Substrate biasing during plasma-assisted ALD for crystalline phase-control of TiO2 thin films

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Substrate biasing has been implemented in a remote plasma atomic layer deposition (ALD) reactor, enabling control of the ion energy up to 260 eV. For TiO₂ films deposited from Ti(CpMe)(NMe₂)₃ and O₂ plasma it is demonstrated that the crystalline phase can be tailored by tuning the ion energy. Rutile TiO₂ was obtained at 200 and 300 °C, typically yielding amorphous and anatase films without biasing. Aspects such as film mass density, [O]/[Ti] ratio and growth per cycle under biased conditions are addressed. The results demonstrate that substrate biasing is a viable method for ALD to tailor ultra-thin film properties.

The experiments were carried out in a remote plasma ALD reactor equipped with an inductively-coupled plasma (ICP) source. The reactor is schematically illustrated in Fig. 1. During the plasma step of the ALD cycle, the substrate stage was electrically grounded or biased by substrate-tuned biasing or RF biasing. With substrate-tuned biasing, only a matching network was connected to the substrate stage (4 inch diameter) and the bias voltage was controlled by adjusting the impedance between the substrate stage and the ground potential.

In the case of RF biasing, a power supply (denoted by the asterisk in Fig. 1) was connected to the matching network. The substrate can be grounded by closing a switch that electrically connects the substrate stage and the grounded reactor walls and substrate stage. As a result, positive ions are accelerated in a thin space charge layer, the plasma sheath, towards the grounded reactor walls and the substrate stage. For the case of a collisionless plasma sheath (i.e. at relatively low pressures), the kinetic energy of the ions Eᵢ can be expressed by Eᵢ = e(Vₛ − Vᵢ), where Vₛ is the plasma potential and Vᵢ is the substrate potential. This expression illustrates that the energy with which the ions arrive at the substrate surface is increased for a more negatively biased substrate stage. Recently, we demonstrated that during remote plasma ALD under regular conditions (i.e. with a grounded substrate stage) the ion energy can be sufficiently high to play a role during the ALD process, e.g. by enhancing adatom migration and ligand removal. With substrate biasing even higher ion energies can be reached and an increased number of physical surface reactions can be expected to play a role during ALD.

For plasma-enhanced chemical vapor deposition (PECVD), substrate biasing has already proven its value in tailoring thin film material properties. For the deposition process of Si, for example, the microstructure, density and crystallinity can be affected by controlling the substrate bias voltage. For PECVD of TiO₂ the effect of substrate biasing has been confirmed as well - the deposition rate and the crystalline phase are affected by a bias voltage applied to the substrate stage. Also for ZnO, the influence of RF substrate biasing was demonstrated and the preferred orientation, the crystal size, and the thermal stability of the films were shown to be affected by the bias power. Being a different deposition method ruled by surface chemistry, it is also interesting to study the influence of substrate biasing for the case of plasma-assisted ALD.

In this letter, we demonstrate that substrate biasing is a viable technique during plasma-assisted ALD to tailor material properties of ultra-thin films. More specifically, it is shown that substrate biasing allows for control over the phase composition of TiO₂ thin films deposited at relatively low substrate temperatures. It is also revealed that substrate biasing affects the mass density, the [O]/[Ti] ratio and the growth per cycle (GPC).
found by extrapolating the average ion energies obtained for substrate-tuned biasing. Planar probe measurements confirmed that the ion flux to the substrate surface is hardly affected by substrate-tuned biasing and is in the order of $10^{14}$ cm$^{-2}$ s$^{-1}$.

Grazing-incidence X-ray diffraction measurements (XRD) were carried out on ~30 nm (200°C series) and ~50 nm (300°C series) thick TiO$_2$ films and the spectra are shown in Fig. 3. For films deposited at 300°C and a substrate potential of 0 V, the XRD spectrum includes the (101), (004), (200), (105), and (211) diffraction peaks corresponding to the anatase TiO$_2$ phase. When a bias voltage of −50 V is applied, the magnitude of these peaks decreases, while the (110) peak related to the rutile TiO$_2$ phase starts appearing. When the bias voltage is further increased, the anatase diffraction peaks gradually disappear and the (110), (101), (111), and (211) diffraction peaks, corresponding to the rutile phase, increase in magnitude. At −200 V solely peaks related to the rutile phase are visible in the spectrum. A difference can be observed between the spectra for −100 V substrate-tuned biasing and −100 V RF-biasing. This difference is expected to originate from a change in the plasma density and electron temperature as a result of the increase in power delivered to the plasma with RF biasing. TiO$_2$ films deposited at 200°C are amorphous, however when −100 V biasing is applied the (110) rutile phase peak appears in the XRD spectrum. Films deposited at 100°C remain amorphous even when substrate biasing is applied (not shown). It is noted that we verified that substrate biasing does not significantly heat the samples, by monitoring the substrate temperature using a thermocouple connected to the substrate stage.

The impact of substrate biasing was furthermore evaluated by Rutherford backscattering spectroscopy (RBS), elastic recoil detection (ERD), and X-ray photoelectron spectroscopy (XPS). Table I shows that films deposited without substrate biasing are stoichiometric, have a mass density typical for ALD-prepared TiO$_2$ films and contain <2 at.% H. The film properties for TiO$_2$ deposited at a bias voltage of −50 V are very similar, however TiO$_2$ films deposited at higher bias voltages show a pronounced change in the compositional material properties. The [O]/[Ti] ratio increases and the mass density decreases with increasing bias voltage. From in-depth analysis of the ERD results, the knowledge is gained that for bias voltages of 0 and −50 V the 1.4 at.% H in the films is mainly present at the TiO$_2$ surface as well as at the TiO$_2$ interface with the substrate. For films deposited at higher bias voltages a considerable amount of H seems to be present in the bulk, particularly as –OH groups, as confirmed by X-ray photoelectron spectroscopy (XPS) measurements. These OH groups are apparently more incorporated under biased conditions and are the reason for lower density films obtained for higher bias voltages. Using ex-situ spectroscopic ellipsometry (SE) the average GPC for the TiO$_2$ is shown in Fig. 3.
films was determined to be 0.86 Å/cycle without biasing, and 0.89 and 0.94 Å/cycle for a −100 V and −200 V RF biased substrate stage, respectively. The growth in terms of Ti atoms per cycle is approximately constant over the range of bias voltages applied (see Table I) and therefore the increased GPC can be attributed to the lower density of the films under these conditions. The N and C impurity levels (determined by XPS, not shown in table) are respectively 0.1 and 0.5 at.% for films deposited without biasing, comparable to TiO2 films previously deposited using the same precursor. When −200 V RF biasing is applied, the N and C contents increased to 0.8 and 1.0 at.%.

This study demonstrates that substrate biasing allows for additional control over thin film material properties during plasma-assisted ALD, by tuning the ion energy. More specifically, it shows that the phase composition of TiO2 thin films can be tailored by substrate biasing, in addition to other parameters reported in the literature such as the reactant pressure, the deposition temperature, the substrate material and post-deposition annealing. Also the compositional properties of TiO2 films are affected by biasing, which allows for tuning the electrical, structural and optical properties of the films. In preliminary studies, effects of biasing on other metal oxide systems have been confirmed as well. For Al2O3 and Co3O4 thin films deposited by plasma-assisted ALD, for example, we found that the GPC and the oxide-to-metal ratio were affected by substrate biasing. Accordingly after the initial second) such that the exposure to high energy plasma pulse during ALD. For instance, the substrate biasing can be enabled only after the ALD surface reactions have taken place (typically after the initial second) such that the exposure to high energy ions can be considered an in-situ film treatment executed every ALD cycle.

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### Table I. Influence of the bias voltage on the material properties of ~50 nm thick TiO2 films deposited at 300 °C. Substrate-tuned biasing was employed for −50 and −100 V, whereas RF substrate biasing was applied for −100, −150 and −200 V (voltages labeled by asterisks). The relative errors in the [O]/[Ti] ratio, the mass density and the number of Ti atoms deposited (all determined by RBS) are 4%, 4% and 3%, respectively. For the H content (determined by ERD), the relative error is 7%.

<table>
<thead>
<tr>
<th>Bias voltage (V)</th>
<th>[O]/[Ti] ratio</th>
<th>Mass density (g cm⁻³)</th>
<th>H content (at.%)</th>
<th>Ti atoms deposited (× 10¹⁴ cm⁻² cycle⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.0</td>
<td>3.7</td>
<td>1.4</td>
<td>2.4</td>
</tr>
<tr>
<td>−50</td>
<td>2.0</td>
<td>3.7</td>
<td>1.4</td>
<td>2.6</td>
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<tr>
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<td>3.4</td>
<td>5.2</td>
<td>2.3</td>
</tr>
<tr>
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<td>3.5</td>
<td>4.4</td>
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<tr>
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<td>4.0</td>
<td>2.3</td>
</tr>
<tr>
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<td>3.3</td>
<td>6.1</td>
<td>2.2</td>
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</tbody>
</table>