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Short Communication

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Tuning the stoichiometry and electrical properties of tantalum oxide thin films

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ABSTRACT

Tantalum oxide has a wide range of applications and has drawn much attention especially for its useful properties in resistive random-access memories, in which the Ta oxide composition plays an important role to control the electrical properties of the TaO_x thin films. In this paper, we present a way to tune the composition of TaO_x thin films by varying the oxygen partial pressure during growth using pulsed laser deposition. TaO_x thin films were deposited at room temperature, under oxygen partial pressures ranging from 10⁻⁶ mbar to 2×10⁻² mbar. Using angle resolved X-ray photoelectron spectroscopy, we show that the composition of the film varies systematically with the oxygen partial pressure during the film growth. We then correlate the oxygen content with the electrical properties of the film and the results show that the composition has a great influence on the resistivity of the TaO_x thin films. As the oxygen partial pressure during deposition increases, the percentage of tantalum pentoxide (Ta₂O₅) as well as the resistivity of the films increases. This experimental approach provides a pathway to control the TaO_x thin film stoichiometry and its electrical properties during growth.

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Tantalum oxide (TaO_x) is a promising candidate for a wide range of applications such as antireflection coatings,^{1,2} optical waveguides,^{3,4} hydrogen generation photocatalysts,^{5,6} and dielectric materials in the microelectronic industry.^{7,8} TaO_x thin film has recently drawn much attention as a non-volatile memory material which makes it suitable for resistive random access memories (RRAMs).^{9–12} Due to the excellent performances of TaO_x based RRAMs such as a large endurance of 10^{12} cycles¹¹ and a fast switching speed of sub-nano second,¹² it becomes one of the promising materials for memory application. Seen from fabrication point of view, since a high-temperature process is not preferable in complementary metal oxide semiconductor (CMOS) fabrication process, TaO_x deposited at room temperature is often preferred. The resistive switching phenomenon in this family of materials is usually achieved by partially switching the TaO_x thin film between a highly resistive state of tantalum pentoxides (Ta_2O_5) and a more conductive state of $\text{TaO}_{x<2.5}$ under external electrical field.^{10,11} Understanding the parameters influencing the different phases of TaO_x and their electrical characteristics is thus essential for memristor device design. The electrical properties of TaO_x have been found to be greatly influenced by the oxygen content and often very small changes in the deposition parameters cause profound change in the functionality of the film. Tantalum oxide films with different stoichiometry have been reported by using several methods, including thermal oxidation,¹³ sputtering,^{14–20} chemical vapor deposition (CVD),^{21,22} photolysis,²³ atomic layer deposition (ALD),^{24,25} sol-gel method,²⁶ and pulsed laser deposition (PLD)^{27–34}. A direct detailed dependence between the stoichiometry of the film and the resistivity of tantalum oxide were so far given mainly for sputtering deposition method^{17–20}, but there are no reports on the relation between the deposition condition and the film performance for PLD based samples. Although tantalum oxide thin films deposited by PLD were widely studied,^{27–39} focus was mainly put on the optical properties,^{27,28,30,31,33,35,36,38,39} leakage current^{27,29,33,35,36} and dielectric constant²⁷ of the oxide films. In order to be able to control the exact phases formed during the deposition, understanding of the relation between the film stoichiometry and the deposition conditions, especially the oxygen partial pressure, are desirable. Here we conduct a systematic experimental study to determine and understand the relationship between the Ta oxidation state and the electrical properties of the film. Understanding this will provide a tool to fabricate highly controlled TaO_x films with tailored properties at room temperature.

TaO_x films were deposited using a PLD setup as described elsewhere.⁴⁰ A KrF excimer laser (248 nm, 10 Hz, 4 J/cm²) was used to ablate a commercial ceramic target of Ta₂O₅ (American Elements) with 99.99% purity and dimensions of 25.4 mm in diameter and 6 mm in thickness.

Two types of commercial substrates were used in this study: (1) <100> silicon substrates with 100± 10 nm silicon di-oxide and 100 nm sputtered TiN film on top, labeled as Si/SiO₂/TiN substrates and (2) single crystal <100> MgO substrates. The TiN layer in the Si/SiO₂/TiN substrate acts as a conducting layer, whereas the MgO substrates were insulating. Both substrates and target were investigated with X-ray diffraction (XRD) to ensure their phase purity prior to the deposition. The deposition was carried out by keeping the target-substrate distance constant at 7.5 cm, while the deposition time was chosen to be either 10 or 60 min at room temperature. The oxygen partial pressure was varied from 10⁻⁶ mbar (base pressure) to 2×10⁻² mbar and five different values of oxygen partial pressures were used in total. X-ray diffraction (XRD) and scanning electron microscope (SEM) were employed on all films to characterize the crystalline quality and the morphology of the films. The oxidation states of Ta in the TaO_x films were determined by angle resolved X-ray photoelectron spectroscopy (ARXPS). The ARXPS analyses were performed on a ESCALAB XI⁺ X-ray photoelectron spectrometer microprobe (Thermo Fisher Scientific, East Grinstead, U.K.) using a monochromatic Al-Kα X-ray source with a 900 μm spot size. A combined ion/electron gun (i.e. a dual beam source) was used to control sample charging. The electrical conductivity was measured on a rectangular shaped sample (10 mm × 10 mm) in a Van der Pauw configuration using a station probe (Imina).

Figure 1 (a) and (b) show the schematic configurations of the deposited films together with a micrograph showing a cross-sectional SEM image of the TaO_x film deposited on TiN substrate (at P_{O2}= 10⁻⁶ mbar, room temperature). The TaO_x thin films deposited at P_{O2}=10⁻⁶ mbar on Si/SiO₂/TiN and MgO substrates show a typical similar surface morphology, as illustrated in Figure 1 (c) and (d), respectively. TaO_x thin films grown at different oxygen partial pressures all show similar microstructures. XRD of TaO_x films deposited at different oxygen partial pressure shows that all the films deposited on top of the Si/SiO₂/TiN substrate have no distinct diffraction peak other than the one belong to substrate peaks, indicating the existence of an amorphous structure (supplementary material, Figure S1).

Since the memristors operate at room temperature, the resistivity of different TaO_x films were measured at this temperature. Figure 2 shows the results of the room-temperature resistivity of TaO_x thin films grown on MgO substrates for 60 min as a function of oxygen partial pressure in the PLD chamber. The resistivity of the films did not show very minor anisotropy in the plane of the film. The result shows that the resistivity increases from 0.33 Ω·cm up to 2.34 kΩ·cm as the oxygen partial pressure increases from 10⁻⁶ mbar to 5×10⁻³ mbar. The resistivity of the TaO_x film grown at an oxygen partial pressure of 2×10⁻² mbar was high above the measurement limit. The oxygen partial pressure can therefore be used as a convenient knob to tune the conductivity towards a more insulating phase as the pressure is increased.

The chemical composition of the TaO_x thin films were examined by ARXPS. High resolution local binding energy spectra, as shown in Figure 3, were obtained for Ta-4f using 20 eV detector pass energy, 50 ms dwell time, 0.02 energy step size, and collected over 5 scans. Fitting analysis of the Ta 4f peaks and thus quantification of the Ta oxidation states is based on the approach by Simpson et al.⁴¹. Peaks were fitted using a 38% Lorentzian/Gaussian function, a 4f5/4f7 spin orbit splitting of 1.9 eV, and a 4f5/4f7 height ratio of 0.788. Figure 3 presents Ta 4f ARXPS spectra obtained at an emission angle of $\theta=0^\circ$ relative to the perpendicular direction to the surface of the sample (i.e. maximum escape depth), showing the main Ta⁵⁺ peak together with lower oxidation states. These are Ta⁴⁺, Ta³⁺, Ta²⁺, Ta¹⁺, and Ta⁰ representing TaO₂, Ta₂O₃, TaO, Ta₂O, and Ta metal, respectively. The main peaks observed are the Ta 4f 7/2 and the Ta 4f 5/2 peaks at binding energies of 26.9± 0.1 eV and 28.8± 0.1 eV, respectively. This confirms that most of the deposited thin films are composed of Ta₂O₅. The fit of the Ta 4f peaks and thus quantification of the Ta oxidation states is based on the approach by Simpson et al.⁴¹. (The comparison between the binding energies for each oxidation states used in the work of Simpson et al.⁴¹ and this paper is shown in the supplementary material Table S1.)

In order to investigate the composition homogeneity along the film growth direction and the surface oxidation conditions of the TaO_x thin films, ARXPS were carried out and the emission angles θ , relative to the perpendicular direction of the surface of the sample, vary from 0° to 90° (grazing angle), which corresponds to the maximum probe depth of ~10 nm and the upper surface layer of the TaO_x thin films, respectively. As show in Figure 4 (a), for TaO_x thin films deposited under high oxygen partial pressure (5×10⁻³ mbar) for a short time (10 min)

corresponding to a film thickness of 23 ± 4 nm, the composition of TaO_x thin film is homogeneous for all emission angles, which means a homogeneous Ta oxidation states composition from surface to approximately 10 nm deep under the surface. As compared to the TaO_x deposited for the same time but under a lower oxygen partial pressure (10^{-6} mbar) corresponding to a film thickness of 6 ± 1 nm, the composition of Ta_2O_5 increases as the emission angle increases, which indicate a higher Ta_2O_5 composition near the film surface, as shown in Figure 4 (b). This finding is in consistence with the work of Sharath et al.⁴² Furthermore, as the thickness of the films increase, the composition of the thin films deposited at high oxygen partial pressure is not homogeneous any longer from surface to approximately 10 nm deep under the surface and a composition gradient along the film growth direction can be seen for films deposited at both high and low oxygen partial pressure, as shown in Figure 4 (c) and (d), respectively.

Figure 5 illustrates the Ta oxidation states in the TaO_x films as a function of oxygen partial pressure. The percentage of Ta oxidation states in the TaO_x films are obtained from the XPS data taken at an emission angle of 0° . The percentage of Ta^{5+} (Ta_2O_5) increases from 75 at.% to 95 at.% as the oxygen partial pressure increases from 10^{-6} mbar to 2×10^{-2} mbar while the contribution from the lower oxidation state reduces. By comparing the XPS results, it is clear that it requires very low oxygen partial pressures to form lower oxidation state than the Ta^{5+} in a significant concentration. Comparing the XPS results of samples deposited at the same oxygen partial pressure, but different deposition duration of 60 min and 10 min (supplementary material S2), the results indicate that combining long deposition duration with low oxygen partial pressure provides the most efficient way to form lower oxidation states in significant concentrations.

In summary, we demonstrated the influence of oxygen partial pressure during PLD growth on the properties and stoichiometry of TaO_x films. This was used to tune the oxygen content in the film and therefore the resistivity of the TaO_x films. Our approach suggests that the future design of the desired initial state of the memory devices which depend very much of the phases used can be attained by choosing the right deposition parameters.

FIGURES

Figure 1. (a) A schematic illustration of TaO_x film deposited on Si/SiO₂/TiN substrate. The inset shows a cross sectional SEM image of the film stack. (b) A schematic illustration of TaO_x film deposited on MgO (100) substrate. (c) SEM picture showing the surface of TaO_x film deposited on Si/SiO₂/TiN substrate. (d) SEM picture showing the surface of TaO_x film deposited on MgO (100) substrate. The TaO_x films shown here are all deposited under 10^{-6} mbar at room temperature.

Figure 2. The relation between TaO_x thin film resistivity and oxygen partial pressure during deposition. The inset figure shows the van der Pauw configuration for resistivity test. Since the figure is plotted in double logarithmic coordinates, the error bars are not included due to lack of visibility. The relative standard deviation (σ/μ) of the resistivity is smaller than 13%.

Figure 3 Ta 4f XPS spectra of TaO_x thin films deposited for 60 min under different oxygen partial pressure of: (a) P_{O2} = 10⁻⁶ mbar, (b) P_{O2} = 5.6 × 10⁻⁴ mbar, (c) P_{O2} = 2 × 10⁻³ mbar, (d) P_{O2} = 5 × 10⁻³ mbar, and (e) P_{O2} = 2 × 10⁻² mbar. The solid black lines are the experiment XPS spectra data and the solid red lines are the fitting envelopes of the XPS spectra data.

Figure 4 The Ta oxidation states of TaO_x films deposited under different conditions revealed by ARXPS spectra. (a) oxygen partial pressure of $P_{O_2}=5 \times 10^{-3}$ mbar for deposition time of 10 min, (b) oxygen partial pressure of $P_{O_2}=10^{-6}$ mbar for deposition time of 10 min, (c) oxygen partial pressure of $P_{O_2}=5 \times 10^{-3}$ mbar for deposition time of 60 min, and (d) oxygen partial pressure of $P_{O_2}=10^{-6}$ mbar for deposition time of 60 min. (e) is a schematic illustration of the principle of ARXPS. The angle θ is the emission angle relative to the perpendicular direction of the surface of the sample. By changing the emission angle, the sampling depth decreases from ~ 10 nm at $\theta=0^\circ$ to the very surface of the film at $\theta=90^\circ$.

Figure 5. The Ta oxidation states inside TaO_x thin films deposited under different oxygen partial pressure for 60 min at room temperature.

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Highlights

Understanding the different phases of TaO_x and their electrical characteristics is essential for future application of these materials in memristor devices but also for a wider range of other applications. However, so far there is no detailed work about the correlation between the process parameters such as oxygen partial pressure during deposition using PLD, the exact composition of TaO_x thin films and their respective electrical properties. Here, we conducted a detailed investigation to understand the relation between the oxygen partial pressure and the properties of the film.