Atomic layer deposition of Nb-doped TiO2: dopant incorporation and effect of annealing

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ABSTRACT

Transparent conductive oxides form an important group of materials that combine high conductivity with high transparency. In this context, the authors designed an atomic layer deposition process for Nb-doped TiO$_2$. The presented process enables accurate control over both the position and concentration of the Nb dopants. The as-deposited films become crystalline (brookite) and low resistive ($4.3 \times 10^{-3} \Omega \text{cm}$) upon a postdeposition anneal with temperatures as low as 300 °C. Variations in annealing ambient and temperature yielded resistivity changes over four orders of magnitude and significant changes in the sub-bandgap absorption of light. Next to doping, annealing is therefore shown to be a powerful tool in controlling electrical and optical properties of TiO$_2$:Nb.

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I. INTRODUCTION

Transparent conductive oxides (TCOs) form an important group of materials that exhibit low resistivity as well as high optical transparency. Typically, the resistivity is in the order of $10^{-4} - 10^{-3} \Omega \text{cm}$ and the transmittance in the visible light range is $\geq 80\%$ for thin films. TCOs find their main applications as transparent electrodes in displays and solar cells. Two very well-known examples include indium oxide (In$_2$O$_3$) and zinc oxide (ZnO). To obtain a good electrical conductivity of these materials, doping is essential. A typical dopant for In$_2$O$_3$ is tin (Sn), leading to Sn-doped In$_2$O$_3$ abbreviated as In$_2$O$_3$:Sn and ITO. To obtain a good electrical conductivity of these materials, doping is essential. Aluminum (Al) is a commonly used dopant for ZnO, forming Al-doped ZnO also known as ZnO:Al and AZO.

Titanium oxide (TiO$_2$) is a material with a wide bandgap (3.0–3.6 eV) enabling transparency in the visible range. It possesses several attractive properties such as a high refractive index, high transmittance in the infrared range of the spectrum, high stability in reducing atmospheres, and photocatalytic activity. It has been shown that the electrical conductivity of TiO$_2$ can be greatly enhanced by introducing dopants (Al, Ag, Co, Nb, Ni, and N) making it an interesting TCO candidate. One of the promising dopants to turn TiO$_2$ into a highly conductive oxide is niobium (Nb). In the last years, Nb-doped TiO$_2$ (TiO$_2$:Nb or TNO) has been explored by various deposition techniques including sputtering, sol-gel processing, pulsed layer deposition, and atomic layer deposition (ALD).

ALD is a cyclic deposition method in which the surface is sequentially exposed to vapors or gases in an alternating fashion. The gases and vapors react in a self-limiting fashion with the surface and thereby grow a film. The self-limiting nature of ALD enables very accurate thickness control, i.e., down to the subnanometer level. Simultaneously, a very high conformality and uniformity are typically achieved due to the fact that the flux of the reacting gas to the surface is irrelevant for the growth rate when working with sufficient large exposures. These unique features make this technique well suited to meet the demands for an increasing number of...
applications, including those requiring TCOs. In many emerging applications it is necessary to cover 3D-nanostructures with thin, yet highly conformal films. Examples include transparent contacts for nanowire solar cells and coating of nanoparticles for catalysis. The low deposition temperature (which can be as low as room temperature in some cases) and soft deposition nature of thermal ALD (i.e., the absence of energetic species) makes it also compatible with sensitive materials and devices that can be easily damaged by deposition techniques such as sputtering.

For the deposition of doped films, ALD is a very interesting option due to its unique way of incorporating dopants. Doping of ALD films is commonly realized by alternating $n$ ALD cycles of the host material with one cycle of the doping material in a supercycle fashion. In the case of Nb-doped TiO$_2$, $n$ cycles of TiO$_2$ are alternated with one cycle of Nb$_2$O$_5$. In theory, this enables very precise control over the amount and position of the dopants in the film although in practice some issues can exist. These distinct advantages have driven the exploration of Nb-doped TiO$_2$ by this particular technique.

The first ALD TiO$_2$:Nb films were prepared by Pore et al. using titanium(IV) methoxide as Ti-precursor, niobium(V) ethoxide as Nb-precursor, and H$_2$O as reactant. Subsequently, others prepared TiO$_2$:Nb as well exploring titanium(IV) chloride as Ti-precursor and tris(diethylamido)(tert-butylimido) niobium (V) as Nb-precursors. In many of these studies, the deposited films have an amorphous nature and typically show a high resistivity in the as-deposited state. A lower resistivity ($\sim 10^{-3} \ \Omega \ \text{cm}$) can be obtained after crystallizing the films to the anatase phase using a postdeposition annealing (PDA) treatment. The latter is typically performed at 500–600 °C in a reducing ambient.

In this work, we have extended the available ALD processes for TiO$_2$:Nb by exploring a recipe based on tetrakis(dimethylamino)titanium, Ti[N(CH$_3$)$_2$]$_4$ (Strem Chemicals Inc., ≥99% purity) as Ti-precursor and H$_2$O as reactant. Subsequently, others allowed by one ALD cycle of an Nb$_2$O$_5$ recipe in a supercycle fashion until the desired film thickness is reached (see Fig. 1). The niobium fraction in the film was changed by varying $n$ between 10 and 80. A brief description of the two ALD processes follows below.

The TiO$_2$ recipe is a thermal ALD process using TDMAT (tetrakis(dimethylamino)titanium, Ti[N(CH$_3$)$_2$]$_4$) (Strem Chemicals Inc., ≥99% purity) as Ti-precursor and H$_2$O as coreactant. TiO$_2$ is kept at 60 °C and bubbled with 100 SCCM Ar (99.999% pure). The first half-cycle of the process consists of 1 s TDMAT dosing while the chamber pressure is kept at 80 mTorr using an automatic pressure controller. Subsequently, the chamber is purged with Ar for 10 s at 20 mTorr. The second half-cycle consists of 100 ms vapor-drawn dosing of H$_2$O, which subsequently resides in the chamber for 1 s at 40 mTorr. The ALD cycle ends with 15 s of Ar purging at 20 mTorr.

The niobium oxide recipe is a thermal ALD process based on the work reported by Basuvalingam et al. using TBTDEN (tris(diethylamido)(tert-butylimido)niobium, [(CH$_3$)$_2$N]$_3$Nb(N(CH$_3$)$_3$]...
(Strem Chemicals Inc., ≥98% purity) as a niobium precursor and H₂O as a reactant. The precursor was kept in a container at 65 °C and bubbled with 100 SCCM Ar. The first half-cycle consists of 8 s dosing of TBTDEN with the pressure in the reaction chamber kept at 80 mTorr. Next, the chamber is purged with Ar for a duration of 5 s at 20 mTorr. The second half-cycle consists of 250 ms dosing of H₂O in the vapor phase followed by a 3 s reaction step in which the H₂O resides in the reactor at a pressure of 80 mTorr. The cycle ends with 60 s of Ar purging at 20 mTorr.

The ALD dopant cycle ratio is defined as
\[
R = \frac{1}{1 + n}
\]  
with \((1 + n)\) the total number of ALD cycles in a supercycle. The concentration of Nb atoms divided by the concentration of Ti and Nb atoms in the TiO₂:Nb film is defined as the doping fraction
\[
DF = \frac{[Nb]}{[Nb] + [Ti]}
\]

The atomic concentrations for Nb ([Nb]) and Ti ([Ti]) were determined by x-ray photoelectron spectroscopy (XPS) depth-profiling. The film thickness and optical properties of the films were obtained from spectroscopic ellipsometry using a J.A. Woollam Co., Inc. M2000 rotating compensator spectroscopic ellipsoider. The ellipsometry data (\(\Psi\) and \(\Delta\)) were modeled with CompleteEASE software. The c-Si substrate with 450 nm SiO₂ layer was modelled using the approach of Herzinger et al. The ~30 nm thick TiO₂:Nb films were modeled with a Cody–Lorentz oscillator (one of the common models for TiO₂ II) extended with a Gaussian oscillator positioned at about 0.8 eV (1550 nm) to account for subgap oscillator. The growth per cycle (GPC) of TiO₂:Nb was determined by dividing the film thickness by the total number of ALD cycles. Alternating current (ac) Hall measurements, performed with a Lake Shore model 8404, provided information about the electrical conductivity, mobility, and carrier concentration of the films. The Hall measurements were performed at room temperature using the van der Pauw method. The crystallinity of the material was analyzed with Raman spectroscopy using a Renerishaw Raman microscope. The intensity of the Raman spectra was normalized using the silicon peak of the substrate at ~520 cm⁻¹. TEM studies were performed using a probe-corrected JEOL ARM operated at 200 kV and equipped with a 100 mm² Centaury SDD energy-dispersive x-ray spectroscopy (EDX) detector. Both bright field TEM and high angle annular dark field (HAADF) scanning TEM modes were used. Cross-sectional TEM samples were made using a standard lift-out focused ion beam preparation protocol. The samples consisted of a TiO₂:Nb film deposited on a 10 nm ZnO film on the Si substrate with 450 nm SiO₂. The TiO₂:Nb was capped with a 30 nm Al₂O₃ film. Both ZnO and Al₂O₃ were prepared by ALD. XPS provided information about the chemical composition of the films. For XPS measurements, a Thermo Scientific KAI066 spectrometer employing monochromatic Al Kα (hv = 1486.6 eV) x-ray radiation was used. The background subtraction method for measured XPS spectra was a Shirley background with the additional constraint that the background should not be of greater intensity than the actual data at any point in the region. The C–C peak at 284.8 eV originating from adventitious carbon is used as a charge correction reference. The PDA treatments described in this work were performed employing a Lipelec Rapid Thermal Annealer (RTA). Various ambients were used during annealing including a forming gas (FGA) (10 Vol. % H₂ in N₂) and oxygen diluted in nitrogen (20 Vol. % O₂ in N₂). Additional details about the specific anneal treatments are provided in the Results section.

III. RESULTS AND DISCUSSION

A. ALD process properties of TiO₂:Nb

The growth per cycle for the undoped TiO₂ (\(R = 0\)) was found to be 0.41 ± 0.01 Å. The GPC of pure Nb₂O₅ (\(R = 1\)) was determined to be 0.36 ± 0.01 Å. Given the fact that these GPC values are quite close, the GPC for TiO₂:Nb was determined by dividing the TiO₂:Nb film thickness by the total number of TiO₂ and Nb₂O₅ ALD cycles. This approach yielded a GPC for the doped films of about 0.40 ± 0.01 Å per ALD cycle for all investigated doping concentrations (see Fig. 2). Evidently, for the investigated range of doping concentrations, the film growth of the doped films is nearly identical to that of pure TiO₂. Therefore, the growth seems to be rather unaffected by the presence of the intermediate Nb₂O₅ ALD cycles in the recipe; i.e., no additional nucleation delays or etching effects are observed, in contrast to, for example, for the extensively studied case of ZnO:Al.

From XPS depth-profiling, the atomic Nb fraction of the deposited TiO₂:Nb films \(DF\) was determined as a function of the ALD cycle ratio \(R\). Figure 3 confirms that Nb atoms are effectively incorporated in the films and that there is a linear relation between the Nb fraction of the film \(DF\) and the fraction of ALD cycles.
The value of $1.40 \pm 0.04$ is the slope corresponding to the linear fit through the data points of Fig. 3(b). These results can be compared with the work of Niemelä et al.\textsuperscript{28} and Pore et al.\textsuperscript{29} Niemelä et al.\textsuperscript{28} used TiCl$_4$ as Ti-precursor and Nb(OEt)$_5$ as Nb-precursor to grow TiO$_2$:Nb films. For pure TiO$_2$, they found a GPC close to this work: 0.47 Å. Like in our work, they also observed a linear relation between $R$ and $DF$ although the slope is somewhat lower ($\sim 0.92 \pm 0.02$). Different from this work is that they observed the effect that the intermediate Nb$_2$O$_5$ ALD cycles in the recipe decreased the GPC. There can be various reasons for a growth delay for TiO$_2$ after one cycle of Nb$_2$O$_5$ (see, e.g., the discussion on the growth delay between ALD ZnO and SnO$_x$ in the work of Hägglund et al.\textsuperscript{47}), but a main difference between our process and the process of Niemelä et al.\textsuperscript{28} is that the Nb-precursor and Ti-precursor have a similar chemical structure in our work while the one of Niemelä et al. involves a combination of a halide and a metalorganic precursor.

Pore et al.\textsuperscript{29} used Ti(OEt)$_4$ as Ti-precursor and Nb(OEt)$_5$ as Nb-precursor to grow TiO$_2$:Nb. The GPC of pure TiO$_2$ with this process is significantly lower than in this work: 0.3 Å. The relation between $R$ and $DF$ was found to be linear in that study as well, with a slope of $-0.81 \pm 0.07$. Consequently, the Nb incorporation of the recipe used in this work is relatively high compared to these two other reports.

**B. Compositional and structural properties**

The chemical composition of the films was analyzed by XPS, and all spectra are provided in the supplementary material.\textsuperscript{69} These measurements revealed that all the as-deposited films have high purity with carbon and nitrogen levels below 2 and 1 at. %, respectively.

To investigate the distribution of the Nb dopants in the TiO$_2$:Nb films, the films were analyzed using cross-sectional transmission electron microscopy (TEM). Through this technique, it appeared that for TiO$_2$:Nb deposited by ALD in a supercycle fashion, the Nb atoms are concentrated in horizontal planes. Figure 4(a) shows the HAADF scanning transmission electron microscopy (STEM) cross section image of an 30 nm TiO$_2$:Nb film with $R = 0.01$ in the as-deposited state. In the image, brighter lines are (weakly) visible, indicating thin Nb$_2$O$_5$ planes separating much thicker TiO$_2$ layers. An energy-dispersive x-ray spectroscopy (EDX) composition profile, shown in Fig. 4(b), clearly shows the localized Nb atoms. This profile remained virtually unaffected upon 60 min forming gas anneal at 300 °C. The Nb dopants in the ALD TiO$_2$ films are, thus, concentrated in planes and not homogeneously distributed throughout the film. This is very similar to what has been observed for the Al-dopants in ZnO:Al by ALD.\textsuperscript{11,48–50} The reason for these layered structures in
TiO$_2$:Nb and ZnO:Al is the supercycle fashion in which the dopants are introduced at well-defined locations in the film.

The crystallinity of the TiO$_2$:Nb films was investigated with Raman spectroscopy, and the results are displayed in Fig. 5. All three crystal phases of TiO$_2$ are considered here: anatase, brookite, and rutile. For both undoped and doped TiO$_2$ films, no Raman peaks associated with any of these crystal phases of TiO$_2$ are observed in the as-deposited state, while only peaks corresponding to the silicon substrate are visible in the Raman spectra; i.e., the as-deposited films are amorphous. The latter has been previously reported for ALD TiO$_2$:Nb films.\textsuperscript{28,29}

Raman peaks associated with brookite TiO$_2$ are observed for the same films after 60 min forming gas annealing at 300 °C; i.e., the films transform into the brookite crystal phase of TiO$_2$. This is different from most earlier reports on ALD TiO$_2$:Nb, which usually report the anatase phase TiO$_2$:Nb.\textsuperscript{28,29,32} The difference in the post-deposition annealing temperature (300 °C instead of 500–600 °C\textsuperscript{28,29,32}) seems to be an important factor in explaining this discrepancy, as increasing the annealing temperature to 600 °C for 30 min did change the brookite films at several spots to the anatase phase as well (see Fig. 5). Prolonged annealing or elevated temperatures may transform the films completely to the anatase phase.

As can be seen in Fig. 5, the Raman peaks become broader and slightly less intense with increasing doping concentration. The latter indicates that the crystallinity decreases with increasing doping concentration, as is also observed by other studies on doped TiO$_2$.\textsuperscript{51–53}

Besides Raman measurements, the crystallization upon annealing is visualized by employing bright field transmission electron microscopy (TEM) cross sections of an ∼30 nm thick TiO$_2$:Nb film deposited at 200 °C with doping concentration $DF = 0.014$. Figure 6(a) shows a homogeneous TiO$_2$:Nb layer, showing no clear crystalline features, confirming the amorphous character of the as-deposited films found by Raman spectroscopy. After annealing the films at 300 °C, the TEM cross section in Fig. 6(b) confirms the crystalline character of the film. Grains are extending throughout the entire thickness of the layer, i.e., across the Nb-doped layers. The many contrast variations in the film indicate the presence of stacking faults in the TiO$_2$:Nb crystal lattice.

C. Electrical properties

The electrical properties of the TiO$_2$:Nb films were investigated using Hall measurements. The electrical properties were examined for the films in the as-deposited state, as well as after several postdeposition annealing treatments. These different annealing treatments include forming gas annealing at 300 °C, forming gas annealing at 600 °C, decreasing the anneal ramp rate from 30 °C/s to 0.08 °C/s, and finally annealing in an oxygen-rich ambient instead of a forming gas ambient. The experimental observations are shown in Fig. 7.

The as-deposited TiO$_2$:Nb films show all a very similar electrical resistivity of 3 $\Omega$ cm. Remarkable is that no effect of the
resistivity on the dopant concentration is observed. Mobility and carrier concentration measurements of these films were unsuccessful, indicating a very low mobility and carrier density of these thin and amorphous films.\textsuperscript{54}

After a forming gas annealing treatment at 300 °C for 60 min, the resistivity of the films decreases by several orders of magnitude, as shown in Fig. 7(a). A clear decrease in the resistivity is observed with increasing doping concentration, leading to resistivity values as low as $\rho = 8.7 \times 10^{-3}$ Ω cm. Exception to this trend is the film with the highest Nb concentration; here a slight resistivity increase is observed compared to the as-deposited state. The TiO$_2$:Nb films annealed at a temperature of 600 °C for 30 min show also a decreasing resistivity as a function of the doping concentration, reaching a minimal resistivity of $\rho = 4.5 \times 10^{-4}$ Ω cm [see Fig. 7(a)]. However, the absolute resistivity values of these films are higher than the resistivity in the as-deposited state.

To get more insight into the electrical conductivity, we have also attempted to determine the carrier density and mobility of these annealed films using alternating current Hall measurements. The lower temperature annealing treatment (300 °C) yielded films that could be measured with our setup, but measurements of the films annealed at the higher temperature (600 °C) did not yield reliable results. The latter is likely due to a lower carrier density than the films annealed at 300 °C.

Hall measurements of the films annealed at 300 °C reveal that the decrease in resistivity with doping concentration is related to a higher free electron concentration $n_e$, which increases up to $n_e \approx 1 \times 10^{21}$ cm$^{-3}$, as shown in Fig. 7(b). The Nb dopants are clearly active after the annealing treatment. With respect to the carrier concentration, it is interesting to note that the undoped TiO$_2$ film exhibits already a reasonably high carrier concentration ($8.7 \times 10^{19}$ cm$^{-3}$). The latter suggests that, besides extrinsic Nb doping, intrinsic doping of the TiO$_2$ is present. This intrinsic doping is likely the consequence of oxygen-related defects or so-called oxygen vacancies.\textsuperscript{55,56} By annealing in an oxygen-rich ambient, the number of oxygen vacancies can be reduced. If these vacancies are important for the conductivity, an annealing treatment in an oxygen ambient should consequently increase the resistivity. The latter seems indeed to be the case. Annealing for 60 min at 300 °C in an N$_2$:O$_2$ (80:20) gas mixture leads to a resistivity that is nearly 10$^4$ times higher than annealing for 60 min at 300 °C in forming gas [Fig. 7(a)].

The electron mobility of the TiO$_2$:Nb films annealed in forming gas at 300 °C appears to be rather independent of the doping concentration and has a value of $\mu_e \approx 0.7$ cm$^2$/Vs as shown in Fig. 7(b). This mobility can be improved significantly by employing lower ramp rates in the postdeposition annealing process. By decreasing the ramp rate from 30 to 0.08 °C/s, the mobility increased with a factor of 3 from $\mu_e = 0.6$ cm$^2$/V s to $\mu_e = 1.9$ cm$^2$/V s. Pore et al.\textsuperscript{29} also observed the formation of larger crystals by decreasing the ramp rate of the postdeposition annealing process. They argued that there might be a lower nucleation density at lower ramp rates, which results in fewer, but larger crystals. Larger crystals decrease the number of grain boundaries at which carriers can scatter, and consequently, it can improve carrier mobility. The increase in mobility could, therefore, well be the result of larger crystals. The carrier concentration also shows a small increase of about 13% upon decreasing the ramp rate. The combination of these effects enables a reduction of the resistivity to the lowest value obtained in this work: $4.3 \times 10^{-3}$ Ω cm.

It is striking that the annealing temperature of 300 °C leads to a greatly reduced resistivity, while 600 °C annealing has led to a higher resistivity than the as-deposited films, something that is in contrast to earlier work.\textsuperscript{28,29} A possible reason for this difference could be a significant presence of intrinsic dopants in our TiO$_2$:Nb films. Like the oxygen annealing treatment, a higher annealing temperature could cure more (oxygen-related) defects in the film and thereby decrease the role of intrinsic dopants in TiO$_2$. Postdeposition annealing of the films studied in this work may, therefore, have two effects: activation of the Nb dopants and decreasing the intrinsic doping. The interplay between these effects determines the resistivity of the film.

A second peculiarity to discuss is the fact that the resistivity of the film with the highest doping concentration (DF = 0.13) does increase upon annealing at 300 °C. An important reason for this is that the film did not crystalize upon this annealing treatment.
(Fig. 5), thereby leaving the dopants inactive and the mobility very low. Although this reason explains the absence of a decrease in resistivity upon annealing, it does not explain the observed increase. The latter might be explained by what was pointed out at the end of the previous paragraph: Annealing has also the effect of reducing defects responsible for intrinsic doping.

It is useful to compare these observations with the existing literature. This work shows that there is no effect of doping on the resistivity for as-deposited amorphous TiO2:Nb films. A postdeposition annealing treatment at both 300 and 600 °C leads to crystallization of the films (Fig. 5) and simultaneously a clearly decreasing trend of the resistivity with doping appears [Fig. 7(a)].

The value of the exponent \( \gamma \) depends on the nature of the optical transitions: \( \gamma = 1/2 \) for indirect bandgap transitions and \( \gamma = 2 \) for direct bandgap transitions. Although there is discussion in the literature about the nature of the optical transition in TiO2,\(^{31} \) we will follow the most common approach in literature, which is to assume an indirect transition.\(^{14,12-14} \)

A few Tauc plots of the TiO2:Nb films studied in this work are shown in Fig. 8. The absorption coefficient \( \alpha \) required to construct these plots is determined from the complex refractive index data obtained by spectroscopic ellipsometry. The bandgap value is determined from the intercept of the linear fit on the absorption edge with the horizontal axis. The resulting bandgap values are given in Fig. 9.

As can be seen in Fig. 9, the effect of the doping concentration on the Tauc plots is minor compared to the changes observed after different annealing treatments; we will, therefore, focus on the latter. Figure 8 represents the Tauc plots for an ~30 nm thick TiO2:Nb film with \( \text{DF} = 0.067 \) after various anneal treatments. The as-deposited films (black curve) exhibit a bandgap of about 3.50 eV. The refractive index \( n \) at \( \lambda = 589 \text{ nm} \) for the as-deposited films was found to be \( \sim 2.3 \). Annealing in either forming gas (blue curve) or oxygen ambient (red curve) at a temperature of 300 °C transforms the amorphous films with \( \text{DF} = 0.067 \) to crystalline films in the brookite phase (Fig. 5) and slightly decreases the optical bandgap to a value of about 3.35 eV. This value falls in the middle of the wide range of bandgap values (3.0–3.6 eV) reported for the brookite crystal phase.\(^{23,57} \) The refractive index \( n \) at \( \lambda = 589 \text{ nm} \) was observed to increase slightly to 2.5, which is similar to values reported by other studies.\(^{30,57} \) The films annealed in forming gas for 30 min at 600 °C are characterized by a mixed phase of brookite and anatase crystals (Fig. 5) and show an optical bandgap of \( \sim 3.25 \text{ eV} \). The latter is close to the value of 3.2 eV that has been reported previously for the anatase phase\(^{14-16} \), where the refractive index \( n \) at \( \lambda = 589 \text{ nm} \) is \( \sim 2.7 \).

D. Optical properties

The optical bandgap of TCOs is commonly determined from so-called Tauc plots.\(^{32} \) In such a plot, \( (\alpha h \nu)^2 \) is plotted against \( h \nu \), where \( \alpha \) is the absorption coefficient and \( h \nu \) is the photon energy. The value of the exponent \( \gamma \) depends on the nature of the optical transitions: \( \gamma = 1/2 \) for indirect bandgap transitions and \( \gamma = 2 \) for direct bandgap transitions. Although there is discussion in the literature about the nature of the optical transition in TiO2,\(^{31} \) we will follow the most common approach in literature, which is to assume an indirect transition.\(^{14,12-14} \) A few Tauc plots of the TiO2:Nb films studied in this work are shown in Fig. 8. The absorption coefficient \( \alpha \) required to construct these plots is determined from the complex refractive index data obtained by spectroscopic ellipsometry. The bandgap value is determined from the intercept of the linear fit on the absorption edge with the horizontal axis. The resulting bandgap values are given in Fig. 9.

As can be seen in Fig. 9, the effect of the doping concentration on the Tauc plots is minor compared to the changes observed after

![Figure 8: Tauc plots from the absorption coefficient obtained from spectroscopic ellipsometry. The plots belong to ~30 nm thick TiO2:Nb films with a doping concentration of \( \text{DF} = 0.067 \) in as-deposited state (black), after 60 min of forming gas annealing at 300 °C (blue), after 60 min of oxygen annealing at 300 °C (green), and after 30 min of forming gas annealing at 600 °C (red).](image)

![Figure 9: Tauc plots based on the absorption coefficient data obtained from spectroscopic ellipsometry measurements conducted on an ~30 nm thick TiO2:Nb film with different doping concentrations after 60 min forming gas annealing at 300 °C.](image)
It is interesting that significant absorption below the bandgap is observed for the TiO$_2$:Nb films in the as-deposited state and also after a 300 °C forming gas annealing treatment (Fig. 8). Literature suggests oxygen vacancies or oxygen defects as likely candidates for this absorption in TiO$_2$. When the films are annealed in an oxygen ambient at 300 °C or when they are annealed at 600 °C, this so-called subgap absorption is significantly reduced. These two types of annealing treatments also give rise to a significant increase in resistivity compared to the as-deposited state or the 300 °C FGA film. The decrease of the intrinsic doping of our TiO$_2$:Nb films due to oxygen vacancies might be responsible for this increase in resistivity, which is a phenomenon that is well established in the literature. Both optical and electrical measurements, thus, seem to suggest that oxygen vacancies or oxygen-related defects are present in our TiO$_2$:Nb films and, consequently, introduce additional electrical conductivity and sub-bandgap absorption due to free carriers. Annealing in an oxygen-rich ambient or at elevated temperatures (600 °C) seems to eliminate these oxygen-related defects and consequently increase the resistivity and decrease the free carrier absorption below the bandgap.

IV. SUMMARY AND CONCLUSIONS

Nb-doped TiO$_2$ films with various doping concentrations have been deposited by atomic layer deposition using TDMA as Ti-precursor and TTDTEN as Nb-precursor. The incorporation of Nb dopants in the TiO$_2$ film correlates linearly with the dopant concentration of the Nb-doped TiO$_2$ films with various doping concentrations ranging from 0.6 to 15 at.%. A lower ramp rate of the annealing treatment showed, however, that this value is improvable by almost a factor 3 ($\mu$ of 1.9 cm$^2$/V s). A lower ramp rate of the annealing treatment showed, however, that this value is improvable by almost a factor 3 ($\mu$ of 1.9 cm$^2$/V s).

The Ndoped TiO$_2$:Nb films are amorphous in nature. They show a relatively high resistivity (p = 3 Ω cm) as well as a relatively large optical absorption in the bandgap. Annealing at 300 °C crystallizes the films to brookite TiO$_2$. It activates the dopants, and it enables resistivities that can be considered low compared to the literature in this doping range (p = 4.3 × 10$^{-3}$ Ω cm). Highly conductive TiO$_2$:Nb films can, thus, be realized with this process. Moreover, high temperature annealing (>300 °C) is not necessarily required to obtain this result. The electron mobility of the films was found to be relatively low compared to the literature ($\mu$ of 0.6 cm$^2$/V s). A lower ramp rate of the annealing treatment showed, however, that this value is improvable by almost a factor 3 ($\mu$ of 1.9 cm$^2$/V s).

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