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# Functional Metal Oxide Thin Films Grown by Pulsed Laser Deposition

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Additional information is available at the end of the chapter

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## Abstract

The aim of this work is to show that material processing by laser-based technologies can lead to the growth of multifunctional thin films with potential in a large area of applications. The synthesis of Hf, Ta, Si, and Al metal oxides described here relies on the use of pulsed laser deposition (PLD), or radiofrequency (RF) assisted PLD. The morphology and structure of the as-grown thin films are investigated by atomic force microscopy, X-ray diffraction, and transmission electron microscopy, whilst the optical properties are determined by spectroellipsometry. The dielectric behaviour of the deposited layers is investigated by electrical measurements.

It is shown that by tuning the deposition parameters, the materials of interest can be synthesized as compact and dense oxide layers. Parameters such as substrate temperature, oxygen pressure, or laser wavelength have a critical impact on the crystallinity of the films, as well as on the characteristic functional properties. For example, hafnium dioxide, tantalum oxide, and aluminium oxide layers grown by RF-PLD at room temperature have low leakage currents, which make them useful for dielectric gates. When high substrate temperatures are involved in the PLD process, these oxide layers have a crystalline structure and smooth surfaces, with potential in antireflective coatings.

**Keywords:** metal oxides, thin films, pulsed laser deposition, radiofrequency assisted PLD, antireflective coatings, high-k dielectrics

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## 1. Introduction

In the past century, the continuous development of human society led to exceptional scientific and technological accomplishments, miniaturization being a key work. Challenges such as the

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decrease in the production costs together with the transition from the micro to the nanoscale represent, at present, the focus of the international scientific and industrial community. Metal oxide materials (in particular Hf, Al, Si, and Ta oxides) have been attracting considerable attention, due to their complexity which originates from their seemingly antagonistic properties that make them attractive in different applications [1]. Hafnium dioxide and aluminium oxide processed as smooth films have been considered for applications such as dielectric mirrors and high-k candidates for next-generation MOS gates [2]; grown as nanostructured materials, they show the potential for biological applications. Tantalum oxide as a smooth thin film had a fast evolution as an important material in opto-electronics, being extensively used in the production of capacitors and anti-reflection coatings [3]. The nanostructured surface morphology of tantalum oxide makes it suitable for solid-state oxygen sensors and thin-film catalysts [4, 5].

The metallic oxides can be obtained as thin films by numerous techniques, such as plasma enhanced chemical vapour deposition [6], chemical vapour deposition [7], atomic layer deposition [8], radiofrequency (RF) sputtering [9], etc. Major disadvantages of these techniques are related to the high processes temperatures, the use of expensive and highly corrosive precursors, and subsequent thermal treatments for crystallization. A reliable method for obtaining thin films of simple or complex compounds is pulsed laser deposition (PLD), also called laser ablation.

PLD has gained worldwide acknowledgement as a reliable method for obtaining thin films of simple or complex materials. The PLD relies on the interaction of the laser beam with a target material (solid or liquid), thus producing a plasma plume through which the material is carried on a substrate, as a thin film. This method has several advantages: (a) the deposition chamber is a "clean" reactor as the energy source (laser) is outside the reaction chamber, (b) the deposition process can be easily controlled because the processes involved are strongly influenced by the laser parameters (wavelength, laser fluence, laser spot area, laser pulse duration, repetition rate, etc.), (c) the thickness of the film can be controlled by the number of pulses that irradiate the material, (d) the laser radiation can be focused/imaged in a very small spot which allows the selective processing regions of interest, (e) the transfer of the target to the substrate can produce new materials in metastable states, that are impossible to be achieved by other techniques.

A general problem when depositing metal oxide thin films is the appearance of oxygen vacancies inside the layer and at the layer-substrate interface. A possible solution to this problem is the usage of a hybrid technique that combines the advantages of conventional PLD with the addition of a RF oxygen gas stream directed toward the substrate. During the growth process, the species from the laser plasma plume (Hf, Ta, Al, or Si oxides, ions, etc.) interact with the excited and/or ionized oxygen species generated by the RF discharge. This complex developed deposition technique is named as RF assisted pulsed laser deposition (RF-PLD) [10].

The plasma beam source consists of a double chamber discharge system supplied by a RF power supply. In the active chamber, the discharge is generated in an oxygen flow between two parallel electrodes. It expands into the ablation chamber as a plasma beam, through an

aperture drilled in the bottom electrode, which acts as a nozzle. RF-PLD is suitable for the synthesis of smooth and compact thin films of metal oxides or nanostructured thin films.

Therefore, in the following sections, the deposition of various metal oxide materials (Si, Ta, Hf, and Al) as thin films by PLD and hybrid PLD (RF assisted), with an emphasis on high-k gate dielectrics and antireflective coatings shall be discussed.

## 2. Experimental methods: PLD and RF assisted PLD

High-purity metal oxide targets (i.e., Hf, Ta, Si, and Al) were used for the ablation experiments using either an ArF excimer laser working at 193 nm wavelength with a variable repetition rate (1–50 Hz), pulse duration of 30 ns, or a Nd-YAG laser Surellite II, working at 355 or 266 nm, 5–7 ns pulse duration, and 1–10 Hz repetition rate. The laser fluence was optimized for each material and the target-substrate distance was 4 cm.

All substrates used for thin-film growth were thoroughly cleaned in successive ultrasonic bath (acetone, ethanol, and deionized water) to remove surface contamination before being inserted into the deposition chamber. Prior to the depositions, the vacuum chamber was evacuated with a turbomolecular pump to pressures below  $10^{-5}$  mbar. Oxygen gas flow during the depositions was adjusted by mass flow controllers. The substrates were heated during the depositions at temperatures between 100–600°C.

To the classic PLD setup, a plasma beam was added in order to enhance the reactivity on the substrate due to the presence of an excited and ionized beam of oxygen atoms and molecules produced by the RF discharge. The plasma beam source consisted of a double chamber discharge system supplied by a RF (13.56 MHz, CESAR 1310, RF maximum power 1000 W) power supply. In the active chamber, the discharge was generated in a flow of oxygen between two parallel electrodes. The oxygen gas stream expanded into the ablation chamber through a nozzle of ~2 mm in diameter drilled in the bottom electrode. The discharge power was 100 W and the distance between the RF discharge gun and the substrate was 4 cm.

Details on the experimental deposition parameters used for processing the metal oxides in this work are given in the corresponding sections.

## 3. Thin-film characterization

The morphology of the as-grown metal oxide thin films was analyzed by atomic force microscopy (AFM) with a XE-100 AFM from Park Systems, on different areas and dimensions. All the deposited thin films were scanned in non-contact mode. Transmission electron microscopy (TEM) images were recorded on a JEOL ARM 200F analytical high-resolution electron microscope operating at 200 kV primary accelerating voltage after gently scraping the deposited films and collecting the product on carbon-covered copper grids.

Spectroellipsometry data were obtained in the 300–1000 nm spectral range at an incidence angle of 70° using a Woollam V-VASE apparatus equipped with a HS-190 monochromator.

Changes in the polarization state of an incident beam were analyzed, from linearly polarized to elliptical. These changes can be expressed by two parameters:  $\Psi$  (amplitude ratio) and  $\Delta$  (phase difference) [11]. The experimental values for  $\Psi$  and  $\Delta$  are acquired in the spectral range of 400–1000 nm, with a step of 2 nm, and at the beam incident at an angle of  $70^\circ$ . Since ellipsometry is a comparative technique, an optical model was required in order to generate the theoretical curves of  $\Psi$  and  $\Delta$ , which are to be fitted to the experimental data. For our films, we assumed an optical model consisting of four material layers: the silicon substrate, the native silicon oxide, the thin film of the metallic oxide layer, and a top rough layer. The values of the optical constants for silicon and native silicon oxide were taken from literature [12]. The top rough layer was considered to be a mix of materials, 50% oxide layer and 50% air (voids), in Bruggeman approximation [11].

X-ray measurements conducted in a Bragg-Brentano geometry ( $\theta$ – $2\theta$ , between  $20^\circ$  and  $100^\circ$ ) were carried out on a PANalytical X'Pert MRD system ( $\text{CuK}\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ).

To evaluate the leakage currents through the thin films, metallic contacts were deposited as top electrodes with 100 nm thickness. The current-voltage characteristic was measured using a Keithley instrument with a precision on the order of nano-amperes.

#### 4. Silicon dioxide thin films

Nowadays, the electronic industry is based on silicon dioxide technology. Since the 1980s,  $\text{SiO}_2$  is used as gate dielectric material for complementary metal-oxide-semiconductor (CMOS) technology. The technological requirements include high speed, low static power, and a wide range of power supply and output voltages [13]. The miniaturization trend, i.e. from the micro to the nano-scale resulted in the fabrication of the field effect transistor (FET), which lead to a high expansion of the technology and communication markets. Therefore, the metal-oxide-semiconductor field effect transistor (MOSFET) based on silicon dioxide gain enormous importance in the development of electronic devices.

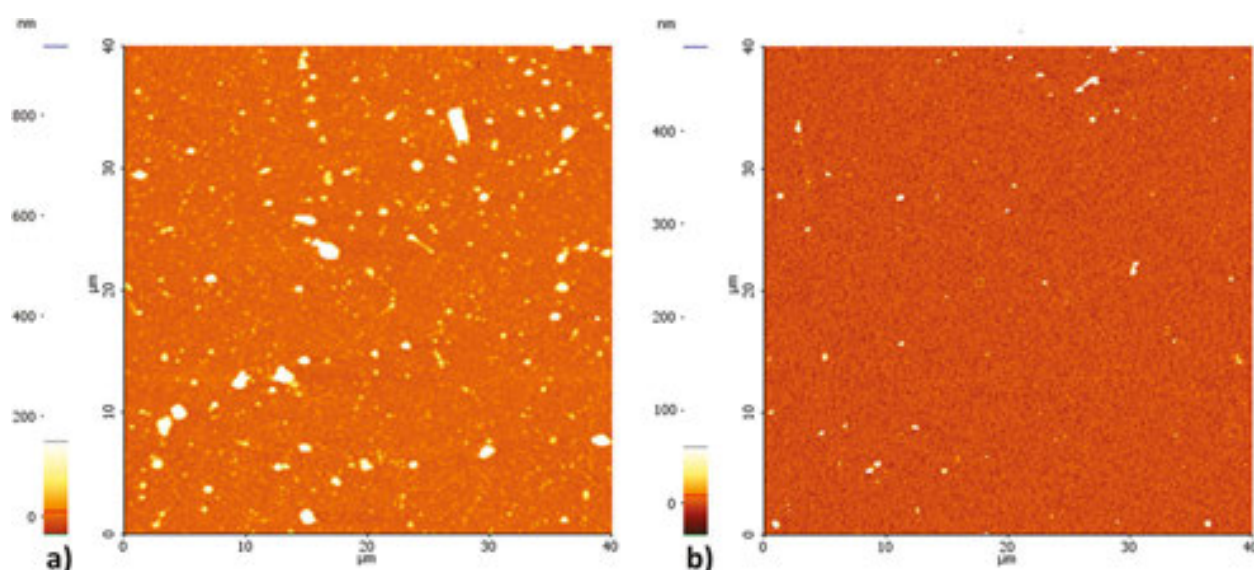
Amorphous  $\text{SiO}_2$  thin films are thermodynamically and electrically stable, having a good quality of the interface with the Si wafer, and superior electrical isolation properties. In the food industry, silicon dioxide is a common additive, used as a flow agent in powdered foods, or for water adsorption in hygroscopic applications. Furthermore,  $\text{SiO}_2$  is a good refractory material, used as antireflective coating for laser optical components.

In this work we focus on the deposition of  $\text{SiO}_2$  thin films to be used in antireflective coating applications. For this application, it is important to obtain featureless  $\text{SiO}_2$  thin films, i.e. free of pores and droplets.

$\text{SiO}_2$  thin films are deposited either by irradiation with a Nd:YAG laser (operated at 266 nm) or an ArF laser (193 nm) of a silicon target (classical PLD). The thin-film depositions are carried out in an oxygen atmosphere (0.01–0.1 mbar) using a laser fluence of  $1.5 \text{ J/cm}^2$ . The silicon substrates used as collectors are heated at  $600^\circ\text{C}$  during the depositions, and are set parallel to the target, at 4 cm distance.

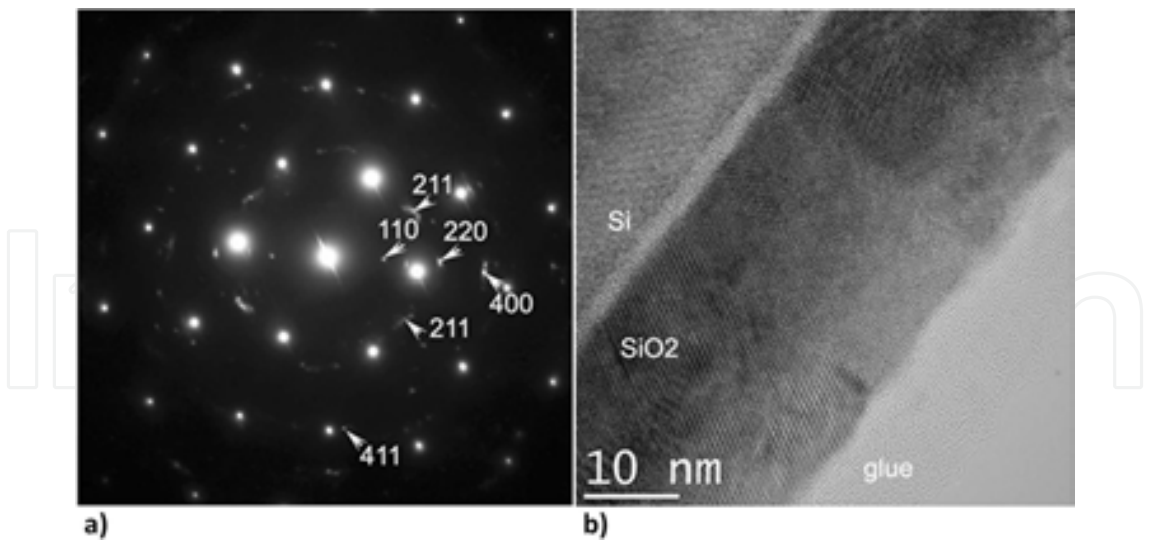


For the applications envisioned here, i.e. antireflective coatings, the thin-film surface morphology characterization is mandatory. It has been found [14, 15] that the laser wavelength plays an important role in the ablation process, influencing the thin film properties. The films grown from the target irradiated with 193 nm laser wavelength, at 0.01 mbar oxygen pressure, present micrometric droplets, with high roughness (RMS) of  $\sim 40$  nm (see **Figure 1(a)**). In contrast, the  $\text{SiO}_2$  thin films deposited from the target irradiated with 266 nm laser wavelength reveal both a reduced number of droplets and roughness ( $\sim 30$  nm). Increased oxygen pressure during thin-film deposition (0.1 mbar) together with irradiation at 266 nm laser wavelength lead to a considerable decrease of the films' roughness (below 10 nm) (see **Figure 1(b)**).



**Figure 1.** AFM images for thin films of silicon oxide grown by PLD at (a) 0.01 mbar of oxygen and  $\lambda = 193$  nm, (b) 0.1 mbar of oxygen and  $\lambda = 266$  nm.

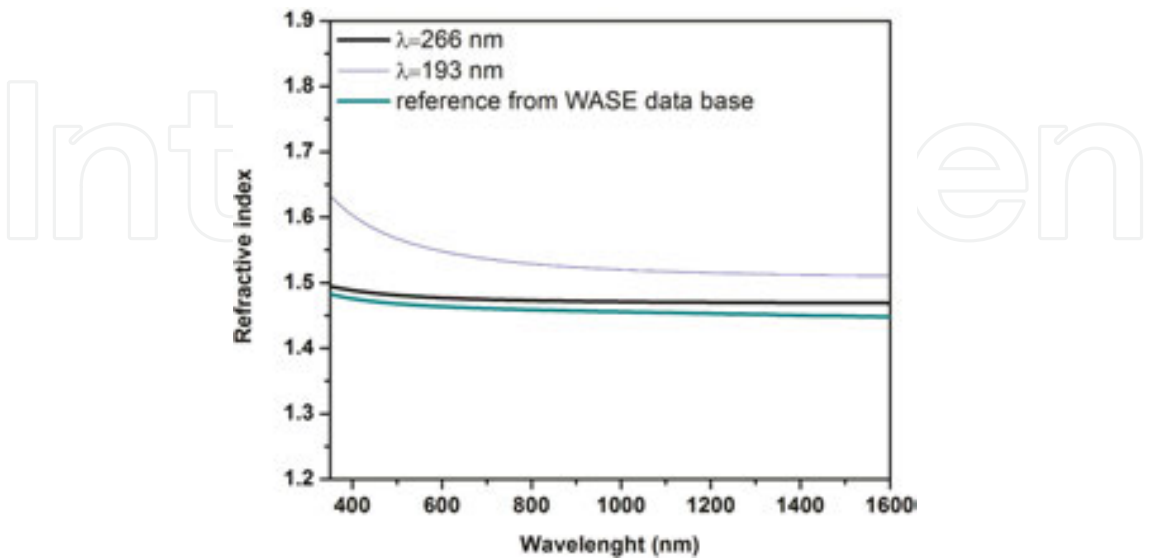
Furthermore, the electron diffraction pattern together with the HRTEM image of the  $\text{SiO}_2$  thin films deposited at 266 nm is shown in **Figure 2**. The electron diffraction patterns shown in **Figure 2(a)** reveal strong diffraction maxima attributed to the Si(100) substrate and weak diffraction maxima corresponding to the  $\text{SiO}_2$  cubic structure, spatial group SG:P2<sub>1</sub>3 and lattice constant  $a = 0.716$  nm (JCPDS file 85-0621). The HRTEM image in **Figure 2(b)** reveals a columnar growth of the  $\text{SiO}_2$  thin films. The differences of hill/valley height are small, below 2 nm. It is noticeable that the columns have almost the same width from the base to the top of the film. The columns differ between them only by the crystallites orientation. At the Si substrate- $\text{SiO}_2$  thin film interface, there is an amorphous  $\text{SiO}_2$  thin layer of 2 nm thickness.



**Figure 2.** (a) Electron diffraction pattern of the SiO<sub>2</sub> thin film deposited onto a Si substrate, (b) cross-section HRTEM of the SiO<sub>2</sub> thin film deposited on a Si substrate. The laser processing wavelength was 266 nm.

The SiO<sub>2</sub> thin films deposited by PLD at different laser wavelengths (193 and 266 nm) are investigated by spectroellipsometry to determine the refractive index.

It has been found that the laser wavelength used to process the thin films plays an important role in the optical properties of the thin films. Using the 266 nm wavelength, thin films with a refractive index  $n \sim 1.45$ , i.e. similar to the values from the data base (reference) are obtained. For 193 nm laser wavelength irradiation, the deposited thin films have a higher  $n \sim 1.55$ , which can be explained by the presence of a higher amount of Si in the SiO<sub>2</sub> thin films (**Figure 3**).



**Figure 3.** Refractive index of the SiO<sub>2</sub> thin films deposited by PLD compared to a reference SiO<sub>2</sub> thin film.

## 5. Tantalum oxide

In the microelectronics field, higher integrated circuit functionality and performance at lower cost are continuous demands. The requirement of an increased circuit density leads to a higher density of transistors on a wafer. SiO<sub>2</sub> has some limitations, for example, high leakage current, therefore new materials are studied. Replacing SiO<sub>2</sub> as gate dielectric in metal-oxide-semiconductor devices with high-k dielectric materials avoids the decrease in the dielectric's thickness to dimensions of angstroms, keeping it in the nanometres range [16].

Tantalum pentoxide (Ta<sub>2</sub>O<sub>5</sub>) quickly evolved as an important material in microelectronics. Due to its high dielectric constant (around 25) and to its chemical and thermal stability, it is a promising candidate as dielectric material in dynamic random-access memory devices. It can be used in microelectronics processing, replacing the conventional thin films of SiO<sub>2</sub> or Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub>. The high refractive index and low absorption coefficient on wide visible range make it suitable in optical devices as antireflective coating for solar cells based on silicon, and as material for waveguides.

Other applications of tantalum oxide include coatings for mirrors, and biological and chemical sensors. Ta<sub>2</sub>O<sub>5</sub> can be used as gate insulator in thin films and MOSFET. Moreover, Ta<sub>2</sub>O<sub>5</sub> has a high refractive index ( $n \sim 2.2$  at 633 nm), a wide band gap (*e.g.*  $\sim 4.2$  eV), and free absorption for wavelengths in the 300 nm to 2.0  $\mu$ m range allowing to be used in "charge coupled" devices. Furthermore, due to its chemical stability, Ta<sub>2</sub>O<sub>5</sub> can be used as protective layer to corrosion.

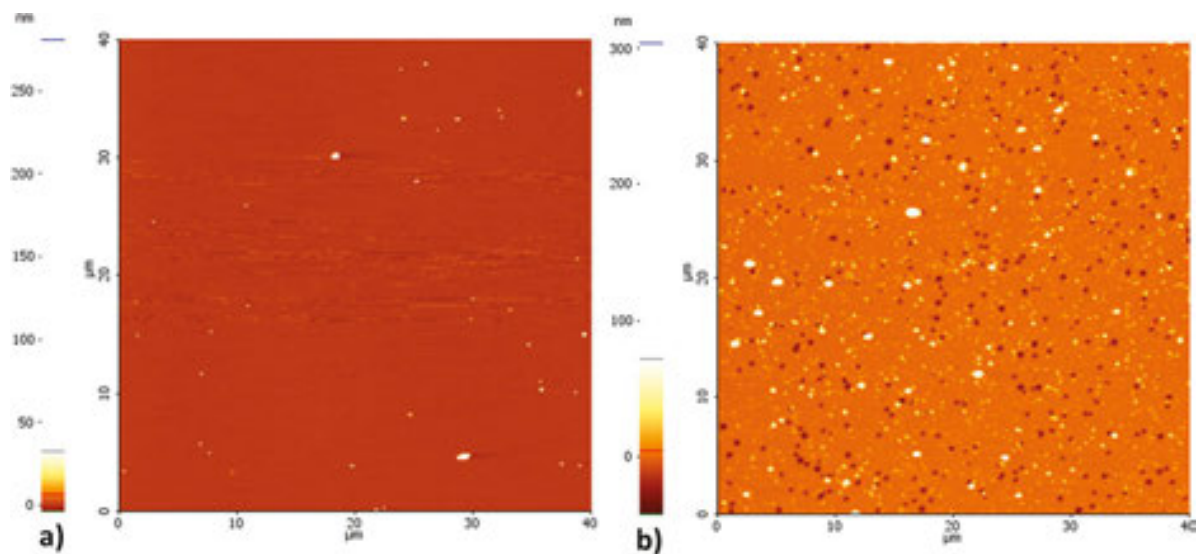
For applications in electronics as gate dielectric, the morphological and electrical properties of Ta<sub>2</sub>O<sub>5</sub> thin films exhibit high interest. The films roughness should be in the order of tens of nanometres and leakage currents should be very low.

Thin layers of Ta<sub>2</sub>O<sub>5</sub> are prepared by PLD and RF plasma-assisted PLD [17]. The laser beam (266 or 355 nm) is focused on a tantalum metallic target to obtain Ta<sub>2</sub>O<sub>5</sub> thin films. The distance between the target and the Si or Pt-coated Si (Pt/Si) substrates is 4 cm. The substrates are heated to 400 or 600°C. Depositions are carried out in oxygen atmosphere, at a constant pressure of 0.05 mbar. The laser fluence is varied between 1–3 J/cm<sup>2</sup> in order to avoid the formation of droplets on the films' surface. Thin films with thicknesses of around 150 nm are obtained as a result of 15,000 laser pulses.

Surface morphology has an important role for the applications presented above, in particular, for gate dielectric and antireflective coatings. The thin films' requirements are low roughness, lack of pores, and uniform thickness over a large area.

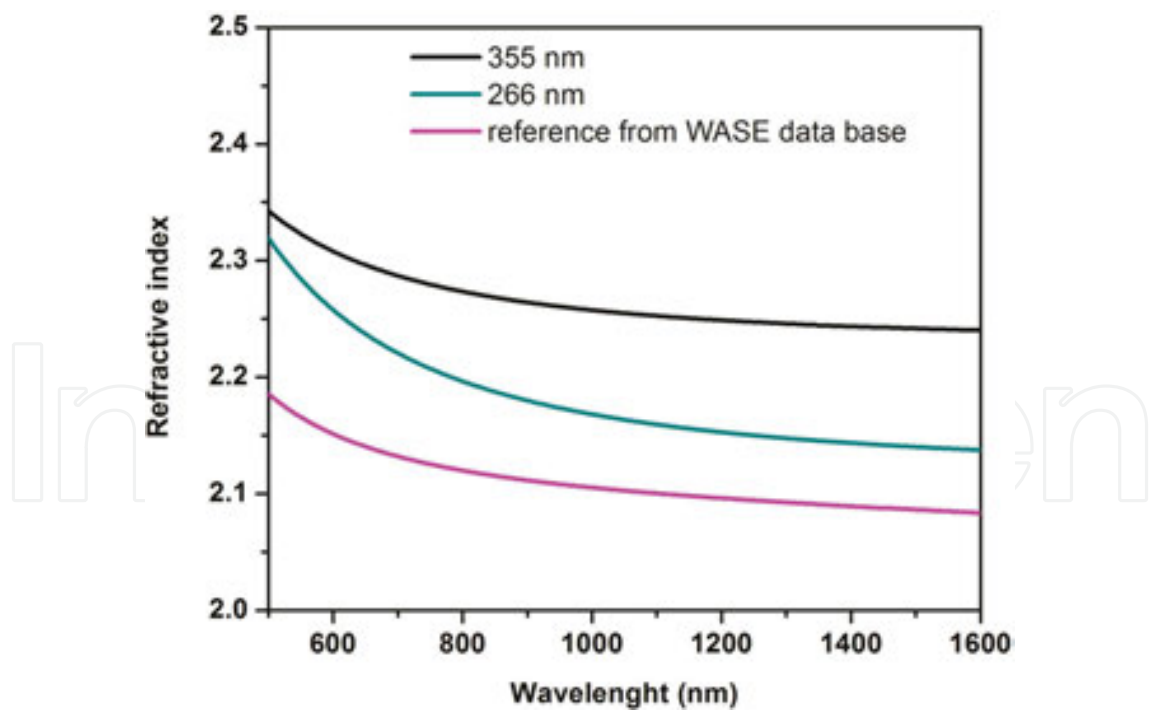
First, we investigate the morphology of two thin films deposited by PLD at 1 J/cm<sup>2</sup> and two laser wavelengths, i.e. 266 nm and 355 nm (**Figure 4**). Compact thin films with only a few droplets and low roughness (below 4 nm) are obtained with 266 nm wavelength (**Figure 4a**). In contrast, thin films with micrometric pores and droplets, and roughness around 10 nm are obtained by using 355 nm laser wavelength, as shown in **Figure 4b**. The tantalum oxide thin films are amorphous as revealed by HRTEM investigation (not shown here).





**Figure 4.** AFM images of Ta<sub>2</sub>O<sub>5</sub> thin films grown on Si substrate at different wavelengths: (a) 266 nm, and (b) 355 nm.

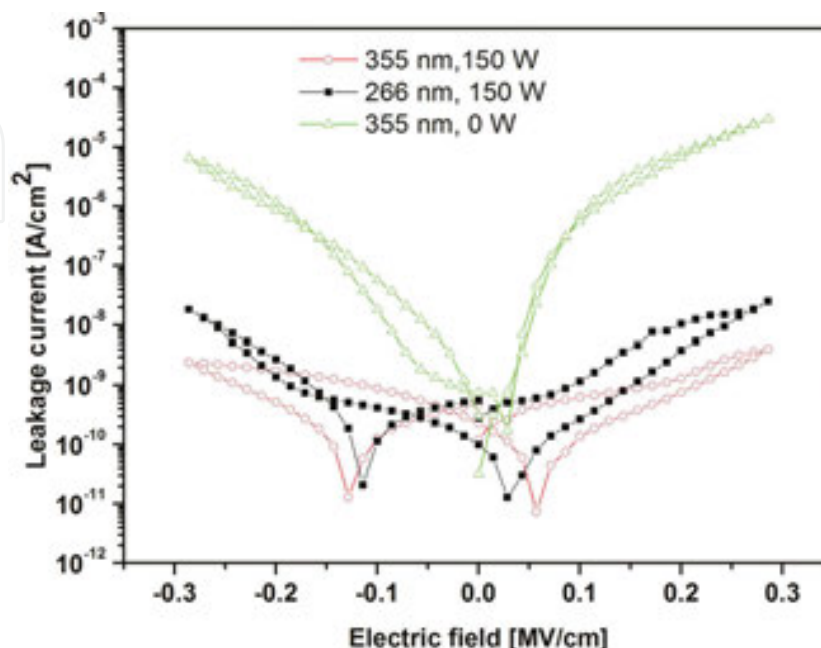
Spectroscopic ellipsometry investigations show that the tantalum oxide layers present refractive indices close to those of tantalum pentoxides (Ta<sub>2</sub>O<sub>5</sub>) from the VASE32 database [18] (Figure 5).



**Figure 5.** Refractive index of the Ta<sub>2</sub>O<sub>5</sub> thin films deposited by PLD compared to a reference Ta<sub>2</sub>O<sub>5</sub> thin film.

The I–V characteristics are measured on tantalum oxide layers deposited on Pt/Si substrate with aluminium top electrodes having areas around 0.22–0.23 mm<sup>2</sup>. The influence of the

wavelength and RF plasma addition to the PLD system on the leakage currents densities for tantalum oxide is studied. The influence of the RF discharge and the wavelength on the electrical properties is highlighted in **Figure 6**.



**Figure 6.** The I-V characteristics of the Ta<sub>2</sub>O<sub>5</sub> thin films [17].

The thin films grown by RF-PLD have low leakage currents densities with three orders of magnitude smaller than for samples grown by PLD. The structural ordering induced by RF plasma addition results in a significant decrease in the leakage current densities. Thin films deposited using the third laser harmonic (355 nm) showed one order of magnitude smaller leakage currents, as compared to those obtained using the fourth laser harmonic (266 nm). These low leakage currents densities corroborated with smooth, low roughness thin films made from tantalum oxide grown by RF-PLD, the suitable candidate for dielectric gates. In addition, our thin films have superior dielectric properties (refraction index and leakage current) when compared to results reported in literature by other deposition techniques (see **Table 1**).

Deposition technique	Refraction index (550 nm)	Leakage current density (A/cm <sup>2</sup> )
RF-PLD (this work)	2.27	$4.8 \times 10^{-10}$
PLD [19]	2.22	-
Thermal oxidation [20]	2.10	$7 \times 10^{-10}$
Atomic layer deposition [21]	2.13	$1 \times 10^{-8}$
Rf magnetron sputtering [22]	2.11	$1 \times 10^{-6}$

**Table 1.** Comparison between the refractive index of Ta<sub>2</sub>O<sub>5</sub> thin films deposited by different deposition methods.

To sum up, the high refractive index (2.27), low absorption coefficient, and the fact that the material is inert makes it useful as antireflection coating and waveguide material [23, 24].

## 6. Hafnium oxide

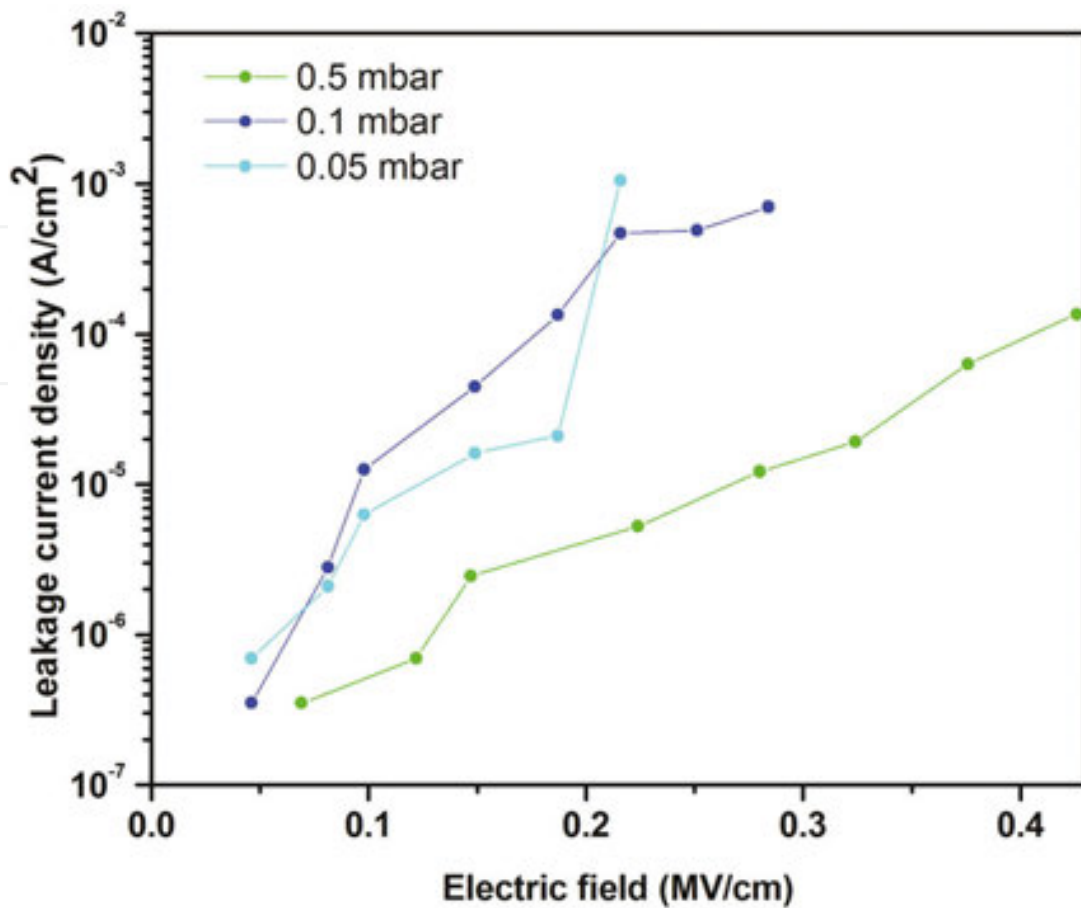
Hafnium dioxide, also called hafnia, is a high-index, low-absorption material used for coatings in the near-UV (below 300 nm) to IR ( $\sim 10\ \mu\text{m}$ ) regions [25]. Typical applications include near-UV laser antireflective coatings and dielectric mirror designs. Adhesion is excellent to glass, quartz, to the most other oxides, and to metals such as aluminium and silver. The refractive index of hafnia thin films changes with respect to the high energy deposition techniques and substrate temperature, because both parameters decrease the void volume by increasing the packing density of the microstructure [26].

The refractive index below 300 nm wavelength is near 2; therefore, hafnia can be combined in multilayers with silicon dioxide ( $n = 1.48$ ) to form high index/low index-contrast multilayer structures with high laser damage thresholds for UV laser applications [27]. Hard, scratch-free, dense, and adherent coatings can be deposited on relatively low temperature substrates. Its abrasion resistance provides the protection of metal mirrors.

$\text{HfO}_2$  is suitable for gate dielectric due to its stability in direct contact with Si at temperatures required for processing and due to its high dielectric constant of 18–25. For this specific application, thin films of  $\text{HfO}_2$  are prepared by RF-PLD on Pt/Si and Si(100) substrates (heated at  $100^\circ\text{C}$ ) [28]. The ablation of a hafnium target is carried out in reactive atmosphere of oxygen. The laser fluence is set to  $5\ \text{J}/\text{cm}^2$ . And, 12000 laser pulses are shot to obtain  $\text{HfO}_2$  thin films with thickness of approximately 150 nm. Different deposition parameters, i.e. laser wavelength (266 or 355 nm) and oxygen pressure (0.5–0.05 mbar) are varied to obtain thin films with smooth morphology and dielectric properties.

It has been found that the laser wavelength does not influence the thin films morphology, only a slight decrease in the surface roughness is being observed in the case of samples deposited at 266 nm. The surface is uniform and compact, with rare droplets (not shown) and roughness below 15 nm [28]. Auger electron spectroscopy reveals thin films with stoichiometry close to  $\text{HfO}_2$  (Hf 35%: O 65%).

In addition, AFM investigations show that the variation of oxygen pressure does not influence the surface morphology. The results of electrical measurements on hafnia thin films prepared in the same conditions but with different oxygen pressures indicate small leakage current density values, between  $10^6$  and  $10^3\ \text{A}/\text{cm}^2$  on a narrow electric field ( $\sim 0.2\ \text{MV}/\text{cm}$ ) for low oxygen pressures (0.05 – 0.1 mbar); the thin films grown at a slightly higher oxygen pressure (0.5 mbar) exhibit lower leakage current densities for a wide electric field (up to  $0.4\ \text{MV}/\text{cm}$ ) (see **Figure 7**).

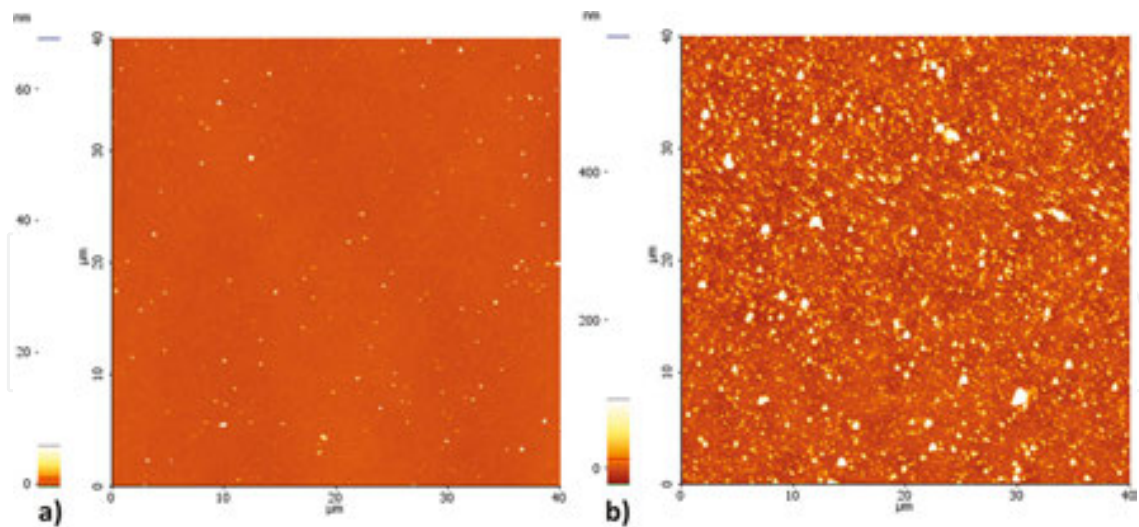


**Figure 7.** Leakage current density vs. electric field of hafnia thin films prepared by RF-PLD at different oxygen pressures [28].

In conclusion, it has been shown that hafnia thin films grown in low oxygen content ( $\leq 0.5$  mbar) have low leakage currents suitable for applications in MOSFET devices.

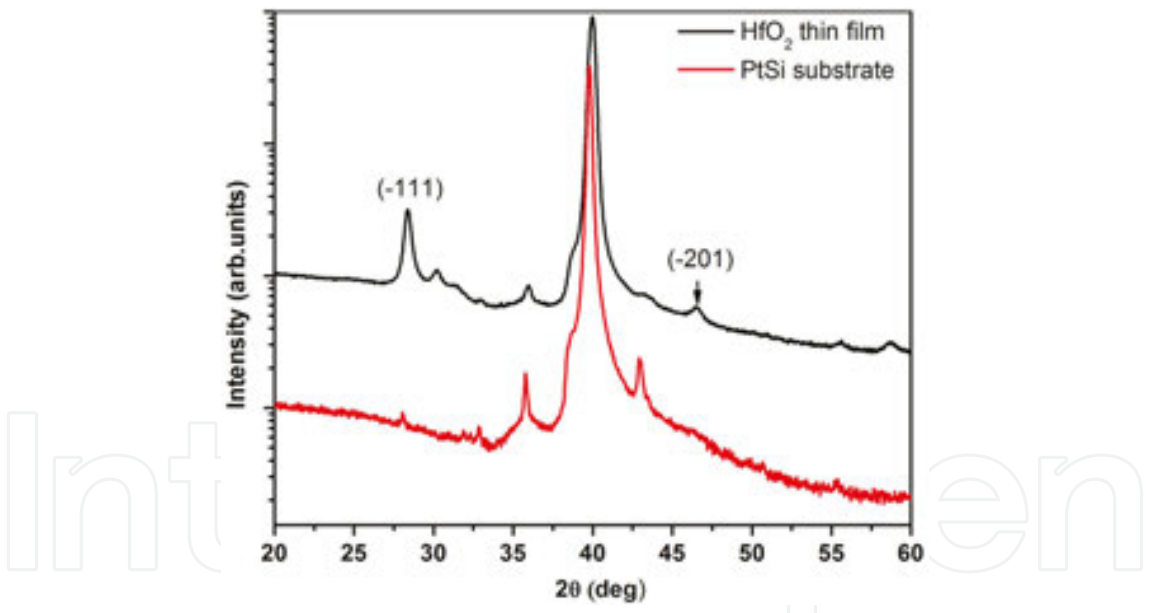
Further on, thin films with low surface roughness and high refractive index are candidates for coatings in dielectric mirrors. For this application, thin layers of hafnium oxide are produced in 0.01 mbar of oxygen, by ablation at different wavelengths (193, 266, and 355 nm). The substrates (silicon and Pt/Si) are kept at 600°C during the depositions. The laser fluence is set at 1.5 J/cm².

Laser wavelength has an important role in obtaining droplet-free thin films. After target irradiation with 193 nm, the obtained films show a low roughness (below 1 nm) for 20 nm film thickness (**Figure 8a**). Thin films produced in the same experimental conditions using 266 nm laser wavelength have higher roughness (about 6 nm), however, for a higher thickness (227 nm) (not shown). Hafnia target irradiated at higher wavelength (355 nm) leads to thin films with micrometric droplets and conglomerates; the surface roughness is very high (25 nm) for a small film thickness (40 nm) (**Figure 8b**).



**Figure 8.** AFM images of hafnia thin films grown on Si substrates at (a) 193 nm and (b) 355 nm laser wavelength.

The structural investigation by XRD shows that the  $\text{HfO}_2$  thin films are crystalline with (-111) orientation (PDF card 00-034-0104) (see **Figure 9**).

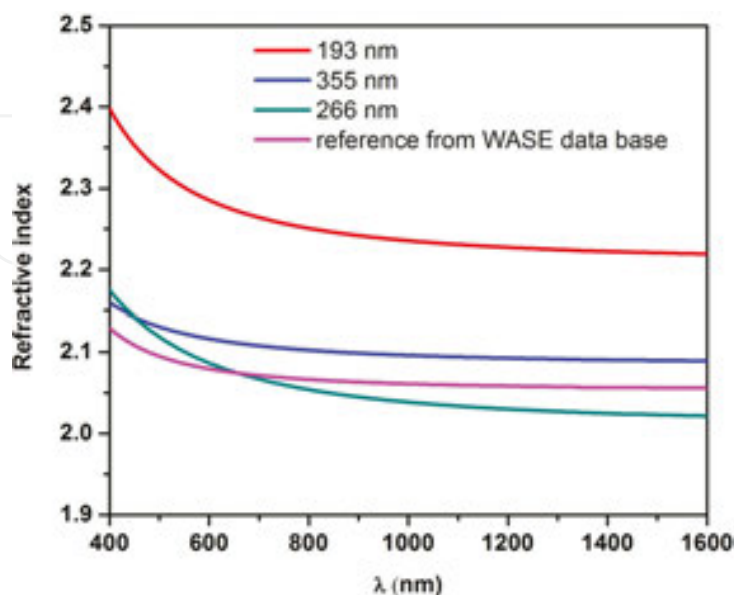


**Figure 9.** XRD patterns of an as-grown  $\text{HfO}_2$  thin film deposited by PLD at 266 nm laser wavelength.

In addition to hafnia surface morphology, the laser wavelength influences the optical behaviour of the hafnia films. Thin films with refractive index values close to the value of  $\text{HfO}_2$  reference from WASE data base are obtained at 266 and 355 nm. The irradiation of the target with 193 nm laser wavelength leads to thin films with a higher refractive index, due to the high roughness (voids presence) corroborated with a higher content of Hf in the oxide layer (**Figure 10**). And, 266 nm laser wavelength has been found as the suitable wavelength for smooth (RMS



= 5.8 nm) thin layers with good refractive index ( $n \sim 2$ ) to be further used in antireflective coating applications.



**Figure 10.** Refractive index of the  $\text{HfO}_2$  thin films deposited by PLD compared to a reference  $\text{HfO}_2$  thin film.

## 7. Aluminium oxide

Another dielectric candidate for replacing silicon dioxide in MOS devices is aluminium dioxide (alumina). It has excellent conduction and valence band offsets on contact with Si [29, 30] being suitable for use with n- and p-type Si over a range of doping levels. Due to its high melting point,  $\text{Al}_2\text{O}_3$  is used as a refractory material; it is a hard dielectric material with a refractive index of 1.77 [31] and presents high corrosion resistance. Aluminium oxide is a good candidate to integrated optics and as antireflection coating [32] due to the possibility to tune its spectral properties [33].

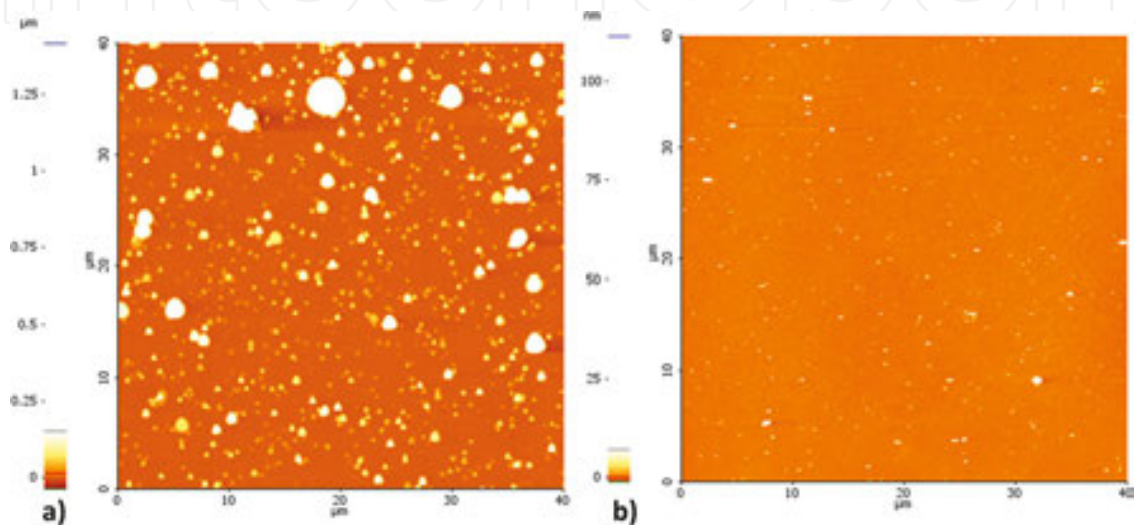
Taking into account the dielectric behaviour, thin films of alumina are deposited by PLD on Ti-coated glass substrates [34]. An alumina target is ablated with 193 nm laser wavelength, in oxygen atmosphere, at a laser fluence of  $4 \text{ J/cm}^2$ .

Nanostructured thin films, droplet-free, with roughness below 5 nm are revealed by AFM investigation. The permittivity and dielectric losses vs. temperature are measured in the range of  $-150$  to  $150^\circ\text{C}$ , in a 42 Hz and 5 MHz frequency range. Thin films with good stability of the permittivity and low loss values are obtained by PLD. For example, at  $0^\circ\text{C}$ , the dielectric constant of  $\text{Al}_2\text{O}_3$  thin films is around 7.2 [34].

The role of aluminium oxide thin films as antireflective coatings is studied from a morphological and optical point of view. In order to obtain thin films suitable for optical

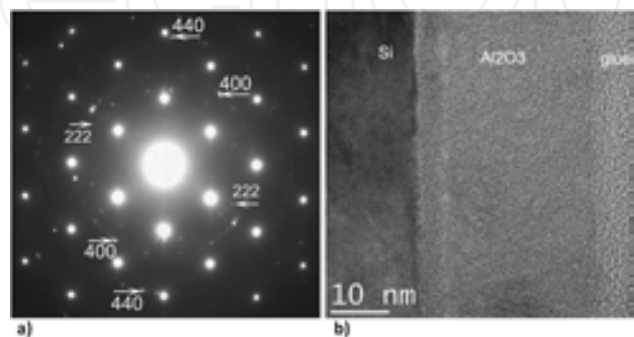
applications, the deposition experiments are carried out in oxygen atmosphere (0.01 mbar), at 193 or 266 nm wavelength. The Si substrates are heated at 600°C during depositions.

The laser fluence is set at 6 J/cm<sup>2</sup> for the depositions carried out at 193 nm and 1.5 J/cm<sup>2</sup> in the case of target ablation with 266 nm. The film surfaces produced with 266 nm wavelength show numerous droplets and high roughness (70 nm) (**Figure 11a**). In contrast, the films obtained by using 193 nm laser wavelength are smooth, without droplets (**Figure 11b**) and roughness below 2 nm.



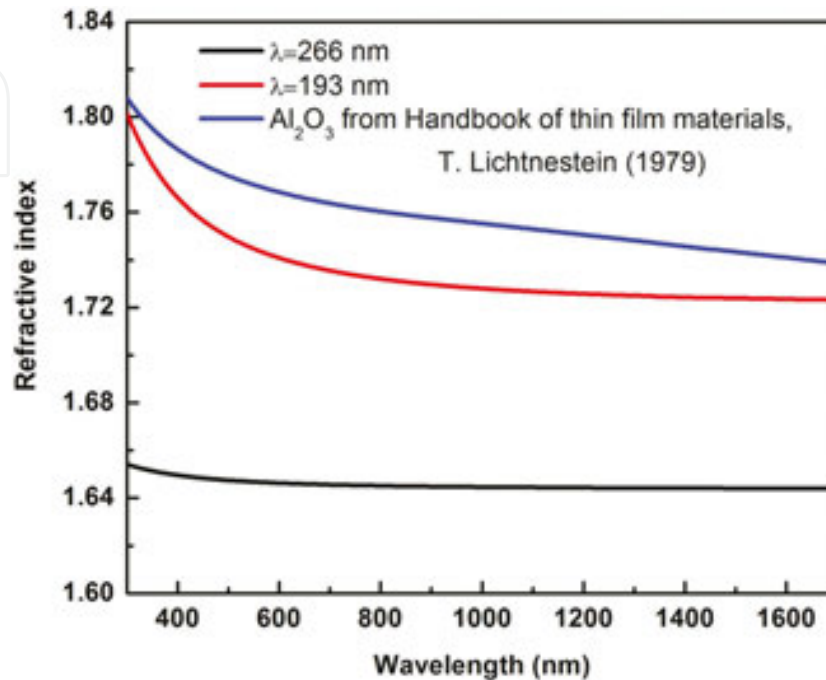
**Figure 11.** AFM images of Al<sub>2</sub>O<sub>3</sub> thin films grown on Si substrates, at different wavelengths and laser fluences: (a)  $\lambda = 266$  nm and  $\Phi = 1.5$  J/cm<sup>2</sup>, and (b)  $\lambda = 193$  nm and  $\Phi = 6$  J/cm<sup>2</sup>.

From HRTEM investigation, polycrystalline Al<sub>2</sub>O<sub>3</sub> thin layers are detected. Strong diffraction peaks corresponding to (110) silicon and weak diffraction peaks attributed to cubic Al<sub>2</sub>O<sub>3</sub> ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) structure (JCPDS file 29-0063) (space group SG:Fd3m and lattice constant  $a = 0.7924$  nm) are shown in **Figure 12a**. The morphology of Al<sub>2</sub>O<sub>3</sub> thin layers is shown in the HRTEM images at high magnification in **Figure 12b**. The layer is formed from small nanocrystallites (<10 nm).



**Figure 12.** (a) Electron diffraction pattern of Al<sub>2</sub>O<sub>3</sub> grown on Si substrate; (b) Cross-section HRTEM image of the Al<sub>2</sub>O<sub>3</sub> thin film.

The optical properties of alumina thin films are studied by spectroellipsometry. Using 193 nm laser wavelength, thin films with refractive indices close to literature values are reported [35]. The thin layers grown from a target irradiated at 266 nm have low refractive indices ( $n \sim 1.65$ ) due to the high presence of voids (**Figure 13**).



**Figure 13.** Refractive index of the Al<sub>2</sub>O<sub>3</sub> thin films deposited by PLD compared to a reference Al<sub>2</sub>O<sub>3</sub> thin film.

## 8. Conclusions

This chapter succinctly reviews the deposition of Si, Ta, Hf, and Al oxide materials as thin films by PLD and RF-PLD. All the results presented in this work are discussed in terms of two main applications, i.e. high-k dielectrics and antireflective coating applications. These applications have specific requirements, for example, the deposition of smooth and droplet-free thin films. This could be achieved by optimizing the laser wavelength, i.e. smooth and droplet-free Al<sub>2</sub>O<sub>3</sub> could be obtained by using 193 nm laser wavelength. In contrast, smooth SiO<sub>2</sub> and HfO<sub>2</sub> thin films with low roughness were obtained by 266 nm laser irradiation. In the case of Ta<sub>2</sub>O<sub>5</sub>, the thin films grown by RF-PLD at 266 nm wavelength have low roughness and in addition they present low leakage currents densities with three orders of magnitude smaller than for samples grown by PLD. Furthermore, the optical properties of the as-deposited metal-oxide thin films were investigated by spectroellipsometry, and, for example, the Ta<sub>2</sub>O<sub>5</sub> thin films deposited by RF-PLD have a high refractive index (2.27) which makes them useful as antireflective coatings and waveguide material. In addition, we have also shown that hafnia thin films grown in low oxygen content ( $\leq 0.5$  mbar) have low leakage currents which make them suitable for applications in MOSFET devices.

To sum up, we have shown that by varying the deposition parameters in the classical and hybrid (RF-assisted) PLD process, it is possible to tune the morphology, structure, and optical properties of the Si, Hf, Ta, and Al oxide thin films to match antireflective coating and high-k dielectric applications.

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