Identification and roles of nonstoichiometric oxygen in amorphous Ta₂O₅ thin films deposited by electron beam and sputtering processes

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Abstract

The morphology and composition of tantalum oxide (Ta₂O₅) thin films prepared by electron-beam (EB) evaporation and radio-frequency sputtering (SP) were investigated by grazing incidence X-ray diffraction (GIXRD), X-ray reflectometry (XRR), atomic force microscopy, Fourier transformed infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). GIXRD revealed an amorphous nature for both films, and XRR showed that the density of the Ta₂O₅-EB films was lower than that of the Ta₂O₅-SP films; both films have lower density than the bulk value. A larger amount of molecular water and peroxo species were detected for the Ta₂O₅-EB films by FTIR performed in ambient atmosphere. XPS analyses performed in vacuum confirmed the presence of hydroxyl groups, but no trace of chemisorbed molecular water was detected. In addition, a higher oxygen nonstoichiometry (higher O/Ta ratio) was found for the EB films. From these results, we conclude that the oxygen nonstoichiometry of the **EB** film accounted for its lower density and higher amount of absorbed molecular water. The results also suggest the importance of understanding the dependence of the structural and chemical properties of thin amorphous oxide films on the deposition process.

Keywords: Oxides; composition; H₂O absorption; nonstoichiometric oxygen, Fourier transformed infrared spectroscopy; X-ray photoelectron spectroscopy

1. Introduction

Tantalum oxide (Ta_2O_5) is used in a diversity of applications ranging from dielectric materials for capacitance applications and integrated semiconductor devices to batteries and coatings [1-3]. Recently, it has attracted interest as a medium for electrochemical transport in solid-state nano-electronics devices like atom transistors or redox-based resistive switching memory (ReRAM) devices [4, 5]. Redox-based ReRAM based on cation migration in a thin oxide film is considered to be a promising candidate for next generation nonvolatile memory applications, owing to its high density, high speed, low power consumption, and back-end-of-line compatibility with complementary metal-oxide-semiconductor technologies, ensured by a basic metal-insulator-metal (MIM) structures with an electrochemically active metal (usually Cu or Ag) electrode on one side. The resistance switching properties are summarized as follows: the creation of metal cations by dissolution from the active metal electrode polarized as the anode, electro-migration towards the cathode, nucleation of metal islands on the cathode, and ultimately formation of a metal filament between the two electrodes [6]. Owing to its similarity to an atomic switch, in which resistance across a nanometer gap between a mixed conductor electrode and an inert counter electrode is controlled by bias voltage sweeping, MIM-structured ReRAM with an active electrode is referred to as a gapless-type atomic switch [7]. This type of ReRAM is also referred to as an electrochemical metallization (ECM) cell, [8, 9] and conductive bridge RAM [10].

Tsuruoka et al. [11] have shown the important effect of the moisture absorption of oxide films on the switching properties of oxide-based atomic switches. Recently, they also reported that the density of Ta_2O_5 film significantly influences the redox reactions at the anode interface as well as the forming process (the first SET process from a pristine high-resistance state to a low-resistance state) [12]. These results indicate that the structural properties of thin oxide films in the MIM structure play a crucial role in determining the switching characteristics of the atomic switch. Ta_2O_5 films used for atomic switch applications have been mainly amorphous in morphology [11-14]. Amorphous Ta_2O_5 films generally show a range of stoichiometries: from sub-oxidized Ta_2O_5 films (O/Ta atomic ratio inferior to 2.5) [15-17] to oxygen rich Ta_2O_5 films (O/Ta ratio superior to 2.5) [18, 19], depending on the deposition method and conditions. Few studies have focused on the consequences of using oxygen rich films on the properties of atomic switches. Tsuchiya et al. [19] have previously studied the composition of oxygen rich Ta_2O_5 films with O/Ta ratios of up to 3, and predicted the corresponding variation in the redox reactions at the anode interface. However, significant

changes in the composition are predicted to occur only for higher ratios of oxygen nonstoichiometry.

In this paper, we report a systematic study of the morphology and composition of amorphous Ta₂O₅ films deposited by two deposition methods: electron-beam (EB) evaporation and radio-frequency (RF) sputtering (SP). To reveal the actual properties of the films used in the atomic switches, Ta₂O₅ was deposited onto Pt/Ti/SiO₂/Si substrates, where Pt was used as the bottom electrode for the atomic switch cells. Various structural and chemical analyses revealed that the deposited films exhibited oxygen nonstoichiometry with high O/Ta ratios and that the formation of unsaturated peroxo dangling bonds and hydroxyl groups are responsible for water chemisorption by thin Ta₂O₅ films. The difference in the structural and chemical properties of the two deposited films is also discussed.

2. Material and methods

All layers were deposited at room temperature. First, Si substrates covered with SiO₂ (300 nm) were cleaned by alternate solvent bathing and O₂ plasma **etching**. Then, 5-nm-thick Ti and 25-nm-thick Pt as the adhesion layer and the bottom electrode, respectively, were deposited by EB evaporation using a home-made deposition chamber. Afterwards, a 15-nm or 20-nm-thick Ta₂O₅ film was deposited by EB evaporation (Ta₂O₅-EB) or RF sputtering (Ta₂O₅-SP). Ta₂O₅-EB films were deposited from Ta₂O₅ pellets formed from 99.99% pure Ta₂O₅ powder at room temperature and a fixed deposition rate of 0.01 nm/s. The deposition rate and film thickness were controlled using a quartz crystal thickness monitor. Ta₂O₅-SP films were sputtered from a polycrystalline 99.99% pure Ta₂O₅ target. A mixture of Ar (5 sccm) and O₂ (2.5 sccm) gases was used. The reactive sputtering process was performed using an ES-250 sputtering apparatus (EIKO Engineering Co. Ltd., Osaka, Japan) and the RF power was maintained at 200 W. The substrate was kept at room temperature. For comparison, Ta₂O₅ films were also deposited onto Si substrates with a thin native oxide layer. The thickness of the deposited films was determined by ellipsometry using a M-2000U spectroscopic ellipsometer (J.A. Woollam, Lincoln, NE USA). Ellipsometric parameters (Ψ , Δ) were acquired over the wavelength range of 400–1000 nm at three different incident angles, 65°, 70°, and 75°, to evaluate the film thickness precisely.

The crystallinity of the films was analyzed by grazing incidence X-ray diffraction (GIXRD) at incidence angles of 0.5° and 1° and a collection range of 10°–65° using a SmartLab® Rigaku diffractometer in $\theta/2\theta$ configuration with a copper anticathode having a wavelength of 1.5418 Å as the X-ray source. X-ray reflectometry (XRR) using a Pan

Analytical X'Pert Pro MPD diffractometer was used to determine film thicknesses and densities. Crystallinity confirmation and composition analyses were performed by Fourier transformed infrared (FTIR) spectroscopy in attenuated total reflectance (ATR) mode to enhance the infrared signature of the thin films. FTIR-ATR measurements were acquired between 500 and 4200 cm^{-1} using a diamond prism in close contact with the sample. A polarized IR beam from a FTIR spectrometer (Nicolet 4700, Thermo Scientific, Waltham, MA USA) was directed into the prism base at an incidence angle of 70° to ensure total reflection. The spectrum of the prism was taken as a reference when no sample was coupled to the diamond prism. Surface morphology and roughness were observed by atomic force microscopy (AFM) using a NanoNavi II apparatus (SII, Chiba, Japan) in tapping mode with phosphorus (n) doped silicon tips (NanoSensors™) equipped with cantilever having a force constant in the 5–37 N/m range. The grain size and root mean square (rms) surface roughness of the deposited films were determined from a scan area of 500 nm $\times$ 500 nm. X-ray photoelectron spectroscopy (XPS) was performed to determine the composition of the films, using a scanning XPS microprobe (PHI Quantera II™, ULVAC-PHI, Inc., Chigasaki, Japan) with a monochromatic ($\text{AlK}\alpha$ at 1.487 keV) X-ray source operated at 15 kV. The photoelectrons were collected at 90° with respect to the surface. The typical operating pressure was 5×10^{-6} Torr. Survey (wide-scan) spectra were obtained with a pass energy of 44.75 eV. Multiplex (narrow-scan) spectra were obtained for the C 1s, O 1s, Ta 4f_{7/2} and Ta 4f_{5/2} photopeaks. The number of scans was fixed to 50. **Mixed Gaussian-Lorentzian line shape** was used for curve fitting, and integrated backgrounds were employed. **The atomic concentrations were estimated from the XPS peaks areas together with their relative sensitivity factors [20].**

3. Results

3.1. XRD

GIXRD measurements were performed to determine the structure of 15-nm-thick Ta₂O₅ films prepared by both deposition methods. Figure 1 shows GIXRD patterns obtained at an incidence angle of 0.5° for the as-deposited Ta₂O₅/Pt stacks at ambient temperature. For comparison, the XRD diffraction patterns of the tetragonal (α -Ta₂O₅) and orthogonal (β -Ta₂O₅) crystalline phases of tantalum oxide and the Pt bottom electrode, as documented by the Joint Committee for Powder Diffraction Studies (JCPDS) [21-23], are also shown in Fig. 1. The diffraction patterns of the two Ta₂O₅ films were similar and contained two diffraction peaks: a peak at 40.2° and a weaker peak at 46.6° . These peaks were identified as from the

(111) and (200) plane, respectively, of cubic phase Pt [23]. No reflections from tantalum oxide lattice planes were observed in the GIXRD spectra, indicating either an amorphous structure of the as-deposited films or highly textured oxide films from which peaks could not be detected because of the GIXRD configuration [24]. However, the presence of a broad and diffuse background was observed in the 15–30° angular region; this is referred to as an ‘amorphous-bump’ and is typical of amorphous oxide thin films [25]. This conclusion is also confirmed by previous studies of tantalum oxide thin films deposited by physical vapor deposition techniques under similar conditions: no substrate heating and no post-deposition annealing, leading to amorphous tantalum pentoxide, excluding the hypothesis of highly oriented films [26].

3.2. XRR

The mass density of the Ta₂O₅ films was determined by exposing the films to an X-ray beam in a grazing incidence configuration with respect to the film surfaces. The mass density of Ta₂O₅ films can be determined at a critical angle, θ_c [27]. For angles below θ_c , the incident X-ray beam is totally reflected. However, if the incidence angle is greater than θ_c , the X-ray beam penetrates into the film, leading to reflection and interference. As a result, the intensity of the reflected beam drops sharply. In this configuration, the thickness and roughness of the films as well as the stack structures could be identified. The experimental and simulated XRR curves obtained for Ta₂O₅ films with a nominal thickness of 15 nm, deposited on Pt/Ti/SiO₂/Si substrates, are shown in Fig. 2. The results for films deposited on Si substrates are also represented for reference and comparison. In the case of Si substrate, the fitting model included the presence of a native SiO₂ layer formed by simple exposure of the substrate in air before deposition. In the case of the Pt/Ti/SiO₂/Si substrate, the XRR curves were fitted using a stack structure consisting of each layer without any interfacial layers. The results of the experimental data fitting are presented in Table I.

The thickness of the Ta₂O₅ layers estimated from XRR was smaller than that determined by ellipsometry. The underestimation for the Ta₂O₅ layers deposited on Si substrates was likely a consequence of the formation of an intermixed Ta–Si–O interfacial layer between the Ta₂O₅ and the SiO₂ native oxide, which was not included in the fitting. Such a layer is expected to form as a result of the intermixing of Ta₂O₅ and SiO₂ [28-29], and can be included for more accurate results [18, 31]. Similarly, the uncertainty observed for the estimated thicknesses of Ta₂O₅/Pt/Ti/SiO₂/Si stacks indicates the presence of nonuniformities or interfacial layers between the Ta₂O₅ and Pt layers or between the Ti and SiO₂ layers. The

density of the Ta₂O₅-EB and Ta₂O₅-SP films deposited on Pt/Ti/SiO₂/Si was estimated to be 6.84 and 7.57 g·cm⁻³, respectively. Similar values were obtained for the EB and SP films deposited on Si substrates: 6.96 and 7.53 g·cm⁻³, respectively. These densities are lower than the reported bulk density of crystalline β-Ta₂O₅, 8.3 g·cm⁻³ [32]. The film roughness tended to diminish on the Pt electrodes, indicating a lower roughness of the Pt electrode compared with that of the Si substrate covered with a thin native oxide. The un-controlled formation of this SiO₂ native oxide caused by intermixing between the deposited Ta₂O₅ and the Si substrate may be the origin of the higher roughness observed for this type of substrate. Independently of the considered substrate, the SP films exhibited a lower roughness than the EB films, indicating a difference in film morphology induced by the deposition process. For amorphous Ta₂O₅ thin films obtained by DC magnetron sputtering deposition, Ngaruiya et al. [26] reported density values lower than that of the bulk density in the range of 7–7.5 g·cm⁻³ depending on the oxygen concentration, determined by XRR. In the case of tantalum oxide deposited by RF sputtering, Lutzenkirchen-Hecht et al. [33] reported similar values of surface roughness and density, 0.56 nm and 7.31 g·cm⁻³, respectively. A density close to 7.6 g·cm⁻³ has been reported for ion beam deposited films of similar thickness [18]. For films produced by reactive electron beam and ion plating, the density of thicker Ta₂O₅ films (10–100 nm) was reported to be in the range of 6.17–7.66 g·cm⁻³ [34].

The deviation between the bulk and the estimated densities led to the assumption that the two films had non-compact structures. Multiple factors could be at play: a highly disordered structure associated with a small Ta–O bond distance [33], nonuniformity of the Ta₂O₅ film originating from island formation, the presence of pores and voids within the films, and nonstoichiometry of the films. Island formation is not expected for either method in the case of amorphous oxides [35]. In the case of reactive Ta₂O₅ films obtained by DC magnetron sputtering, oxygen rich films have been reported to be concomitant with a decrease in their density [18]. We believe that the present XRR results suggest an oxygen rich composition of the films, as discussed in detail later.

3.3. AFM

Figure 3 shows three-dimensional (3D) surface topographic images obtained from the AFM measurements performed in tapping mode. The morphology observed in the AFM images was measured in multiple regions for each film and confirmed to be similar and uniform. A smooth surface with no presence of grains or facets was observed, excluding the presence of a poly-crystalline phase for Ta₂O₅ and thus confirming their amorphous nature, as

evidenced by the XRD patterns. No voids or pores were seen on the films, but this does not exclude the presence of internal voids and pores. Moreover, in a previous study, transmission electron microscopy could not distinguish the presence of nanocrystallites in the amorphous matrix of either type of film deposited under identical conditions [36]. The presence of island-like (or mound) structures on the surface was observed, but they must not be confused with poly-crystalline tantalum oxide grains, nanocrystallites, or pillars. A similar morphology has been confirmed for amorphous tantalum oxide films deposited on Pt or SiO₂, independently of the deposition process used [26, 35, 37-39]. The mean width of the mounds was estimated to be 20.8 nm and 15.32 nm for the Ta₂O₅-EB and Ta₂O₅-SP films, respectively. The thickness of these mounds, which can be defined as the height difference between peaks and valleys was up to 4.82 nm for the 15-nm-thick Ta₂O₅-EB films and 1.85 nm for the 15-nm-thick Ta₂O₅-SP films.

The average surface roughness R_a and root mean square roughness R_{rms} were estimated to be 0.48 nm and 0.6 nm for the Ta₂O₅-EB films and 0.16 nm and 0.21 nm for the Ta₂O₅-SP films, respectively. These roughness values are quite low and in good agreement with those reported for other amorphous films [38]. The Ta₂O₅-EB films exhibited higher roughness than the Ta₂O₅-SP films, as clearly observed in Fig. 3. **This tendency is consistent with the XRR results (see Table I).** In the case of the Ta₂O₅-EB films, the mounds had a height deviation greater than 3 nm from the nominal thickness of the films. Comparing the roughness results with those obtained from XRR, cf. Table I, we notice that the roughness measured by XRR is slightly overestimated. For example, in the case of the Ta₂O₅-EB thin films, the R_a extracted from AFM images was 0.48 nm, compared with 0.99 nm determined by XRR. It has already been reported that XRR experiments tend to overestimate the values of surface roughness [40, 41]. Additionally, the inclusion of interfacial layers in the XRR fitting model would probably improve the certainty. The R_a obtained from the AFM images should be considered to be more reliable.

3.4. FTIR-ATR

Figure 4 presents the FTIR-ATR absorbance spectra for 20-nm-thick Ta₂O₅ films deposited on a Pt/Ti/SiO₂/Si stack by both deposition methods. The spectra exhibited similar features, and the main peaks were located at 781 and 817 cm⁻¹ for the Ta₂O₅-EB and Ta₂O₅-SP films, respectively. For the Ta₂O₅ deposited by the pulsed laser deposition method, the absorbance band with a maximum located at 774 cm⁻¹ was attributed to the stretching vibration mode of Ta–O–Ta bonds [39]. Hence, the peaks at 781 and 817 cm⁻¹ can be

assigned to this stretching mode of Ta–O–Ta bonds for amorphous tantalum oxide [42-44]. Previous studies of 100-nm-thick amorphous tantalum oxide films have reported a main absorption peak at 650 cm^{-1} , which is characteristic of the $\text{Ta}\equiv\text{O}$ stretching mode [45,46]. This feature is absent in our spectra, indicating either a change in morphology or a preferential Ta–O configuration for our amorphous thin films compared with those of films over 100-nm-thick. For pulsed laser deposited Ta_2O_5 , Zhang et al. [47] reported a broad absorption band around 1000 cm^{-1} attributable to the presence of tantalum sub-oxides. The lack of this absorbance band indicates the absence of sub-oxide in our films. This result is in good agreement with the XRR results suggesting O-rich Ta_2O_5 films for both deposition methods.

The spectrum of the Ta_2O_5 -EB film exhibited a shoulder peak at 880 cm^{-1} as part of the main peak at 781 cm^{-1} . The Ta_2O_5 -SP film also exhibited a similar shoulder peak at the almost same wavenumber but with a lower intensity. This shoulder peak has also been observed for Nb_2O_5 and has been attributed to the stretching vibration of O–O bonds originating from peroxo species ($-\text{O}_2^{2-}$) [48-50]. The bending vibration of MO–H bonds (M means the metal), which vibrate in- and out-of-plane, has been reported to correspond to the presence of an absorbance peak located near 890 cm^{-1} arising from a highly hydrated environment [51]. A combination of these two contributions may be responsible for the shoulder peak observed for both films. These contributions are usually observed for oxygen rich films or in a humid environment. Although a slight deviation of $\sim 36\text{ cm}^{-1}$ was found between the position of the main absorbance peaks of the Ta_2O_5 -EB and Ta_2O_5 -SP films, the shoulder peak was observed at the almost same wavenumber ($\sim 880\text{ cm}^{-1}$). This indicates that both films partially shared an identical environment of Ta–O–Ta covalent bonds but had locally varied bonding states. The change in local environment may have been related to the lower density and the less compact structure of both films.

A small absorption peak was observed at $\sim 1150\text{ cm}^{-1}$ for both films. Pai et al. [52] reported the presence of a Ta–O terminal group vibrating mode at 1100 cm^{-1} for Ta_2O_5 films obtained by reactive RF magnetron sputtering, which is not seen as the main contribution in our spectra. However, the small peaks at $\sim 1150\text{ cm}^{-1}$ might be assignable to similar Ta–O terminal groups. They may also be attributable to another vibration mode of O–O bonds associated with the shoulder peak near 880 cm^{-1} [48,53]. Two absorbance peaks located near 1400 and 1580 cm^{-1} have been reported elsewhere for tantalum oxides obtained by the decomposition of organometallic precursors in plasma-enhanced chemical vapor deposition [42,54]. These have been argued to be related to the interaction of carbon based groups with metallic atoms of the

oxide film. The peaks can be assigned to the following vibrational modes: --COO bidentate bridging asymmetric stretching, --COO bidentate chelating asymmetric stretching, --COO bidentate chelating symmetric stretching, --COO bidentate bridging symmetric stretching, and CO_3^{2-} vibration. Because no carbon source is expected to be present in physical vapor deposition, these small peaks may be attributed to carbon contamination on the surface caused by adsorption of atmospheric carbon-containing species.

Finally, a broad absorbance band was observed in the $2600\text{--}3600\text{ cm}^{-1}$ region for both $\text{Ta}_2\text{O}_5\text{-EB}$ and $\text{Ta}_2\text{O}_5\text{-SP}$ films. The maximum of the band was located around 3400 cm^{-1} and was associated with stretching vibrations originating from both hydrogen-bonded water molecules and free water molecules [55,56]. Because both FTIR-ATR spectra are normalized, the higher intensity of the spectrum from the $\text{Ta}_2\text{O}_5\text{-EB}$ film indicates that the EB films contained a larger amount of absorbed water than the SP films. Small absorbance peaks at 3775 cm^{-1} for the $\text{Ta}_2\text{O}_5\text{-SP}$ films and 3780 cm^{-1} for the $\text{Ta}_2\text{O}_5\text{-EB}$ films may be related to a vibrational mode of the hydroxyl groups. However, as reported by Takeuchi et al. [55], further discussion on the presence of compounds related to H_2O molecules with different chemical states in the $2600\text{--}3700\text{ cm}^{-1}$ absorption band is difficult.

3.5. XPS

XPS measurements were performed on the 15-nm-thick $\text{Ta}_2\text{O}_5\text{-EB}$ and $\text{Ta}_2\text{O}_5\text{-SP}$ films. The two samples were simultaneously introduced to the XPS chamber. The obtained photoelectron spectra are indicated by the solid curves in Figs. 5–8. No argon sputter cleaning was performed before XPS spectra acquisition to avoid preferential removal of oxygen, which could have induced changes in stoichiometry [57, 58]. Both films exhibited a C 1s core level peak near 284.8 eV, as shown in Fig. 5. The peak intensity was not negligible, and the presence of carbon based species on the film surfaces independently of the chosen deposition process indicated surface adsorption arising from air exposure. The deconvolution of the C 1s core level peak was similar for both films and identified a main peak located at 284.7 eV, corresponding to the bonding energy of C–C and C–H bonds. A second peak was noted at a binding energy near 286.3 eV and was attributed to simple C–O bonds. The third peak located at higher energy near 288.9 eV can be identified as the contribution of O–C=O species or Ta–O–C–O chelating and bridging bonds [47]. However, the presence of C–Ta or C–O–Ta bonds, noted in the IR spectra, should have led to a peak near 283.5 eV [47] but was not observed in the C 1s spectrum of either sample.

The Ta 4f photoelectron spectra of both films are presented in Fig. 6. The Ta 4f core level exhibited a doublet peak that could be deconvoluted into two peaks located at 26.47, 28.35, 26.17, and 28.07 eV for the Ta₂O₅-EB and Ta₂O₅-SP films, respectively. These contributions are representative of the Ta 4f orbital splitting into Ta 4f_{7/2} and Ta 4f_{5/2}, and exhibited a separation energy of about 1.9 eV and an area ratio of 1.4 [59]. The fitting parameters used for the deconvolution of all peaks, their binding energy position, and full width at half-maximum are displayed in Table II. For both films, the binding energies of the doublet corresponded to the Ta⁵⁺ oxidation state. No other doublet peaks, which are regularly encountered in the presence of suboxides and characteristic of tantalum at lower oxidation states, were observed at lower binding energy [60]. The Ta 4f core level signal for the Ta₂O₅-EB film exhibited a slight deviation toward higher binding energy compared with that of the Ta₂O₅-SP film.

Figure 7 depicts the O 1s photoelectron spectra of both films located around the bonding energy of 530.5 eV. The shape of the O 1s peak was independent of the deposition process employed and consisted of an asymmetric Gaussian type curve with a pronounced tail toward the higher energy side. Therefore, the O 1s peak was resolved into two Gaussian peaks. The first peak consisted of an intense peak located at 530.72 and 530.47 eV for Ta₂O₅-EB and Ta₂O₅-SP films, respectively. This peak is representative of the O²⁻ species occurring in Ta₂O₅ [61]. Several papers [19, 60] have reported a shift to higher bonding energy, beyond 530.5 eV, in the case of the presence of sub-oxides, which has been investigated as an effect of oxygen vacancies. However, this effect was not observed in either of the O 1s core level spectra, indicating the absence of tantalum sub-oxides in our films.

The location of the second contribution was aided by the position of the tail. The peak was located at 532.20 and 532.03 eV for the Ta₂O₅-EB and Ta₂O₅-SP films, respectively. This peak was assigned to O–C bonds originating from various species present in the organic carbon overlayer on top of the oxide films. The presence of O–H groups was expected to appear in these spectra according to the FTIR-ATR analysis, as shown in Fig. 4. It has been proposed that the peak corresponding to O–H groups is located at an identical binding energy to that of the C–O groups [62]. Thus, the distinction between the C–O and O–H contributions is difficult at this binding energy.

According to McCafferty et al. [63], the bonding of water molecules causes energy shifts of more than 3 eV relative to the position of the O²⁻ 1s peak. Although the presence of absorbed water was detected in the FTIR-ATR spectra of both films, no corresponding peaks were observed in the photoelectron spectra. The XPS measurements were performed in high

vacuum, which probably led to water desorption from the films. This resulted in no detection of absorbed water by XPS.

Simmons and Beard [64] performed quantitative analysis of XPS spectra to determine the density of hydroxyls present on oxide surfaces. They introduced a general oxide surface structure consisting of a stacking of organic carbon layer/chemisorbed water layer/hydroxylated layer including O–H groups on an oxide surface. Based on this model, the first order approximation of the peak intensity $I_{O1s}(C-O + O-C=O)$ corresponding to C–O and O–C=O groups in the O 1s spectra is given using the atomic fractions $x_{C1s}(C-O)$ and $x_{C1s}(O-C=O)$ for the C–O and O–C=O contributions to the C 1s peak, respectively, and the contribution of C–O and O–H groups, $I_{O1s}(O-H; C-O; O-C=O)$ [61]:

$$I_{O1s}(C-O + O-C=O) = (x_{C1s}(C-O) + x_{C1s}(O-C=O)) I_{O1s}(O-H; C-O; O-C=O) \quad (1)$$

The atomic fractions $x_{C1s}(C-O)$ and $x_{C1s}(O-C=O)$ are determined using the following relations:

$$x_{C1s}(C-O) = \frac{I_{C1s}(C-O)}{I_{C1s}(C-O) + I_{C1s}(O-C=O) + I_{C1s}(C-H; C-C)} \quad \text{and} \quad (2)$$

$$x_{C1s}(O-C=O) = \frac{I_{C1s}(O-C=O)}{I_{C1s}(C-O) + I_{C1s}(O-C=O) + I_{C1s}(C-H; C-C)}, \quad (3)$$

where $I_{C1s}(C-O)$, $I_{C1s}(O-C=O)$ and $I_{C1s}(C-H; C-C)$ represent the peak intensity of C–O, O–C=O and C–H, C–C groups in the C 1s signal, respectively. Then, by combining the above equations, the corrected intensity $I_{O1s}(O-H)$ corresponding solely to the contribution of hydroxyl groups can be expressed using the following relation:

$$I_{O1s}(O-H) = (1 - x_{C1s}(C-O) - x_{C1s}(O-C=O)) I_{O1s}(O-H; C-O; O-C=O) \quad (4)$$

Figure 8 presents the deconvolution of O 1s photoelectron spectra by three peaks representing the O^{2-} , O–H, and C–O + O–C=O contributions. The associated fitting parameters are presented in Table II. The C–O + O–C=O contribution to the O 1s core level signal appeared to be limited for both the Ta₂O₅-EB and Ta₂O₅-SP films, indicating a major contribution from hydroxyl groups. The Ta₂O₅-EB film showed a slightly higher intensity for the hydroxyl contribution than that of the Ta₂O₅-SP film.

The atomic concentrations obtained by taking into account the sensitivity factor for each element [20] are presented in Table II. Both the Ta₂O₅-EB and Ta₂O₅-SP films exhibited a high concentration of O^{2-} species, resulting in O/Ta ratios of 3.02 and 2.78, respectively.

These values are higher than the O/Ta ratio expected for stoichiometric Ta₂O₅ (= 2.5). Although the presence of carbon was considered to originate from the atmospheric pollution, its atomic concentration was higher for the Ta₂O₅-EB film. The carbon species introduced to the Ta₂O₅-EB film may have come from the tungsten carbide crucible used for the deposition process, but further investigations are needed to clarify the origin of the higher carbon concentration.

4. Discussion

The XRD and XRR measurements revealed an amorphous nature for both the Ta₂O₅-EB and the Ta₂O₅-SP films and a lower film density for the Ta₂O₅-EB film. The AFM images indicated a higher roughness for the EB film, but the absence of pores or voids on the surface of both films, which implied a low porosity for the films. The FT-IR spectra exhibited the existence of peroxo species and a larger amount of absorbed water in the EB film. Finally, the XPS analyses revealed oxygen rich compositions for both films, with estimated O/Ta ratios of 2.83 and 3.16 for SP and BE films, respectively. From these results, how can we relate the deposition method to the structural/chemical properties of the deposited film?

A high oxygen stoichiometry (TaO_x, x > 2.5) is characterized from the coordination number and the O²⁻ multiplicity factor of the oxide. The former corresponds to the number of covalent bonds between the central Ta atom and surrounding oxygen atoms of polyhedral units, while the latter is the number of polyhedral units (or Ta atoms) around each O²⁻. For O/Ta ratios in the range of 2.5–3.0, as in case of the Ta₂O₅-SP film, it has been proposed that excess oxygen is stabilized by the formation of TaO₆ octahedra with lower O²⁻ multiplicity factors (but superior to 2), instead of the formation of bi-pyramidal TaO₇ [65-67]. Tsuchiya et al. [19] confirmed the presence of TaO₆ octahedra and the absence of TaO₇ polyhedra for an O/Ta ratio of 3. The same group [69] has also proposed that amorphous Ta₂O₅ films having O/Ta ratios in the 2.5–3.0 range possess an altered oxidation state induced by the following protonation and deprotonation reaction:

suggesting the presence of hydroxyl groups in the film with this O/Ta range. Indeed, we observed a contribution of hydroxyl groups in the O 1s core level spectra of both Ta₂O₅-SP and Ta₂O₅-EB films, as seen in Fig. 8. The existence of hydroxyls was also confirmed by Rutherford backscattering spectroscopy measured for O-rich amorphous Ta₂O₅ films [19]. When the films are exposed to air, the presence of (Ta⁵⁺O²⁻_{2.5}OH⁻)⁻¹ bonds may have led to the formation of H₂O bidentate bridges and weak chemisorption of water molecules through

the formation of hydrogen bonds. This resulted in a hydrogen-bonded network in the amorphous films. Such a hydrogen-bond network is considered to be volatile and easily desorbable under vacuum conditions, as reported by Tsuruoka et al. [11]. This behavior is consistent with our results of no signal attributed to free water in the O 1s core level spectra measured in high vacuum (Figs. 7 and 8), and of the intense signal of absorbed water in the FTIR-ATR spectra performed in air (Fig. 4).

When the O/Ta ratio becomes equal to 3, the O^{2-} multiplicity factor takes a minimum value of 2, where each oxygen atom is bonded to two polyhedral units (two Ta atoms). If the O/Ta ratio increases further, as in case of the Ta₂O₅-EB film, the film is expected to form dangling bonds with the amorphous matrix. Under these circumstances, excess oxygen is likely to bond weakly with O atoms coordinated with Ta and do not interact directly with Ta atoms [68]. As a result, the increase in O stoichiometry leads to the formation of superoxo species: Ta–O–O[•] or Ta–O–O[−], both which are referred to as Ta–O–O*. These unsaturated bonds can lead to the formation of Ta–O–O–H bonds by a protonation reaction:

which is analogous to the formation of Ta–O–H bonds, as described in Eq. (5). This reaction should have led to a rise in the O–H concentration of the Ta₂O₅-EB film compared with the Ta₂O₅-SP film. The XPS analyses (Table II) showed that the atomic concentration of the O–H contribution was estimated to be 7.40 and 10.06% for Ta₂O₅-SP and Ta₂O₅-EB films, respectively. Although the difference between the concentrations is not great, the higher concentration of hydroxyl groups for the EB film qualitatively supports our expectation. Moreover, the FTIR spectra indicated the presence of peroxo species (shoulder at 880 cm^{−1}), confirming that the Ta–O–O* bonds were not terminated directly with molecular water in either film. The larger amount of absorbed water resulted in the lowered film density of the EB film determined by XRR.

Dupin et al. [70] have determined the presence of metallic peroxide type bonds, M–O–O, from a peak with a binding energy in the range of 530.5–531.1 eV in the O 1s photoelectron spectra of various transition metal oxides. Another group has also reported, for LiMO oxides, the presence of a peak near 530.5 eV attributed to formal O_2^{2-} species like peroxo or superoxo species, indicating short O–O bonds or under-coordinated oxygen atoms in the oxide matrix [71]. However, we have not succeeded in identifying the Ta–O–O* contribution to the O 1s spectra in the current study. As another possible explanation for the volatile water absorption, the unterminated Ta–O–O* bonds may have supported dipole–charge interactions between

the weakly bonded $-O^*$ and molecular water, leading to the formation of H_2O bidentate bridges:

Then, water molecules are chemisorbed on the H_2O bidentate through the formation of hydrogen bonds. These interactions also support the formation of a volatile hydrogen-bond network. However, we cannot derive any more conclusions at this stage. Further investigations are needed to clarify the dominant interactions between the polyhedral units and molecular water at higher O/Ta ratios.

The origin of the larger oxygen nonstoichiometry of the Ta_2O_5 -EB film is not clear. An oxygen rich composition of the deposited films was also observed in the case of amorphous titanium oxide deposited by EB evaporation from oxide pellets [72]. Therefore, we infer that the nonstoichiometry arose from excess oxygen gas during the deposition. The Ta_2O_5 pellets were melted by electron beam irradiation, and oxygen would have desorbed easily from the pellets [73]. The Ta_2O_5 film was grown in this desorbed oxygen atmosphere, resulting in a uniform oxygen rich composition along the film thickness direction. In contrast, the introduction of oxygen into the Ta_2O_5 -SP film may have originated from the target and oxygen gas introduced in the sputtering chamber. The difference in the reactivity of the oxygen during the deposition process should have contributed to the different stoichiometry and density of the present Ta_2O_5 films. **The higher binding energies of the Ta 4f and O 1s peaks observed for EB films can be attributed to higher oxygen content.**

Finally, we would like to remark on the speed of moisture absorption in amorphous oxide films. Because almost no pores and voids were expected in the amorphous matrix from the AFM observations, the protonation reaction between the O atoms of TaO_6 units and the Ta-O-O* bonds was likely to progress slowly. This means that the results examined here may have been affected by the period of time for which the films were exposed to the atmosphere. The effects of air exposure time on film properties are subject to further investigations.

5. Conclusion

In conclusion, the morphology and composition of Ta_2O_5 thin films deposited on Pt/Ti/SiO₂/Si substrates by EB evaporation and RF sputtering processes have been investigated by various characterization methods. The XRD patterns showed an amorphous nature for both films. The XRR measurements revealed that the Ta_2O_5 -EB films had a lower density than the Ta_2O_5 -SP films, and both densities were lower than that of bulk Ta_2O_5 ,

characteristic of amorphous films. AFM images indicated homogenous layers with low surface roughness and no pores or voids. The presence of absorbed water was confirmed by FTIR-ATR spectra measured under atmospheric conditions. From the XPS analyses, the O/Ta ratio was estimated to be higher than the 2.5 expected for stoichiometric Ta₂O₅. The observed O/Ta ratios indicated oxygen rich compositions for both films, which were responsible for their high O–H bond concentrations. These hydroxyl groups could support the weak chemisorption of water molecules. Such water molecules originated from moisture absorbed by the Ta₂O₅ matrix from its surroundings in atmosphere, but they easily desorbed from the film in vacuum, resulting in no detection of water species in the photoelectron spectra. The higher amount of nonstoichiometric oxygen accounts for the lower density and the higher amount of chemisorbed molecular water of the Ta₂O₅-EB film than the Ta₂O₅-SP film. The formation of unsaturated peroxo dangling bonds (Ta–O–O*) may support the chemisorption of water by charge-dipole interactions. Our results are considered to be applicable to other amorphous oxide materials and suggest the importance of understanding the dependence of the structural and chemical properties of thin amorphous oxide films on the deposition process.

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Figure Captions

Figure 1: X-ray diffraction patterns of as-deposited sputter (red curve) and electron beam deposited (blue curve) Ta₂O₅ thin films on Pt/Ti/SiO₂/Si substrates. The powder diffraction files of orthorhombic β -Ta₂O₅ (JCPDS card No. 25-0922), tetragonal α -Ta₂O₅ (JCPDS card No. 21-1199), and cubic Pt (JCPDS card No. 04-0802) are also shown as references.

Figure 2: Experimental (black curves) and simulated oscillating X-ray reflectivity intensity obtained for 15-nm-thick Ta₂O₅ films deposited on Si substrates (EB: blue dashed curve; SP: red dashed curve) and Pt/Ti/SiO₂/Si substrates (EB: blue curve; SP: red curve).

Figure 3: 3D-AFM roughness in a 500 nm $\times$ 500 nm area for as-deposited Ta₂O₅-EB (top) and Ta₂O₅-SP (bottom) thin films on Pt/Ti/SiO₂/Si substrates. The AFM images have been corrected to normalize the mean roughness to the nominal thickness (15 nm) of the films.

Figure 4: FTIR-ATR spectra of 20-nm-thick Ta₂O₅-EB (blue curve) and Ta₂O₅-SP films (red curve) deposited on Pt/Ti/SiO₂/Si substrates.

Figure 5: Decomposition of C 1s core level spectra of Ta₂O₅-EB (blue curve) and Ta₂O₅-SP (red curve) thin films on Pt/Ti/SiO₂/Si substrates.

Figure 6: Decomposition of Ta 4f core level spectra of Ta₂O₅-EB (blue curve) and Ta₂O₅-SP (red curve) thin films on Pt/Ti/SiO₂/Si substrates.

Figure 7: Decomposition of O 1s core level spectra of Ta₂O₅-EB (blue curve) and Ta₂O₅-SP (red curve) thin films on Pt/Ti/SiO₂/Si substrates.

Figure 8: Decomposition of O 1s core level spectra of Ta₂O₅-EB (blue curve) and Ta₂O₅-SP (red curve) thin films on Pt/Ti/SiO₂/Si substrates, obtained by separating the O–C and O–H contributions using Eq. 4.

Table I: Film thickness, density, and roughness extracted from XRR results.

Table II: Summary of XPS measurements and analyses.

Table I

Samples	Thickness (nm)	Density (g.cm ⁻³)	Roughness (nm)
Ta₂O₅-EB-15nm / Pt/Ti/SiO₂/Si	15.95	6.84	0.99
Ta₂O₅-EB-15nm /Si	14.42	6.96	1.04
Ta₂O₅-SP-15nm / Pt/Ti/SiO₂/Si	15.65	7.57	0.23
Ta₂O₅-SP-15nm /Si	13.79	7.53	0.41

Table II

Peaks		Binding Energy (eV)	Intensity (cps)	FWHM ¹ (eV)	Atomic Concentration (%)	O/Ta ratio			
Ta ₂ O ₅ -EB	Ta 4f	Ta 4f 7/2	26.47	23112	1.37	17.99	3.16		
		Ta 4f 5/2	28.35	19709	1.37				
		O ²⁻ 1s	530.72	30696	1.54			56.91	
		O-H 1s	532.20	4676	1.54			10.06	
	O 1s	C-O 1s	532.20	903	1.54	1.83			
		C-C; C-H 1s	284.70	2104	1.70	11.16			
	C 1s	C-O 1s	286.29	274	1.70	1.34			
		O-C=O 1s	288.96	135	1.70	0.71			
		Ta 4f	Ta 4f 7/2	26.17	27865	1.36		21.41	
	Ta 4f 5/2		28.07	23382	1.36				
	O 1s		O ²⁻ 1s	530.47	35969	1.54			60.53
			O-H 1s	532.03	3873	1.54			7.40
C-O 1s		532.03	771	1.54	1.42				
C 1s	C-C; C-H 1s	284.73	1626	1.70	7.72				
	C-O 1s	286.44	194	1.70	0.92				
	O-C=O 1s	288.97	130	1.70	0.60				

¹ Full Width at Half Maximum

Figure

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Graphical Abstract