of titanium (and silver) together with plasma-activated oxygen is described. The thermal evaporation of silver forms most likely Ag distribution on atomic level. The effect on the physical properties of the obtained films by varying the substrate temperature during growth between −190 and 200 °C was studied. The deposition of $TiO_2$ films below room temperature was not investigated so far. In the literature substrate temperatures mostly above 400 °C have been used to form well-crystalline films. In a few studies the formation of amorphous $TiO_2$ films using substrate temperatures below 200 °C are described [22]. For the synthesis of $TiO_2$ [15] and Ag-doped $TiO_2$ [31] films via solution processes, substrate temperatures ≥80 °C were used with subsequent calcination steps. Synthesis of Ag-doped $TiO_2$ films by simultaneous evaporation of titanium and silver together with activated oxygen is not described in the literature until now.

## 2. Experimental details

$TiO_2$ and Ag–$TiO_2$ films were prepared using an UHV (ultra high vacuum) chamber (Fig. 1) containing a turbo molecular and cryo-pump system including a liquid-nitrogen filled cold trap. Titanium (99.95%, Smart Elements, Austria) was evaporated by an electron beam gun (single pocket 218, Telemark Inc., USA) using a molybdenum crucible and an electric power of 0.78 kW. Silver (99.99% Heraeus GmbH, Germany) was evaporated from a PBN-crucible using an effusion cell (Dr. Eberl MBE-Komponenten GmbH, Germany) at 750 and 760 °C. Oxygen (purity 5.0; Westfalen AG, Germany) mass flow was controlled to 0.8 sccm, and the stream into the chamber passed through a microwave plasma source (ECR-Plasma source, Tectra GmbH, Germany) operating at 2.45 GHz and 50 mW. This excess of oxygen results in an oxygen/titanium ratio of around 50:1. The films were synthesized on sapphire substrates which are epitaxially polished on both sides (orientation (0001), CrysTec GmbH, Germany). Simultaneous deposition of titanium (and silver) together with oxygen was performed for a period of 5 to 7 h at substrate temperatures of −190, 30, and 200 °C. The process pressure was $1.0 \times 10^{-5}$ mbar. The residual gas was analyzed and monitored by quadrupole mass spectrometers (Prisma Plus QMG 220, Pfeiffer Vacuum GmbH, Germany).

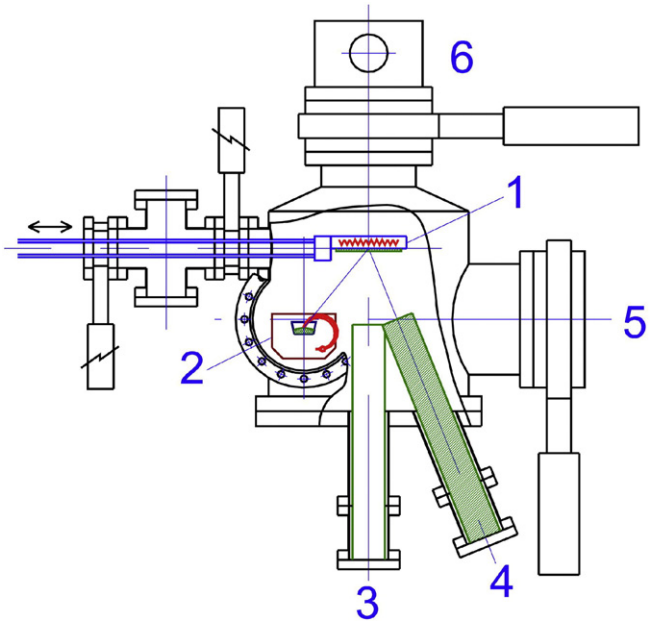


**Fig. 1.** Experimental set-up of the preparation chamber; 1: sample holder, 2: electron beam gun, 3: effusion cell, 4: ECR plasma source, 5/6: gate valve (pumps).

Fig. 1 represents the arrangement of the evaporation sources regarding to the sample holder inside the preparation chamber. The sources are aligned by an angle of 25° (electron beam gun 35°) to the center and have a distance of 150 mm from top to the substrate. The sample holder contains two tubes for the cooling with liquid nitrogen, a resistance heater, and a PT-100 temperature sensor for the temperature control. During experiments the temperature of the substrate on bottom of the sample holder was kept at T = −190, 30, or 200 °C. Via a transfer system, the substrate bearing the deposited sample was transferred from the preparation chamber to a diffractometer while maintaining vacuum and cooling [48]. Here *in situ* X-ay patterns and Raman spectra of the samples were detected as deposited and after increasing the temperature step by step. After annealing with a slope of ~10 °C/min. the sample cools down to room temperature before the next measurement started. Normally a temperature screening with 200 °C steps were used for the characterization of the samples. In special cases minor steps of 50 °C were applied. The sample holder allows a maximum temperature of 430 °C.

The optical appearance of the films on sapphire substrates (photos taken by Canon EOS 350D, Canon, Germany) varied with the deposition temperature. The film thicknesses were analyzed by focused ion beam milling in a microscope (Zeiss 1540 EsB, Germany) together with X-ray absorption spectroscopy (Sol-X energy-dispersive detector, Bruker AXS, Germany) on the X-ray diffractometer. The silver contents of the Ag–$TiO_2$ films were determined using the XPS measurements (see below) and an inductively coupled plasma optical emission spectrometer (ICP-OES; Vista Pro, Varian, Germany). The samples were completely dissolved in $HNO_3$ (conc.) for the ICP-OES measurements. The values in the text represent content in percent atom on metal basis (at.%).

The *in situ* X-ray powder patterns were measured by a $\theta/\theta$-diffractometer (D8-Advance, Bruker AXS, Germany) with a Goebel mirror (Cu–$K_\alpha$) inside a vacuum chamber (~$10^{-7}$ mbar) in reflection mode; for further details see [49]. The lattice constants were refined by the Rietveld method using crystal structure data from the literature via the TOPAS software (TOPAS Vers. 4.2, Brucker AXS, Germany) [50] with phase contents in percent weight (wt%). From the profile shape analysis (TOPAS) the crystallite sizes were calculated by the Scherrer equation. A laser-microscope Raman spectrometer (iHR 550 spectrometer; BXFM microscope, Horiba, Germany) with confocal geometry was used for the in situ Raman measurements. The incident laser beam (532 nm at 10 mW) passes through a window in a vacuum chamber (~$10^{-7}$ mbar) and was focused by an objective (100×) on the samples. X-ray photoelectron spectra (XPS) were recorded (AXIS ULTRA, Kratos Analytical, UK) by using monochromatic Al-$K_\alpha$ radiation (1486.58 eV). The vacuum was kept below $1 \times 10^{-9}$ mbar during the measurements. The samples were transferred under Argon atmosphere into the XPS chamber and analyzed as received and after surface sputtering with Ar-ions (4 kV, 5–15 min., depth profiling). All spectra were calibrated to the C (1 s) line at a binding energy of 284.6 eV and the peaks were fit to Gaussian functions. The transmission electron microscope (TEM)