We investigate chemical and physical properties of crystalline Ta$_2$O$_5$ films grown on Si substrates by radio frequency magnetron sputtering. We first grew three Ta films and, to induce the crystalline phase of Ta$_2$O$_5$, two of them were exposed to a post-deposition annealing at 1273 K in air for 1 h. Coating characterization was performed by X-ray diffraction, scanning electron microscopy, Raman scattering spectroscopy, and X-ray photoelectron spectroscopy. The microstructure of the crystalline films is granular and the atomic structure corresponds to orthorhombic Ta$_2$O$_5$. XPS depth profiles for Ta 4f and O 1s core-levels were carried out in order to assess the chemical states of all samples. Upon analysis at the surface of the films, we observe the Ta 4f spectrum characteristic of Ta$_2$O$_5$. However, as one goes deeper into the films, oxygen vacancies are generated by ion bombardment and reconstruction processes are induced; resulting in the formation of metastable Ta oxide phases with oxidation states Ta$^{1+}$, Ta$^{2+}$, Ta$^{3+}$, Ta$^{4+}$, and Ta$^{5+}$. Exposing the films, after sputtering, to ambience for some days stimulates the amorphous phase of Ta$_2$O$_5$ at the very surface suggesting that the suboxides of Ta are unstable. We discuss that these suboxides are only generated during sputtering and at the very surface. The Raman results indicate the presence of the orthorhombic Ta$_2$O$_5$ phase and also a straightforward transition from Ta amorphous to crystalline Ta$_2$O$_5$. 

I. INTRODUCTION

Recent investigations in high dielectric constant materials point to tantalum pentoxide (Ta$_2$O$_5$) as one of the most promising candidates to deal with modern technological challenges. Due to its low leakage current and high dielectric constant tantalum pentoxide has been used as a storage capacitor, insulator, catalyst and gas detector. In addition to its electrical properties, Ta$_2$O$_5$ possesses high refraction index ($n = 2.18$ at $\lambda = 550$ nm) and a wide band gap of $\sim$4.0 eV which makes it an excellent material for optical applications.

In regard to its atomic structure, Ta$_2$O$_5$ solidifies in either amorphous or crystalline structure; the latter showing two phases below 1500 K. The study of the crystalline properties of Ta$_2$O$_5$ films is of great importance not only from the technological perspective but also from the scientific one. In an earlier work the existence of several polymorphs were established and although most researchers agree that the system crystallizes in either hexagonal ($\delta$ phase) or orthorhombic ($\beta$ phase) structures, the exact spatial group is still under investigation. The atomic structure and the chemical and physical properties of Ta$_2$O$_5$ strongly depend on the fabrication methods. In the last two decades experimental techniques such as PLD, LPCVD, sputtering,
ion assisted deposition, and EBE have been used\textsuperscript{13-15}. Moreover, to ensure the full oxidation of films most techniques involve post-deposition heat treatments under oxygen flow and temperatures above 473 K\textsuperscript{19,21}. If the temperature is high enough, crystalline phases are favoured resulting in a transition of the chemical and physical properties. While there are several reports dealing with the chemical properties of amorphous Ta\textsubscript{2}O\textsubscript{5} films\textsuperscript{14,22,23}, there are a few reports focused on studying these properties for the crystalline phases of Ta\textsubscript{2}O\textsubscript{5}\textsuperscript{20}. Therefore, we believe it is of great importance to investigate the microstructure, vibrational modes and chemical properties of orthorhombic Ta\textsubscript{2}O\textsubscript{5} films. Special attention is paid to the chemical state of the samples as a function of depth profiling. To this end Ta films were grown on Si substrates by RF magnetron sputtering and the crystalline phase was induced by exposing the films to a heat treatment at 1273 K. The crystalline structure and microstructure were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. X-ray photoelectron spectroscopy (XPS) in combination with ion sputtering were used to create a depth profile of the films and to evaluate the chemical properties for the different depths. Finally, the vibrational modes were assessed by Raman scattering spectroscopy.

II. EXPERIMENTAL

A. Film growth and annealing

Three amorphous Ta films were grown (at different sessions) at room temperature on 5 mm × 7 mm–Si(100) substrates by the RF magnetron sputtering technique. To eliminate superficial contamination, the substrates were cleaned up with several baths of distilled water, acetone, and ethanol. After cleaning, each substrate was placed on a rotary base inside the vacuum chamber at a target-substrate distance of 13 cm. For the deposition we used a 2.5 inch-Ta target (99.95% purity) and evacuated the vacuum chamber to a base pressure of 5 \times 10^{-5} Torr. Afterwards, argon gas was flushed into the chamber to a working pressure of (2.0 \pm 0.1) \times 10^{-2} Torr. The native oxide layer on the target surface was eliminated by a 5 min pre-sputtering process at 60 W. Immediately the power was raised to 120 W and the rotary base was activated with a speed of 0.2 rpm. During deposition there was no intentional substrate heating or cooling. After deposition, two films were exposed to heat treatments in air for 1 h at 1273 K using a Thermo Scientific Thermolyne cylindrical furnace (model F21135). These films were labeled as F05, F33; the numbers referring to the deposition rate \(D_v\) are tabulated in Table \[1\].

B. Characterization and depth profiling

To study the crystalline structure of the coatings we used a Siemens diffractometer model D-5000 with Cu K\textsubscript{\alpha} radiation (\(\lambda = 1.5406 \) Å). A Bragg-Bretano configuration was used and XRD patterns were obtained at steps of 0.02° with a time per step of 3 s; with operating parameters of 34 kV and 25 \(\mu\)A. A field emission microscope JSM7000F was used to evaluate the morphology and particle size of the samples.

Chemical state and atomic concentration of the films at different sputtered times were determined from the spectra of the Ta4f and O1s core-levels using a Thermo Scientific K-Alpha XPS spectrometer with an Al K\textsubscript{\alpha} X-ray source set to 12 kV and 40 W. The beam spot has a diameter of 400 \(\mu\)m and made an angle relative to the sample of 30°. For the XPS scans we used steps of 0.1 eV. Oxygen to tantalum ratio in the films was determined by peak deconvolution of the XPS curves. Oxidation states of Ta were estimated by deconvolution of the XPS spectra. Deconvolution and determination of peak parameters were realized with AAnalyzer software using Voigt functions [Gaussian \(\sigma = (1.43,0.9)\) eV and Lorentzian \(\gamma = 0.02\) eV] and a Shirley-Sherwood background\textsuperscript{24}. The sputtering profiling of the films was carried out by an argon ion beam with a voltage of 3 kV and an electric current of 10 \(\mu\)A. The incidence angle between the sample and the ion gun was 90°. The etched area was 2 mm × 1 mm and the sputtered times were: 0 min, 3 min, 6 min, and 9 min.

III. RESULTS AND DISCUSSION

A. Crystalline Structure and morphology

As expected the as-deposited film F0 displays no peaks in the XRD pattern indicating an amorphous structure; for this reason its pattern is not shown here. On the contrary, the patterns for the films F05 and F33 reveal a crystalline structure (see Fig. 1). These patterns can be indexed to the orthorhombic phase \(\beta-\text{Ta}_2\text{O}_5\) (PDF 00-025-0922 with lattice parameters \(a = 6.1980 \) Å, \(b = 40.2900\) Å, \(c = 3.8880\) Å, and \(\alpha = \beta = \gamma = 90°\) for the spatial group \(P2_12121\)). As of now, there is still an ongoing discussion regarding the specific space group for the crystalline phases of Ta\textsubscript{2}O\textsubscript{5}\textsuperscript{12,17,28,33}. It is worth noting, however, that the patterns show no traces of other Ta oxides.

\begin{table}[h]
\centering
\caption{Annealing temperature \(T_{\text{ann}}\), film thickness \(t\), and deposition rate \(D_v\) for the films.}
\begin{tabular}{|c|c|c|c|}
\hline
Film & \(T_{\text{ann}}\) & \(t\) & \(D_v\) \\
\hline
F0 & 298 & 2.4 & 2.8 \\
F05 & 1273 & 0.5 & 2.4 \\
F33 & 1273 & 3.3 & 2.8 \\
\hline
\end{tabular}
\end{table}
FIG. 1. X-ray diffraction patterns for the crystalline films F05 and F33. The lower pattern corresponds to the reference PDF 025-0922.

According to the literature\cite{1}, Ta$_2$O$_5$ is the most stable oxide of Ta exhibiting amorphous and crystalline phases; the other oxides such as TaO, Ta$_2$O, Ta$_2$O$_2$, Ta$_3$O$_3$ (except for TaO$_2$) have shown to be difficult to obtain as pure phases. Moreover, except for Ta$_2$O$_3$ and TaO$_2$, all suboxides are crystalline. We will come back to this in our discussion of chemical states. The crystallite size $D$ was estimated using the well-known Scherrer equation

$$D = \frac{K\lambda}{\Gamma \cos \theta},$$

where $K = 0.9$, $\lambda = 1.5406 \, \text{Å}$ and $\Gamma$ is the full width at half maximum of a given peak. Accordingly, taking the peak at $2\theta = 28.3^\circ$ for both films, we found that $\Gamma = (0.22, 0.27)^\circ$ and hence $D = (36, 30) \, \text{nm}$, respectively. This result demonstrates the nanometric microstructure of the films.

B. Morphology and particle size

In Fig. 2 the SEM images for the three films are shown. As we can observe, film F0 shows a smooth and cloudy pattern. The other films also exhibited this pattern before annealing.

As the films were exposed to the heat treatment grains showed up for F05 and F33, both samples resembling the powder microstructure of Ta$_2$O$_5$. It is worth noticing that both annealed samples exhibit some black spots. To elucidate the nature of these spots we took backscattering electron images (not shown). The results suggest that the spots may belong to another oxide phase of Ta, most probably the $\delta$ phase of Ta$_2$O$_5$ or a suboxide. We performed an EDS (Energy dispersive x-ray spectroscopy) analysis on these spots but the atomic concentration of O and Ta did not change significantly and therefore conclusions cannot be drawn. As for the particle size, according to these images, we estimated a diameter varying from 100 nm to 500 nm with a mode of 300 nm. Despite that
the binding energies of our spectra were calibrated with respect to carboxyl XPS depth profiles on all samples. The bindsurface contamination from the C 1s and annealing processes are quite reproducible.

of the black spots, suggesting that both the deposition morphology are quite similar as well as the manifestation both films have different thickness, the particle size and levels that there is a spin-orbit doublet corresponding to the Ta 4f core-level (spectra shown in the left column of Fig. 3). The splitting of (27.75±0.10) eV with spin-orbit splitting of (1.89±0.01) eV in agreement with those reported for Ta 5+ in stoichiometric amorphous Ta2O5 films, suggesting that at the surface Ta2O5 forms. This is expected because in an oxygen rich environment the surface would be more oxidized than the rest of the film. We checked this by sputtering the surface of the samples for 30 s and observed the light green spectra where new features appear. We then exposed the samples to ambience for seven days and observed again the same black spectra without etching demonstrating that the surface oxidized anew. A closer look at the spectrum for zero etching of F0 and the spectra of F05 and F33 for 30 s etching indicates the presence of a satellite in the low energy region (around 24.6 eV ± 0.3 eV). This satellite is known to be caused by screening of 5d electrons in amorphous TaOx (x = 1.86, 2.00) suggesting the presence of TaOx in our films.

This state of affairs could be predicted if we keep in mind the following. Assuming the presence of Ta2O5 on the very surface, one would expect, immediately after sputtering the surface, the depletion of O atoms and thus the temporary generation of O vacancies. This in turn forces the reordering of the surface atoms, favoring either reconstruction or relaxation processes to take place in order to maintain not only the structural stability of the superstructure at the surface but also electroneutrality. Subsequently, this atomic reconfiguration promotes the formation of metastable phases of Ta oxides such as TaO, Ta2O3, Ta2O5, or Ta2O7.

However, as time goes by (it could be some minutes or days depending on both the oxygen concentration around the surface and the physi and chemisorption processes taking place and due to the instability of these phases, the surface tends to readsorb O atoms and, as we have just discussed above, oxidizes constituting the most stable phase of Ta oxide, i.e., Ta2O5. In this scenario, we realize that, at the very surface, there is amorphous Ta2O5; and for the rest of the bulk, we mainly have TaOx for F0 and the β-Ta2O5 phase for F05 and F33 —incidentally, as is well known, XPS is not capable of distinguishing between the crystalline and amorphous phases. Hence, as one sputters away the topmost atoms, one destroys the amorphous Ta2O5 phase and the chemical states of Ta change. The rich additional features that appear in the profiling spectra as we go deeper lend support for this view (0.5 min to 9 min spectra in Fig. 3). The deconvolution analysis performed on the spectra reveal that there are six sets of peak splitting (see Fig. 4). These kind of spectra have been reported in ab-initio calculations for the δ phase of Ta2O5 films and have been described by four doublets with the 4f7/2 binding energies of (22.0, 23.2, 24.6, and 26.1) eV and spin-orbit splitting of 1.9 eV. These peaks were attributed to Ta1+, Ta2+, Ta3+/Ta4+, and Ta5+, respectively, mainly originated by induced oxygen vacancies generated during the ion bombardment in amorphous Ta2O5 films. In our case we were able to distinguish six doublets corresponding

C. Chemical states: XPS depth profile
1. Ta 4f core-level

To investigate the chemical states of the coatings we carried out XPS depth profiles on all samples. The binding energies of our spectra were calibrated with respect to the O 1s peak at 532 eV. After calibration we checked for surface contamination from the C 1s core-level (spectra not shown). The spectra revealed the presence of carbon contamination which is quite ubiquitous in most samples. We then proceeded to study the core-level depth profiling spectra for Ta 4f, shown in the left column of Fig. 3. Starting with the Ta 4f core-level for the three films without etching (0 min, black spectra) we observe that there is a spin-orbit doublet corresponding to the levels 4f7/2 and 4f5/2. The binding energies for the doublets is around (27.75±0.10) eV with spin-orbit splitting of (1.89±0.01) eV in agreement with those reported for Ta 5+ in stoichiometric amorphous Ta2O5 films, suggesting that at the surface Ta2O5 forms. This is expected because in an oxygen rich environment the surface would be more oxidized than the rest of the film. We checked this by sputtering the surface of the samples for 30 s and observed the light green spectra where new features appear. We then exposed the samples to ambience for seven days and observed again the same black spectra without etching demonstrating that the surface oxidized anew. A closer look at the spectrum for zero etching of F0 and the spectra of F05 and F33 for 30 s etching indicates the presence of a satellite in the low energy region (around 24.6 eV ± 0.3 eV). This satellite is known to be caused by screening of 5d electrons in amorphous TaOx (x = 1.86, 2.00) suggesting the presence of TaOx in our films.

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![Figure 3](image-url)
FIG. 4. (Color online) Deconvolution of Ta 4f XPS spectra for the three films. Left column for F0, central column for F05, and right column for F33.

The spectra correspond to the states Ta\(^0\), Ta\(^{1+}\), Ta\(^{2+}\), Ta\(^{3+}\), Ta\(^{4+}\), and Ta\(^{5+}\) with binding energies at (21.7±0.3, 23.0±0.2, 23.8±0.4, 25.2±0.4, 26.2 and 27.8) eV, respectively, and peak splitting of 1.89 eV each. These values are slightly higher than those reported earlier but follow the same trend. These discrepancies may be due to differences in the calibration criteria adopted for the measuring instruments.

In order to quantify the contribution of Ta oxide to the whole spectrum, we computed, from the deconvolution of the Ta 4f spectra, the percentage of oxidation state of Ta (see Fig. 5).

Due to the complexity of the spectra, the peak fitting may not be entirely accurate and over interpretation of the results should be avoided. Nonetheless, some general trends can be indeed summarized. In Fig. 5 we can observe that, at the surface of all samples, Ta in Ta\(^{5+}\) has the major contribution; with more than 70% in all cases. As expected the content of Ta\(^{5+}\) in F0 is much less than that one in F05 or F33. As we go deeper, the state 5+ decreases between 15% and 35% whereas the other states increase, suggesting the presence of Ta suboxides. Ta in metallic state (Ta\(^0\)) is barely present in all cases with less than 1% and the presence of suboxides varies from 10% to 35%. These values are credible according to previous reports.\(^{26}\)

We also estimated the stoichiometry of our samples. In stoichiometric Ta\(_2\)O\(_5\) the O to Ta ratio is 2.5. We have plotted the atomic percentage ratio for Ta\(_2\)O\(_5\) in figure 6. There we can see that all samples are non-stoichiometric. The ratio of F0 ranges from 0.80 to 0.95 as sputtering time increases which seems reasonable since this sample was not exposed to a heat treatment and one would expect the same atomic concentration all over the sample (except at the surface where there is slightly more oxygen available). This finding suggests that most of the film is TaO\(_x\), reaffirming our discussion above. The ratio
FIG. 5. (Color online) Percentage of oxidation state of Ta as function of sputtering time for the three films.

for F05 goes from 1.50 to 0.90 as the sputtering time increases and that one for F33 goes from 1.75 to 1.20; these values indicate an overall higher oxygen content. We believe that the non-stoichiometry is consequence of two important factors, namely: the lack of an oxygen rich atmosphere during the manufacturing process of the samples; and the oxygen depletion taking place during ion bombardment. It is evident from the plot that the latter factor has a major impact on the oxygen depletion. Since argon and tantalum have larger atomic numbers than oxygen one would expect the oxygen to be removed first during sputtering.

We remark that the reconstruction processes, that leads to the appearance of Ta suboxides, only takes place at the very surface (a few monolayers thick). This is because, in the first place, the suboxides only appear after sputtering the surface, even for short sputtering times (30 s) and, in the second place, because if they were present all over the bulk of the film, they must show up in the XRD patterns; however the XRD patterns show no signs of impurity phases of Ta oxide (excluding Ta$_2$O$_3$ and TaO$_2$, which are amorphous). To further check these assertions, after sputtering F33 for 9 min, we exposed it to air for three days and obtained again its Ta 4f spectrum at the surface; the results showed anew the spectrum corresponding to amorphous Ta$_2$O$_5$ (not shown).

2. O 1s core-level

We can extract even more information on the chemical states analyzing the oxygen core-levels. The depth profiles for the O 1s core-level for all films are displayed in the right column of Fig. 3. Starting with the black spectra (no etching) we observe a satellite at high energies, around 533.8 ± 0.2 eV. We also note a low energy line at 532 eV which is typical from Ta-O binding.

The situation for the sputtered films is different for the satellite seems to disappear. The deconvolution reveals the presence of two components, indicating that even for bottom layers the satellite is still present although its intensity is small (see figure 7). This feature has been observed before by some researchers. On one hand, O. Kerrec et al. grew amorphous Ta$_2$O$_5$ films and exposed them to distilled water. They attributed the satellite to hydroxylic groups and/or water adsorbed at the surface. On the other hand, Atanassova et al. grew also amorphous Ta$_2$O$_5$ thin films (6 nm to 13 nm) on Si substrates and sputtered the samples for different times. They claimed that the satellite was due to Si-O binding rather than contamination. In a recent investigation, R. Simpson et al. studied the effect on the chemical composition of Ar$^+$ sputtered amorphous Ta$_2$O$_5$ films (30 nm thick) grown on Ta foil and found that the C 1s core-level disappears after 3 nm depth. Thus since our coatings are thick and the intensity of the satellite diminishes considerably as the depth increases, we attribute this feature to surface contamination, must probably a carbon compound due to the presence of carbon on the surface.
D. Raman: Vibrational modes

The Raman scattering spectra of the crystalline samples are shown in Figure 8. Due to its metallic nature, the Raman spectrum of F0 does not show up characteristic peaks and for this reason is not shown in the graph. However, we include as a reference the Raman spectrum of β-Ta$_2$O$_5$ powder which was acquired from Alfa Aesar with purity of 99.99%. Before the measurement, the humidity in the powder was eliminated by a heat treatment at 1273 K for 1 h in air. By comparing the Raman spectra for films F05 and F33 we notice that both agree quite well with the reference spectrum and the spectra reported in the literature, indicating that the β phase has been achieved.

According to previous work, the region below 150 cm$^{-1}$ can be assigned to lattice modes, while the bands between 150 cm$^{-1}$ and 500 cm$^{-1}$ are due to bending modes δ(Ta-O-Ta) and δ(O-3Ta). In the region between 400 cm$^{-1}$ and 1000 cm$^{-1}$ we find the stretching modes, attributed to ν(O-3Ta) and to ν(Ta-O-Ta). Bands under 100 cm$^{-1}$ are related to interactions of several Ta polyhedra. In our spectra we see a peak at 635 cm$^{-1}$ that can be assigned to vibrations in the TaO$_6$ octahedra while the peak at 844 cm$^{-1}$ suggests the presence of TaO$_5$ (pentagonally coordinated groups). Based on these observations and given that F0 showed no characteristics peaks, we deduce that there is a straightforward transition from Ta amorphous to β-Ta$_2$O$_5$ in agreement with XRD analysis.

IV. CONCLUSIONS

The microstructure and atomic structure of Ta and β-Ta$_2$O$_5$ films were studied by X-ray diffraction and scan-
FIG. 8. (Color online) Raman spectra for Ta$_2$O$_5$ powder, F05, and F33.

ning electron microscopy. The results show a granular structure for the crystalline samples resembling the powder morphology. Using XRD we also determined the formation of the orthorhombic phase of Ta$_2$O$_5$ for the crystalline films and found no traces of Ta suboxides in the bulk of all samples. Meanwhile the film F0 was found to be amorphous. Both XRD and Raman scattering analyses indicate a structural transition of the films F05 and F33 from Ta amorphous to crystalline Ta$_2$O$_5$ in orthorhombic phase. We carried out XPS depth profiling studies in order to study the chemical states of our samples. From the deconvolution of the Ta 4f spectra it can be concluded that the chemical states of Ta vary from Ta$^{5+}$ to Ta$^{1+}$. Our findings strongly suggest the manifestation of Ta suboxides generated at the very surface by reconstruction processes derived by the creation of vacancies during ion bombardment. We found evidence that the suboxides are unstable and the surface restores the amorphous phase of Ta$_2$O$_5$ after several days of air exposure. We conclude that all films have an amorphous Ta$_2$O$_5$ phase at very surface and, in the rest of the bulk, TaO$_x$ and crystalline $\beta$-Ta$_2$O$_5$ remain the dominating phases for the film F0 and the films F05 and F33. We found that the crystalline samples are non-stoichiometric either on the surface or the rest of the depth. We mainly attributed this to oxygen depletion during ion bombardment and to the lack of an oxygen rich environment during both growth and annealing.

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