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Suppressed grain-boundary scattering in atomic layer deposited Nb:TiO₂ thin films

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We have fabricated high-quality thin films of the transparent conducting anatase Nb:TiO₂ on glass substrates through atomic layer deposition, and a subsequent reductive heat treatment of the as-deposited amorphous films. Hall-effect measurements and Drude-fitting of the Vis-NIR spectra indicate that for lightly doped films deposited at temperatures around 170 °C, grain boundary scattering becomes negligible and the mobility is predominately limited by phonon-electron scattering inherent to the anatase lattice and by impurities. Simultaneously, such lighter doping leads to reduced plasma absorption, thereby improving material's performance as a transparent conductor.

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Niobium-doped anatase TiO₂ is a promising transparent conducting oxide (TCO) owing to its large band gap of 3.2 eV and electrical resistivity as low as $2 \times 10^{-4} \Omega \text{ cm}$; the high refractive index and high IR transmittance make it then particularly an attractive material candidate for applications such as solar cells and blue light emitting diodes.^{1–3} Typically, high-mobility thin films with large and oriented crystal grains can be fabricated on epitaxial substrates. However, for many real-life applications, the thin films should be fabricated on glass substrates, when the control over the crystallinity of the films becomes more challenging.

High-enough fabrication temperatures allow for deposition of crystalline Nb:TiO₂ thin films on glass; the films, however, typically suffer from small grain size and consequently higher resistivity. In principle, the resistance of these crystalline films could be decreased by a post-deposition annealing treatment, enabling the grain size to increase *via* grain coalescence. However, as TiO₂ is prone to the phase transition from the low-resistivity anatase to the high-resistivity rutile structure at temperatures above 600 °C,^{4,5} the grain coalescence is not easily achieved. Fortunately, it has been shown for films fabricated with physical deposition methods that lowering of the deposition temperature allows for fabrication of amorphous films, for which a subsequent reductive annealing then yields crystalline materials with large-enough grain size and notably enhanced conductivity.^{6,7}

As an increasing number of applications require for the thin films to be deposited onto high-aspect-ratio nanostructures, physical line-of-the-sight coating methods fail in terms of providing the demanded conformality. Contrary to this, in chemical gas-phase deposition techniques, the precursors can diffuse onto the coated surfaces *via* random trajectories, such that the coating closely adopts the shape of the substrate surface. Particularly suitable for conformal and large-area

coatings is the atomic layer deposition (ALD) technique, where the self-limiting surface reactions furthermore guarantee Ångström-level thickness control over the film growth.^{8,9}

So far, ALD has been used to deposit Nb:TiO₂ thin films at temperatures higher than 200 °C,^{10,11} that is, above the crystallization temperature for the as-deposited undoped TiO₂ films.^{12,13} At these temperatures, Nb-doping suppresses the crystallization of the highly doped films when the subsequent post-deposition annealing treatment yields large-enough crystal grains, and grain-boundary scattering plays a negligible role for electron mobility. However, simultaneously the high Nb concentration leads to excessive Nb-impurity scattering and reduced IR transmission *via* plasma absorption.¹⁴ At the same time for the low Nb-to-Ti ratios, for which the impurity scattering and plasma absorption are at an acceptable level, the Nb content is not sufficient to suppress crystallinity, and the post-deposition annealing treatment leads to small-grained films that suffer from grain-boundary scattering.¹⁴

In this work, we probe the low-temperature limits of the TiCl₄/Nb(OEt)₅/H₂O ALD process by depositing Nb:TiO₂ films at temperatures as low as 100 °C. By analysing the optical mobility, obtained by fitting of the visible-near-infrared (Vis-NIR) reflectance and transmittance, and Hall mobility (2–300 K) data, we show that lightly doped Nb:TiO₂ films free from grain boundary scattering can be fabricated by annealing amorphous films deposited at around 170 °C, and that then the conduction electrons are predominately scattered by optical phonons inherent to the anatase lattice and by impurities. Moreover, by analysing the Vis-NIR optical spectra, we conclude that for the lightly doped films, plasma absorption decreases—a fact that improves the IR transparency of the films.

We deposited a series of Nb:TiO₂ thin films on borosilicate glass substrates at temperatures from 100 to 280 °C (Picosun R-100 ALD reactor). First, we confirmed the film growth for the binary TiO₂ and Nb₂O₅ thin films *via* the TiCl₄/H₂O and Nb(OEt)₅/H₂O processes, respectively. Then,

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aiming at the light Nb-doping level of 5%, comparable to the optimal Nb content of 6% for PLD-fabricated Nb:TiO₂ films 2000-ALD-cycle thick were deposited by repeating the supercycle of 19 TiCl₄/H₂O cycles + 1 Nb(OEt)₅/H₂O cycle 100 times. This resulted in films with thicknesses around 70 nm as confirmed by X-ray reflectivity (XRR; PANalytical X'Pert Pro MPD diffractometer) measurements. Further details on the deposition process can be found from our previous reports.^{11,14}

Incorporation of the Nb dopants into the TiO₂ films was investigated by determining the composition of the Nb:TiO₂ films by X-ray fluorescence (XRF; PANalytical Axios^mAX). Different from our previous study, where for the films deposited at 210 °C practically one-to-one relation was obtained between the ALD-cycle ratio and Nb/(Nb+Ti) atomic ratio, here we found that the amount of Nb incorporated into the films by a single Nb(OEt)₅/H₂O cycle dramatically increases at temperatures ≤150 °C (Fig. 1(a)). Such an increase could be explained in terms of the growth-per-cycle (GPC) values for the doped films; however, the GPC values for the doped films increase only slightly below 150 °C (Fig. 1(b)). On the other hand, for the binary Nb(OEt)₅/H₂O process, a more pronounced increase of the GPC value is seen at 100 °C, which could be ascribed to physisorption of H₂O and/or Nb(OEt)₅ precursors. Yet, this increase in the GPC for the binary process is only 30%, while the Nb content in the doped films increases roughly by 500%. It is known that the hydroxyl group density on the TiO₂ surfaces increases with decreasing temperature;^{15,16} therefore, at low temperatures, increasing amounts of Nb by single Nb(OEt)₅/H₂O cycles could be incorporated into the Nb:TiO₂ films, as the number of active binding sites for the Nb(OEt)₅ precursor increases. We hence believe that the increased Nb content at low temperatures is a result of both increased chemisorption and physisorption of the Nb(OEt)₅ precursor. Consequently, we only consider the Nb:TiO₂ films fabricated above 150 °C as lightly doped.

Our ALD process yielded amorphous Nb:TiO₂ thin films below 190 °C as was evidenced from grazing incidence X-ray diffraction (GIXRD; PANalytical X'Pert Pro MPD diffractometer) measurements (Fig. 1(c)). To crystallize the as-deposited films and to introduce the final electronic properties, the films were then annealed at 600 °C in an H₂/Ar (5%/95%) gas flow for 6 h (Nabertherm GmbH RS 80/500/11). It is clearly revealed from Fig. 1(c) that the annealing transforms the initially amorphous films into crystalline anatase TiO₂ structure for the films deposited at 100, 150, and 175 °C, whereas for the initially crystalline film deposited at 240 °C little change is seen in the GIXRD pattern upon annealing.

In order to study the transport properties of our annealed Nb:TiO₂ thin films, we first measured room-temperature four-point resistivity in van-der-Pauw geometry for the full series of samples deposited between temperatures of 100 and 280 °C (Fig. 2(a)). It was found out that the resistivity values exhibit a clear minimum at around 170 °C with notably higher values for the lower and higher deposition temperatures. Moreover, 3% and 8% Nb-doped films deposited at 175 °C showed low resistivity values of 1.7 mΩ cm and 1.9 mΩ cm, respectively; these values were though slightly higher than those for the 5% doped sample. Note that the minimum value seen here for the 5%-doped film deposited at 175 °C compares to our previously reported minimum value for a 22%-doped film deposited at 210 °C, and that it is remarkably lower than the previously measured value for a 5%-doped film deposited at 210 °C.¹⁴

We first focused on the charge transport in the films exhibiting the resistivity minimum and performed the Hall-effect measurement between 2 and 300 K (Quantum Design Physical Property Measurement System; ±9 T magnetic flux density) for the film deposited at 175 °C. Typically, for a degenerate semiconductor, the carrier electron density is independent of temperature (Fig. 2(c)), whereas resistivity

FIG. 1. (a) Nb/(Nb + Ti) ratio as a function of deposition temperature (T_{dep}) for nominally 5% Nb-doped TiO₂ films determined by XRF. (b) Growth-per-cycle (GPC) values for the binary TiCl₄/H₂O and Nb(OEt)₅/H₂O processes, as well as for the nominally 5% Nb-doped TiO₂ films. (c) Illustrative GIXRD patterns for 5% Nb-doped TiO₂ films deposited at 100, 150, 175, and 240 °C before and after annealing at 600 °C in H₂/Ar.

FIG. 2. (a) Room-temperature four-point resistivity for nominally 5% Nb-doped films deposited between 100 and 280 $^{\circ}\text{C}$ (T_{dep}) and annealed in H_2/Ar at 600 $^{\circ}\text{C}$. (b) Resistivity (ρ), (c) carrier density (n), and (d) Hall mobility (μ_{Hall}) as a function of temperature (T ; 2–300 K) for the annealed 5%-Nb-doped film deposited at 175 $^{\circ}\text{C}$, as obtained from the Hall measurements. (d) Also shows the fit based on Eqs. (1) and (2) for mobility considering impurity and phonon scattering.

(Fig. 2(b)) and mobility (Fig. 2(d)) experience decreasing and increasing trends with decreasing temperature, respectively, before a saturation-type behavior below 100 K. Such a negative slope of the mobility curve is typically ascribed to phonon scattering, while the saturation region is a signature of impurity scattering.

Considering that the mobility is predominately affected by phonon and impurity scattering, the total mobility can be written as

$$\mu_{\text{tot}}^{-1}(T) = \mu_i^{-1} + \mu_p^{-1}(T). \quad (1)$$

Here, μ_i is the temperature-independent impurity contribution and $\mu_p(T)$ is the temperature-dependent phonon contribution¹⁷

$$\mu_p(T) = AT \sinh^2 \left(\frac{\hbar \omega_0}{2kT} \right), \quad (2)$$

where $\hbar$ is the reduced Planck constant, k is the Boltzmann constant, ω_0 is the angular phonon frequency, and A is a variable used here as a fitting parameter. We fitted Eq. (1) to the mobility data for the 175 $^{\circ}\text{C}$ deposited film, as is shown in Fig. 2(d), obtaining a good match between the experiment and the theory with the fitting-parameter values of $\mu_i = 3.7 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, $A = 1.8 \times 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, and most importantly, with $\omega_0 = 7.0 \times 10^{13} \text{ Hz}$. The value for ω_0 translates to a wave-number value of $\nu = 372 \text{ cm}^{-1}$ ($\nu = \omega_0/(2\pi c)$, where c is the speed of light) that corresponds to the optical phonon modes of anatase TiO_2 (367 cm^{-1} transverse A_{2u} and 366 cm^{-1} longitudinal E_u)¹⁸—a fact that confirms that for the films fabricated around 170 $^{\circ}\text{C}$ impurity scattering and grain boundary scattering can be notably suppressed, and that then the carrier electrons are to large extent scattered by phonons at room temperature. Such a behavior is also characteristic for the epitaxial anatase Nb: TiO_2 films.¹⁹

In order to get more insight to the origin of the increased resistivity values below and above 170 $^{\circ}\text{C}$, as shown in Fig. 2(a), we selected the samples deposited at 150, 175, 210, and 240 $^{\circ}\text{C}$, and compared the Hall-mobility values measured at room temperature to the optical-mobility values obtained by the Drude-fitting of the Vis-NIR transmittance and reflectance spectra. As the Hall-mobility values are sensitive to grain boundary scattering and the optical-mobility values do not, comparison of the Hall and optical mobility values—as described in detail in our previous report¹⁴—can be used to separate the effect of intra-grain and inter-grain scattering to the charge transport.^{20,21}

A good fit between the Drude model and the measured transmittance and reflectance data was obtained as is shown as an example in Fig. 3(a) for the film deposited at 175 $^{\circ}\text{C}$. In the fitting procedure, the scattering time τ and the electron effective mass m^* were used as the fitting parameters, while the high-frequency dielectric constant was set as 5.9 (Ref. 22) at 240 and 210 $^{\circ}\text{C}$, 5.7 at 175 $^{\circ}\text{C}$, and 5.5 at 150 $^{\circ}\text{C}$ (the values <5.9 improved the fit slightly); the carrier electron density values retrieved from the Hall-effect measurements were used as an input to the calculation. The scattering time τ shows a moderate decrease with decreasing deposition temperature (Fig. 3(b)); this can be ascribed to the moderately increased density of Nb-point-scattering centers (see Fig. 1(a)). The other fitting parameter, the electron effective mass m^* , shows a similar though less pronounced trend due to non-parabolicity of the conduction band (Fig. 3(b)).²³ Fig. 3(c) shows the comparison of the optical mobility μ_{opt} and the Hall mobility μ_{Hall} for the films deposited at temperatures between 150 and 240 $^{\circ}\text{C}$ (the 210 $^{\circ}\text{C}$ data are from Ref. 14); for the high deposition temperatures (210 and 240 $^{\circ}\text{C}$) μ_{Hall} is more than an order of magnitude lower than μ_{opt} , indicating that charge transport is limited by grain-boundary scattering. For the film deposited at 175 $^{\circ}\text{C}$, μ_{opt} and μ_{Hall} obtain

FIG. 3. (a) Transmittance and reflectance as a function of wavelength (λ) together with the corresponding Drude model fit for the 5%-Nb-doped TiO₂ film fabricated at 175 °C and annealed at 600 °C in H₂/Ar; the inset shows the Vis-NIR absorbance comparison between the 22% Nb-doped film fabricated at 210 °C¹⁴ and the 5% Nb-doped TiO₂ film fabricated at 175 °C. (b) Effective mass m^* and scattering time τ as a function of deposition temperature (T_{dep}). (c) Hall mobility (μ_{Hall}) and optical mobility (μ_{opt}) as a function of T_{dep} .

similar values, meaning that the charge transport is governed by intra-grain scattering, that is, by the optical phonon scattering as demonstrated earlier and as shown in Fig. 2(d). For the deposition temperature of 150 °C, μ_{opt} and μ_{Hall} deviate again as a sign of the dominance of grain boundary scattering.

We propose that the strong role played by the grain-boundary scattering for deposition temperatures ≥ 210 °C stems from the small grain size due to the crystalline character of the films *prior* to the annealing treatment. For the deposition temperature 175 °C, the as-deposited film is amorphous and the crystal grains are able to freely grow larger during the post-deposition annealing, without preset boundaries by the initial crystallites. Indeed, the grain size for the annealed 175 °C deposited sample is estimated to be on the order of 10 μm from polarized light microscope (Olympus BX50) image shown in Fig. 4, that is, an order of magnitude larger than observed before for the lightly doped samples deposited at 210 °C.¹⁴ On the other hand, the film deposited at 150 °C is also amorphous as deposited, but it still shows a clear signature of grain-boundary scattering; it

FIG. 4. The polarized light microscope image for the 5% Nb-doped TiO₂ film deposited at 175 °C and annealed at 600 °C in Ar/H₂.

may be that at these even lower deposition temperatures increasing amounts of impurities could have an inhibiting effect on the crystal growth during the annealing step. In this respect, the Cl/Ti atomic ratios (in %) as obtained with XRF were 5.8 (100 °C), 2.7 (125 °C), 1.6 (150 °C), 1.7 (160 °C), 2.1 (175 °C), 2.3 (190 °C), 1.5 (210 °C), 1.2 (240 °C), and 1.1 (280 °C), that is, the amount of Cl in the films increases for the low deposition temperatures, but drastically only at 100 °C. In our previous report,¹⁴ we obtained amorphous films with a high Nb content and crystallized them with an annealing treatment; in those films μ_{opt} and μ_{Hall} were indeed found similar, and the role of the grain-boundary scattering minimal—therefore, it is unlikely that increasing Nb content at low temperatures would inhibit grain growth during the subsequent annealing. However, it could be noted that higher amounts of carbon incorporate into the films deposited at the lower temperatures, which could inhibit grain growth during the annealing treatment. However, this could not be confirmed by XRF due to lack of sensitivity of the method to carbon.

Finally, it is emphasized that, as the present suppression of the grain-boundary scattering for the 5% Nb-doped (7% by XRF) film deposited at 175 °C allows for achieving equally low resistivity value as previously with the higher Nb content (22%),¹⁴ and as simultaneously the NIR transmittance can be improved, the overall TCO performance of the films is improved (inset of Fig. 3(a)).

In conclusion, high-mobility ALD-grown Nb:TiO₂ thin films, virtually free from grain-boundary scattering, can be fabricated from amorphous as-deposited films *via* an annealing treatment. The amorphous Nb:TiO₂ films can be obtained at high level of Nb doping at the higher deposition temperatures, and, in particular, at the lower deposition temperatures for the lower levels of Nb doping. When the deposition temperature is optimal, that is around 170 °C, the electron mobility is predominately limited by optical phonons inherent to the anatase TiO₂ lattice and by impurities. Furthermore, the

lower doping levels enable improved NIR transmittance *via* decreased plasma absorption, thereby enhancing the overall performance of the materials as transparent conductors.

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