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Transparent and low surface roughness HfO_2: Tb^{3+}, Eu^{3+} luminescent thin films deposited by USP technique

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Abstract

In this work, the optical and morphological properties of HfO_2: Tb^{3+}, Eu^{3+} thin films deposited by the Ultrasonic Spray Pyrolysis technique from metal-organic precursors are reported. The films showed optical average transmittance values in the visible region greater than 90%, with surface roughness lower than 3.9 nm. The films deposited at 500 °C showed the lowest average roughness with a value of 0.9 nm, and the smallest thickness was 35 nm for sample deposited at 500 °C during 45 s. XRD measurements indicate a hafnium oxide monoclinic phase for films deposited at substrate temperatures higher than 500 °C. All films deposited showed the luminescent emissions (PL and CL) characteristic of Tb^{3+} and Eu^{3+} ions. A luminescence concentration quenching was observed for both Tb^{3+} and Eu^{3+} ions. The HfO_2: Tb^{3+} (5 at%) and HfO_2: Eu^{3+} (10 at%) films deposited at 500 °C, showed the highest PL and CL emission intensity. Quantum Efficiency measurements (up to about 35%) were measured for these films which have a refractive index between 1.97 and 2.04 and band gap of 5.4 eV. The chemical composition of the films as measured by XPS is also reported. In addition, decay time measurements were performed on some HfO_2: Tb^{3+}, Eu^{3+} samples.
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Keywords: Thin films; Transparency; Low roughness; Luminescence; Spray pyrolysis

1. Introduction

The increasing use of electronic devices with displays, demand the research of luminescent materials that can be used as raw materials for the manufacture of luminescent devices with some advantage such as higher brightness and small size. A luminescent material for such applications should have high transmittance in the visible region, wide bandgap (> 3 eV) to avoid re-absorption of the visible radiation emitted, low roughness (to avoid dielectric breakdown), high chemical and thermal stability, low thickness and high luminescent emission [1]. There are several flat panels of technological importance, including the plasma display panels (PDPs), field emission displays (FED) and the thin film electroluminescence displays (ELD) [2–4]. In recent years there has been a lot of interest in the progress of film-type phosphors for flat panel displays such as MISIM (Metal–Insulator–Semiconductor–Insulator–Metal) electroluminescent structures. The typical values of the refractive index for the luminescent materials used in an electroluminescent device are approximately among 1.5 and 2.5. Phosphors such as ZnS: Mn which is very efficient with a bandgap of 3.7 eV has been used for this type of devices. Also, phosphors with bandgaps higher than 5 eV have been used with good results as Y_2O_3:Eu^{3+} [5] and Y_2O_2S: Tb^{3+} [6]. In some cases, it is necessary to incorporate electron

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donor films to improve their efficiency, such as in the case of Y_2O_3:Eu^{3+} used together with a ZnS film [7]. Film-type luminescent materials have some advantages such as high image resolution, thermal stability, long-term stability and better adhesion to the substrate compared to powder-type phosphors [1].

Metallic oxides are very versatile materials that play an important role in the phosphors technology. Among them, the hafnium oxide (HfO_2) is a material that has been widely used in optical applications, when synthesized as thin film has a relatively high refractive index (~2.1) and a wide band gap (~5.7 eV) [8] which makes it transparent over a wide spectral range from ultraviolet to the mid-infrared [9–11]. Recently, this oxide has been used as host lattice for rare earth and transition element ions to produce phosphors. HfO_2 films activated with some trivalent rare earth ions possess remarkable luminescence characteristics [12–15]. Several techniques have been used to deposit HfO_2 thin films, including Metal-Organic Chemical Vapor Deposition (MOCVD), High Pressure Reactive Sputtering (HPRS), Atomic Layer Deposition (ALD), Assisted Ion Beam Deposition, Sputtering and Sol–Gel [16–21]. The Ultrasonic Spray Pyrolysis technique (USP) has proved to be a simple, efficient and inexpensive method that does not require vacuum systems and allows deposition of homogeneous and transparent films with low roughness and small thickness when metal-organic reagents are used as precursors. In addition, this technique is simple for the making of large area film phosphors [21]. Hafnium oxide films deposited by USP using hafnium chlorides as precursors have been studied as host material for rare-earth activators, such as Eu [12], Tb [13] and Ce [22]. The films deposited from these precursors are thick, rough and opaque; consequently they are inadequate for the applications above mentioned (flat panel displays). On the other hand, the deposition of hafnium oxide films by USP, using metal-organic precursors, results in films with excellent flatness, transparency and density characteristics. In general, rough films, induce localized dielectric breakdown because they often create weak spots in multilayered devices (MISIM for example), especially when the layers are very thin. Also, film transparency is important because a reduction of absorption and scattering of the emitted light by the luminescent material produces an improvement of the external efficiency of the luminescent devices [23].

In this contribution, the morphological and optical qualities of Tb^{3+} and Eu^{3+}-doped hafnium oxide thin films, deposited by USP process using acetylacetonates as precursors and synthesized at temperatures up to 550 °C, are reported. Specially, the dependence of the PL and the CL emission intensities from these – transparent and low roughness – thin films as a function of doping concentration (Tb and Eu) and deposition temperature is reported.

2. Experimental details

The un-doped and Tb^{3+}, Eu^{3+}-doped HfO_2 thin films were deposited by USP technique, Fig. 1 shows a schematic drawing of the deposition system used for this research, which

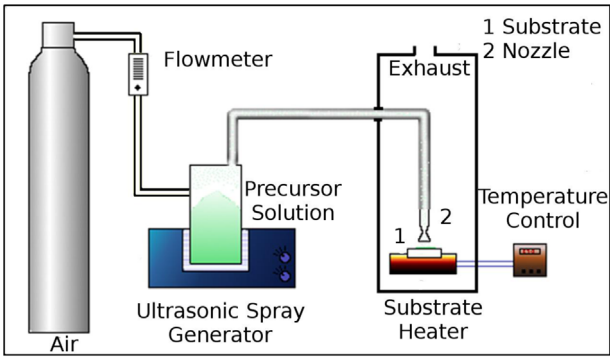

Fig. 1. Schematic diagram of the ultrasonic spray pyrolysis system for deposition of the HfO_2:Tb, Eu, thin films.

is capable to deposit films on substrate up to 20 × 20 cm. This system consists of an ultrasonic spray generator to produce the aerosol from the proper solution that is transported by a carrier gas onto the substrate placed on a tin bath whose temperature is electronically controlled. It should be mentioned that the ultrasonic spray pyrolysis technique has been reported to be used for film deposition on large areas [21]. The films, in this case, were deposited on glass, quartz and silicon single crystal (100) substrates of approximately 2 by 2 cm, these substrates were washed according to the protocol reported by Acosta [24]. The starting reagents were Hf acetylacetonate (Hf acac) dissolved in dimethylformamide (DMF) at a molar concentration of 0.035 M and Tb and Eu acetylacetonates at molar concentrations of 0, 2.5, 5.0, 7.5 and 10 at% (at%) with respect to hafnium content. The films were deposited at substrate temperatures (T_s) of 400, 450, 500 and 550 °C, with a carrier gas flow of 10 l/min (filtered air). The deposition times were 45, 90, 180 and 300 s (s). No further thermal treatments were given to the as deposited samples because there was a concern to keep the energy budget employed in the processing of these materials as low as possible. The crystalline structure of the deposited films was measured by X-Ray Diffraction (XRD) using a Bruker D8-Advance diffractometer with a Cu k_α radiation (1.5406 Å). The chemical elements present in the HfO_2: Tb^{3+}, Eu^{3+} thin films were determined by X-ray photoelectron spectroscopy (XPS). In order to corroborate the presence and incorporation of Tb^{3+} and Eu^{3+} in the films X-ray photoelectron spectra were collected using aK-Alpha spectrometer from Thermo Scientific with monochromatic AlKa (1486 eV) radiation with an energy resolution of 0.5 eV. Survey and high resolution spectra were collected at 160 and 60 eV pass energy analyzer respectively, using an X-ray spot size of 400 μm^2. The surface of the samples was ion beam etching (IBE) cleaned with Ar at ion acceleration potential of 500 eV for 15 s in order to remove the major part of adsorbed species onto the surface prior to XPS analysis. The recorded spectra were fitted through a Gaussian–Lorentzian combination based on an Offset Shirley background type. The surface morphology and roughness of the films was analyzed through Auto Probe CP Atomic Force Microscope (AFM) from Park Scientific Instruments in a contact mode (these measurements were carried out in samples deposited on silicon

substrates). A Cary Varian 50 UV–Visible spectrophotometer at wavelength range from 200 to 800 nm was used to obtain the transmittance spectra of the un-doped films (deposited on quartz substrates). From these spectra was possible to obtain the refractive index and the bandgap of the films deposited at 500 °C through the Swanepoel method [25]. Photoluminescence (PL) spectra (excitation and emission) were obtained by means of a Horiba Jobin Yvon Fluoromax-P spectrofluorometer. Cathodoluminescence (CL) measurements were carried out in a Luminoscope equipment model ELM-2 MCA, RELION Co., which has a stainless steel vacuum chamber with a cold cathode electron gun. The electron beam was deflected through a 90-degree angle to bombard the thin films normal to the surface. The produced light was collected by an optical fiber bundle and fed into the spectrofluorometer abovementioned. The electron accelerating voltage was varied (from 3 to 8 kV) and the applied current of the electron beam was constant at 0.03 mA, the spot size of the electron beam on the surface of the samples was 0.2 cm in diameter approximately. All luminescence measurements were performed in samples deposited on glass substrates. The thickness of films deposited at different times and substrate temperatures was measured using a SLE Stokes Gaertner ellipsometer with a He–Ne 6328 Å laser. Decay times spectra were recorded with an Edinburgh Instruments FLS 980 spectrofluorometer, also equipped with an integrated sphere to QE-measurements and finally SEM images were recorder with a JEOL scanning electronic microscopy, model JSM-6390LV and a Carl Zeiss model Supra 55VP.

3. Results and discussion

The Fig. 2 shows the XRD diffractogram of a film deposited at 550 °C with Miller indexes of the corresponding planes owing to hafnium oxide monoclinic phase (ICSD 027313). The most intense peak is located at 31.70°, indicates a preferential growth in the direction to the plane (1 1 1); similar behavior has been observed in other studies [26,27]. A little shoulder in the peak located at 30° suggests a small crystallization of a meta-stable tetragonal phase of the HfO_2 films [28]. Films deposited at 400 and 450 °C were completely

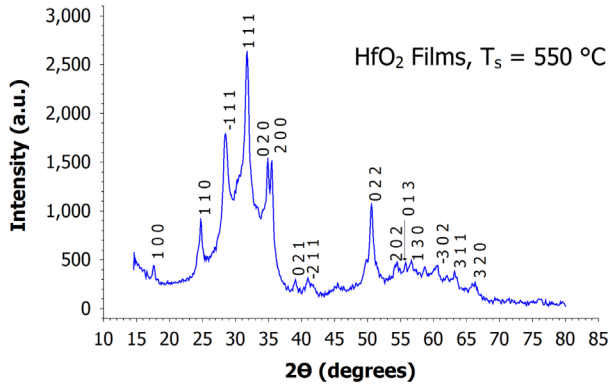

Fig. 2. XRD diffractogram for the HfO_2 film deposited at 550 °C on glass substrate for a deposition time of 300 s. Monoclinic crystalline phase is observed.

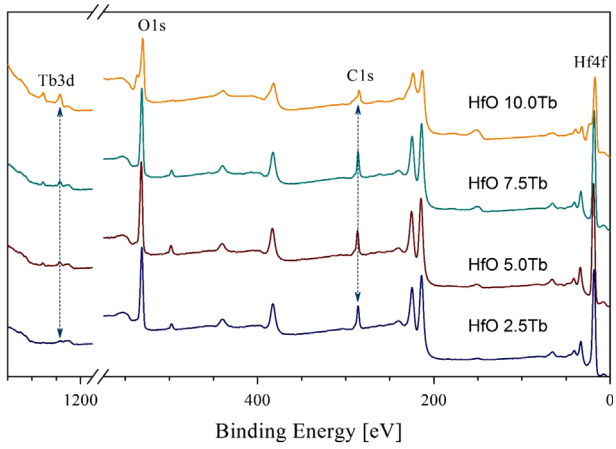

Fig. 3. XPS survey spectra for 2.5, 5.0, 7.5 and 10 at% of terbium content in HfO_2: Tb^{3+} films. For clarity, *X*-axis break was introduced in order to appreciate the increase in content of Tb in the different films.

amorphous and crystallization started in samples deposited at 500 °C. The crystals size in the film synthesized at 550 °C was estimated by means of Scherrer's formula, considering the above described peak (31.70°). The obtained crystallite size was 8.068 nm.

The chemical elements present in the HfO_2: Tb^{3+}, Eu^{3+} thin films were obtained using the XPS technique; the presence and quantification of Tb^{3+} and Eu^{3+} ions into HfO_2 films was confirmed by this technique. Fig. 3 show the XPS survey spectra obtained after the analysis of diverse Tb content incorporated in the hafnium oxide thin films. Smaller amounts of carbon were observed and considered as residual elements of the synthesis process [29]. To determine in more detail, the Hf and Tb oxidation states presented by the HfO_2: Tb^{3+} films, analysis by decomposition modeling of the high-resolution XPS narrow scans for the Hf4f and Tb3d were performed and showed in Fig. 4. Moreover, to detect and compensate the charge shift of the core level peaks, C1s peak position at 248.5 ± 0.2 eV was used as an internal standard. XPS narrow scan of $Hf4f_{7/2}$ and $4f_{5/2}$ doublet spectra for the different films, Fig. 4a, were fitted with one double contribution associated with HfO_2, 16.7 and 18.4 ± 0.2 eV. Fig. 4b shows a comparative of Tb3d high-resolution spectra of HfO_2:Tb films series. Two peaks at energies of 1241.5 and 1276.4 ± 0.2 eV belonging to $Tb_{3/2}$ and $Tb_{5/2}$ were observed, the difference of 35 eV between these energies it is caused by a spin–orbit splitting. In this regard, the literature is limited and/or vague in the interpretation of Tb3d, a wide range of values for Tb(III) are proposed, e.g. 1242.4, 1243.6 eV for Tb(III) [30,31]. We propose that $Tb3d_{5/2}$ peak corresponds to Tb(III) Fig. 4b peak (b) and a mixture of Tb(III)–Tb(IV) peak (a), 1241.5 and 1238.4 ± 0.2 eV, respectively. On the other hand, the spin–orbit splitting of 35 eV together with the precise position of the peak $Tb3d_{5/2}$ indicated an oxidation state of Tb(III) [31,32]. Similar measurements were carried out for HfO_2: Eu^{3+} films.

The atomic percentages of hafnium, oxygen, terbium and europium were obtained by XPS. The ratio O/Hf was close to 2 which is the ideal value for a stoichiometric composition for HfO_2 films. The atomic percentages of Tb and Eu ions

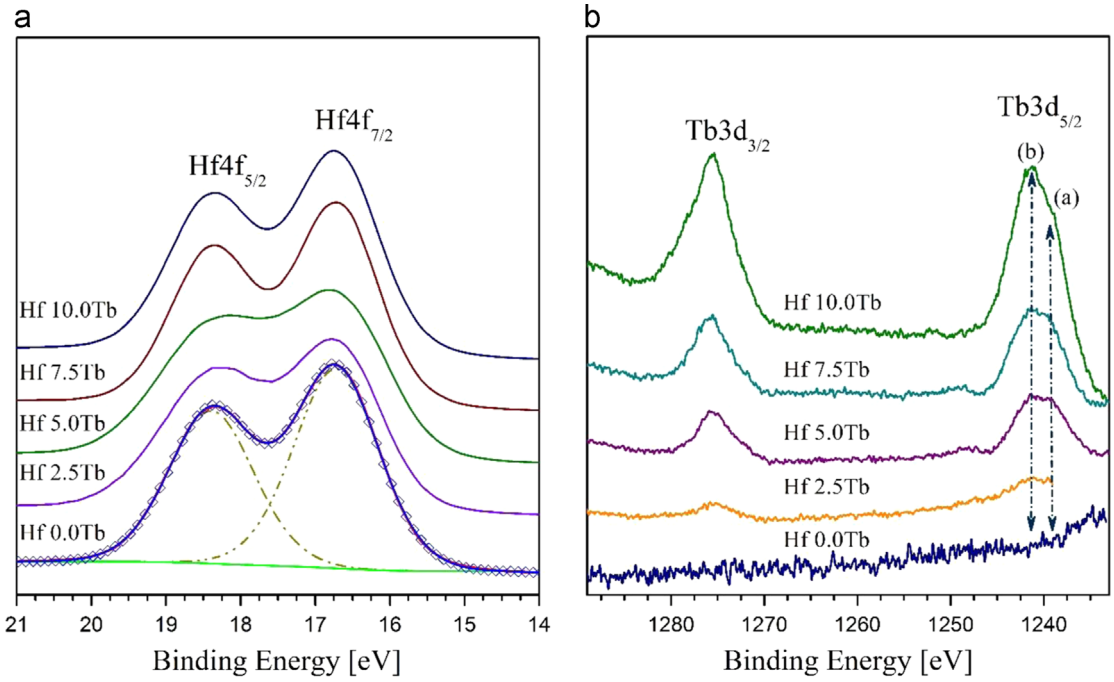

Fig. 4. High-resolution XPS spectra of: (a) Hf4f and (b) Tb3d in which, the HfO_2 was confirmed and can be observed the evolution of Tb content in the HfO_2:Tb^{3+} films.

Table 1
Atomic percentages of terbium and europium in HfO_2:Tb^{+3}, Eu^{+3} films deposited at different substrate temperatures during 300 s. The doping concentrations in the deposition solution were 5 at% for Tb and 10 at% for Eu.

T_s (°C)	400	450	500	550
Terbium	2.3	2.01	1.8	0.4
Europium	2.7	2.1	1.6	0.3

Table 2
Atomic percentages of terbium and europium in HfO_2:Tb^{+3}, Eu^{+3} films deposited at 500 °C during 300 s with variations in the doping concentrations.

Tb, Eu(acac) in deposition solution (at%)	2.5	5	7.5	10
Tb at% inside the films (at%)	1.1	1.8	2.3	3.4
Eu at% inside the films (at%)	0.9	1.6	1.9	2.8

incorporated into the HfO_2 films as measured for samples deposited at different substrate temperatures and with variations in the initial doping concentrations are shown in Tables 1 and 2. It is remarkable to observe a decrease of the atomic percentages of Tb and Eu ions as the deposition temperature is increased up to 500 °C. A dramatic fall of these percentages is observed for samples deposited at 550 °C. This effect is surely related with the growth kinetics of the films as the substrate temperature is increased. At low deposition temperatures the aerosol arrives to the substrate surface in liquid form, the solvent is evaporated and the film is deposited; for higher substrate temperature the aerosol, due to the heat radiated by the substrate, is converted to gas and the kinetics of the deposit process changes (CVD stage). For even bigger deposition temperature the heat radiated by the substrate can prevent that certain elements of the aerosol be incorporated into the films. This could be the case of the activators (Tb and Eu) whose compounds (Tb, Eu acetylacetonates) have smaller melting points (Tb acac, M.P.=135 °C; Eu acac, M.P.=140 °C) compared with the melting point of Hf acetylacetonate (Hf acac, M.P.=193 °C). More investigation is necessary to completely elucidate this point.

AFM images of the HfO_2 films deposited on silicon single crystal (100) substrates at different temperatures (the deposition time was 300 s) are shown in Fig. 5a. The deposited films exhibited a smooth surface at low deposition temperatures (400 °C) and a granular morphology for higher deposition temperatures (550 °C), such growth is typical of the films deposited by USP technique when metal-organic precursors are used [23]. This surface morphology is also obtained when other more expensive and complex deposition techniques as CVD and ALD are used [33,34]. According to Langlet et. al. [21] the diverse morphologies of the films are attributed to the different stages of the pyrolytical reaction occurring in this type of synthesis when the substrate temperature is changed. The USP technique involves a chemical phase deposition (CVD) process which, in general, consists successively in solvent evaporation, precipitate (solute) sublimation and surface diffusion of the vapor generated on the substrate to form the film. The kinetic of this process is critically related to the surface temperature of the substrate. The CVD stage induces the best films properties such as high density, good adherence to substrate, high optical quality, etc. When the substrate temperature is higher than those for CVD process the size and crystalline quality of the grains forming the film vary considerably until reaching an appearance of a powder deposit. In this case, the films show a high roughness. As a consequence, films deposited at 400 are grown at CVD conditions

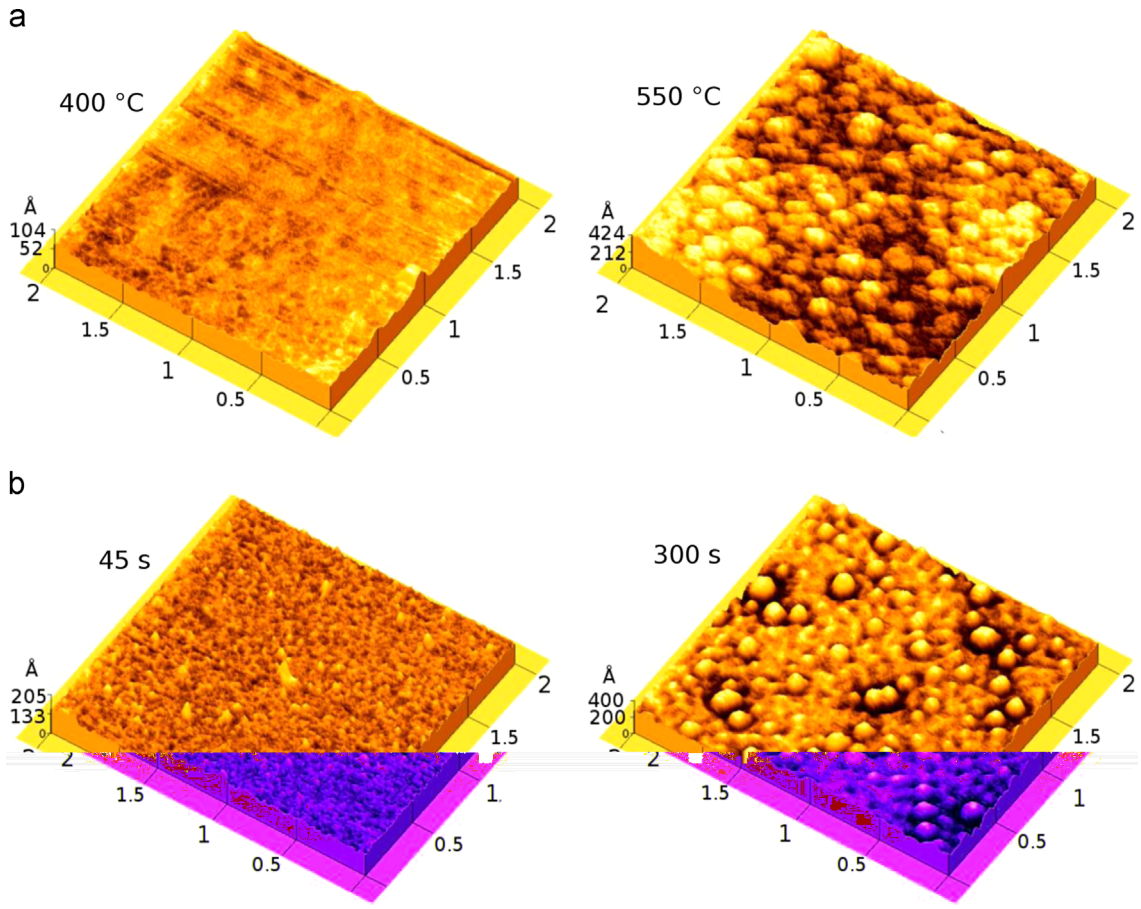

Fig. 5. AFM images of HfO_2 films deposited over silicon substrates (a) at different temperatures with a deposition time of 300 s and (b) at different deposition times at a temperature of 500 °C.

showing flat surfaces and those deposited at higher substrate temperature are not grown in the CVD stage and result with a higher roughness [21]. Fig. 5b shows the AFM images obtained for HfO_2 films deposited at 500 °C with different deposition times. The surfaces of these films evolve from a very smooth surface to a rougher morphology as the deposition time increases. The increase of deposition time results in the appearance of clearly observable agglomerates on the film surface. This effect is mainly due to the changes in crystal structure of the film. Amorphous films grow in the initial stage of deposition (short deposition times), as the deposition time is increased the thickness of the film increases and some crystallites appears; the surface roughness increases together with the film thickness. Similar effect has been observed by Aarik et. al. for HfO_2 thin films deposited by ALD technique [27]. On the other hand, films deposited under similar conditions have been tested in MOS devices as described in previous work [35] where the surface roughness was a critical parameter to avoid dielectric breakdowns.

Table 3 shows the values of average roughness (R_a) of the films as a function of the substrate temperatures and the deposition times. These values were determined over a 5×5 μm area. It is possible observe that the roughness of the films changes more slowly with the deposition time that with the increasing of the substrate temperature. This behavior could guide us to obtain more smooth films when are deposited at lower substrate temperatures and short deposition times. R_a values were obtained in the range between 0.9 and 3.9 nm, being the film deposited at 500 °C during 180 s which had the lowest roughness with a value of 0.9 nm.

Table 3
Average roughness (R_a) of the films as a function of the substrate temperatures and the deposition times.

Time (s)	Roughness (Å)	Temperature (°C)	Roughness (Å)
45	18.6	400	15.5
90	16.9	450	15.1
180	8.97	500	29.2
300	29.2	550	36.9

The thicknesses of the films deposited at different temperatures as measured by ellipsometry technique have the following values: 103.3, 227.1, 274.1 and 905.6 nm for films deposited during 300 s at 400, 450, 500 and 550 °C respectively. Deposition rate was calculated, the resulting values were 0.34, 0.77, 0.91 and 3.0 nm/s. For the films deposited at 500 °C with deposition times of 45, 90, 180 and 300 s, the obtained thickness values were 35.0, 50.0, 91.2 and 274.1 nm, respectively, with an average deposition rate of 0.88 nm/s. It is possible to observe that thickness of the films increases as the