

Structural characterization of mixed Ta–Re oxide films

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Abstract

Thin films of mixed Ta and Re oxides have been produced by reactive dc magnetron co-sputtering of pure Ta and Re metal targets in Ar–O₂ atmosphere. The structural evolution of these films has been studied as a function of the composition, starting from a pure tantalum oxide film up to about 82% rhenium content. The composition and the structure of the films have been investigated by using X-ray diffraction and micro-Raman spectroscopy. For low Re content (20%), islands of a well crystallized phase, based on ReO₄ groups, appear in the films still composed by pure amorphous tantalum oxide, while a mixed disordered solid phase is found for the highest Re concentration (82%).

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1. Introduction

Rhenium trioxide (ReO₃) belongs to a family of proton conductors (H_xMeO₃ where M is Re, W or Mo), which have applications as electrochromic, gasochromic, superionic and photochromic materials [1–4] as well as rectifying layers for the electro-optic response of liquid crystal cells [5,6]. Besides, ReO₃ is a quite intriguing compound because of its character of Drude-like conductor [7–9] and its typical structure of corner-sharing octahedra [10]. ReO₃ has an undistorted perovskite-type (ABO₃) structure at ambient conditions with the A-sites being empty [10]. The peculiarity of the perovskite structure is the highly anisotropic vibrational motion of oxygen atoms perpendicular to the B–O–B atomic chains, which could lead to phase transitions.

It is well known that rhenium ions can exist in a wide number of oxidation states (from +2 to +7), with three stable anhydrous oxide forms of rhenium (ReO₂, ReO₃ and Re₂O₇) and, probably, with many metastable forms as Re₂O₅ and Re₃O₁₀, showing fast disproportioning reactions at room temperature in the presence

of water [11]. However, the real structure of nonstoichiometric polycrystalline ReO_{3+x} as well as of films obtained by powder evaporation seems to present additional complexities, due to the appreciable chemical interaction of the pure oxide with oxygen and water from the atmosphere, leading to the formation of a proton-containing H_xReO₃ and very thin layer of HReO₄ [12]. Details of such interactions, resulting in the formation of different amorphous or crystalline species at the surface, will be described elsewhere. As preliminary statement, we can say that the structure of rhenium oxide thin films is probably different from that of the bulk compound, anyway it is still unknown, taking into account that only one study on rhenium oxide thin films has been reported so far [13].

In the present work, we deal with the structural evolution of mixed Ta–Re oxide films, obtained by dc magnetron sputtering, as a function of composition, starting from pure TaO_x and increasing the concentration of rhenium oxide up to 82%. The purpose of such mixing is to control the reactivity of pure rhenium oxide and to obtain more stable (pure rhenium oxide films are unstable in air) and homogeneous films for various applications.

Physical properties of tantalum oxide depend crucially on its structure [14]. An amorphous tantalum oxide (a-Ta₂O₅) finds many applications as, for example, dielectric material for

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dynamic random access memory (DRAM) capacitors [15] and as ion conductor for batteries [16] and electrochromic devices [17]. Since only short range order exists in $a\text{-Ta}_2\text{O}_5$, it is important to know precisely the local environment around tantalum (or impurity) atoms.

Engineering on the atomic level of mixed transition metal (TM) oxide-based materials with superior properties for industrial applications is impossible without detailed knowledge of the atomic and electronic structure of these materials and of the processes occurring on microscopic level. The goal of this study is to characterize the structure of mixed Ta–Re oxide thin films by X-ray diffraction (XRD) and micro-Raman spectroscopy, taking into account the visual map and the Raman spectral map of the deposited films.

2. Experimental

Pure TaO_x and mixed Ta–Re oxide thin films were deposited on glass substrates by reactive magnetron sputtering in a plasma-focusing dc magnetic field at a discharge power of 100 W. Metallic tantalum (99.9%) and rhenium (99.99%) plates were used as sputtering targets. A gas mixture of argon and oxygen was used as the sputter atmosphere. The argon partial pressure was set at 0.040 Pa, while the oxygen partial pressure at 0.0067 Pa. The distance between the target and the substrate was 8 cm. The working pressure in a vacuum chamber during the sputtering process was 4 Pa. The film's thickness was in the range of 400–1000 nm. The nominal content of rhenium was varied from 0% to 35% by changing the ratio of two target areas. The real rhenium content was estimated from the ratio of the Re-to-Ta X-ray absorption L_3 -edges jumps: it was in the range from 0% to 82%.

Structural phase analysis of the films was performed by X-ray diffraction (XRD) technique using PANalytical X'Pert PRO diffractometer, working in the Bragg–Brentano θ – θ configuration. Conventional X-ray tube with Cu anode, operated at 45 kV and 40 mA, was used as an X-ray source.

The vibrational properties of mixed films were characterized by micro-Raman spectroscopy, taking into account the visual map and the Raman spectral map of the deposited films. A microprobe Jobin-Yvon Labram was used, equipped with a Charge Coupled Device (CCD) detector. The low frequency detection limit, due to the notch filter, was at about 190 cm^{-1} . In all the experiments a $50\times$ Mplan Olympus objective with numerical aperture of 0.70 was used. The power of the He–Ne laser (632.8 nm emission) out of the objective was about 5 mW and the laser spot size was about 2–3 μm . To avoid unwanted laser-induced transformations, neutral filters of different optical densities (OD) were used, usually OD2 and OD1.

3. Results and discussion

XRD patterns for pure TaO_x and mixed Ta–Re oxide films with increasing rhenium content up to 82% are shown in Fig. 1. At low Re content, the XRD pattern is close to that of pure TaO_x film. Upon an increase of the Re concentration above 50%, the broad peaks at $\sim 24^\circ$ and $\sim 56^\circ$ become more pronounced and a

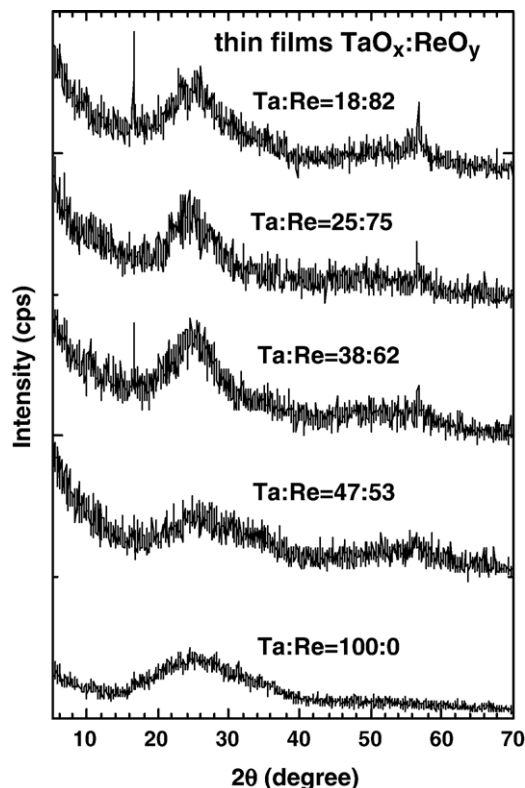


Fig. 1. XRD diffraction patterns for mixed Ta–Re oxide thin films with different Re content.

narrow but weak peak at $\sim 16.5^\circ$ appears for some samples. Comparison of the obtained XRD patterns with those for known rhenium oxide phases (Re_2O_7 , ReO_3 , ReO_2 , etc.) suggest that the thin films are mostly amorphous. However, an increase of the rhenium content facilitates partial crystallisation, with the appearing of a small amount of some crystalline phase.

The micro-Raman spectroscopy allows to observe the formation of separate regions, even when the rhenium doping is not so high, and to discriminate the composition and the structure between the “background” of the films and the small islands, observed at low dopant concentration. Only quite homogeneous regions are found for pure tantalum oxide (see Fig. 2(a)). For low rhenium content (20% and 37%), an almost total phase separation can be observed: rare big structures of the order of 20 μm (see Fig. 2(b)) are scattered on the homogeneous background.

The different chemical and structural characters of the islands with respect to the background are revealed by micro-Raman spectroscopy. In Fig. 3 the spectrum of pure tantalum oxide film (curve (a)) is compared with the spectrum of the island (curve (b)) of different colour, found in a mixed film. The spectrum of pure TaO_x films consists of broad bands at about 220 , 520 and 640 cm^{-1} and smaller features at 380 and 940 cm^{-1} . It is clearly different from the spectra reported for room temperature Ta_2O_5 ceramic and crystalline samples [18]. Moreover, it has been already observed that crystallization of tantalum oxide thin films occurs only at $710\text{ }^\circ\text{C}$ [19].

In the case of the island, visible in Fig. 2(b), some very sharp Raman peaks at 894 , 918 and 969 cm^{-1} and a lower frequency

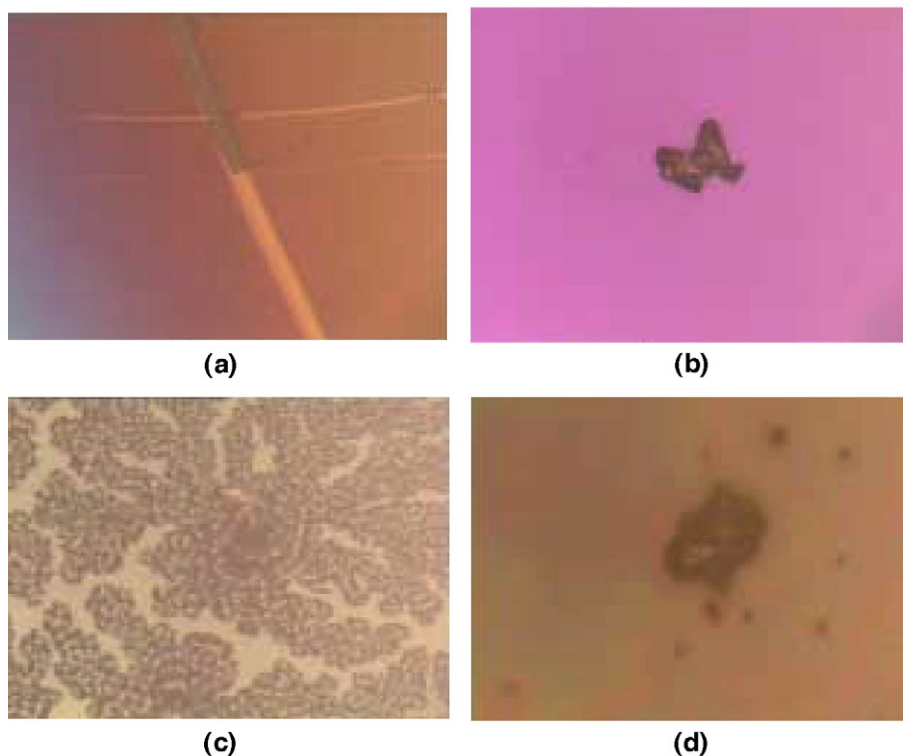


Fig. 2. Microscopic pictures of thin films (horizontal size is 120 μm): (a) pure TaO_x thin film (the observed scratches have been made intentionally, to discriminate the colour of the film from the substrate); (b) mixed Ta–Re oxide film with Re content 20%; (c) the dendritic growth of mixed Ta–Re oxide film with Re content 62%; (d) image of the mixed Ta–Re oxide film with Re content 70%.

doublet at 336 and 345 cm^{-1} are superimposed to the broad spectrum of amorphous TaO_x . Such peaks can be reasonably related to the typical modes of a tetrahedral group, i.e. the $[\text{ReO}_4]^-$ group [20–22]. The spectrum of the homogeneous background, collected far from the islands, was identical to that of pure tantalum oxide film, reported in Fig. 3(a).

The sharp Raman peaks observed in the specific spots of the Re doped film (up to 53%) correspond well to the spectra found for microcrystals grown from vapour phase after heating treatments of pure ReO_3 powders (reported for comparison in Fig. 3(e)). The sharpness of the Raman peaks at 970, 918 and 897 cm^{-1} and of the low frequency doublet at 338 and 347 cm^{-1} indicate well ordered microcrystals, and the modes seem again reasonably assignable to stretching and bending vibrations of $[\text{ReO}_4]^-$ groups. The simple Raman spectrum excludes its assignment to Re_2O_7 crystals, exhibiting a quite higher number of Raman modes [23]. In fact, this latter compound, in its solid phase, includes two types of rhenium coordination—octahedral and tetrahedral, resulting in a more complex Raman spectrum with peaks in the range 800–900 cm^{-1} and above 900 cm^{-1} .

Considerations on the possible surface chemistry occurring for both the sputtered mixed films and the crystals evaporated from ReO_3 lead to the hypothesis of perrhenic acid crystals, containing some water molecules, which is also further supported by comparisons with alkaline perrhenates Raman spectra [24].

The striking correspondence between the spectra of evaporated crystals (Fig. 3(e)) and those of the microcrystalline

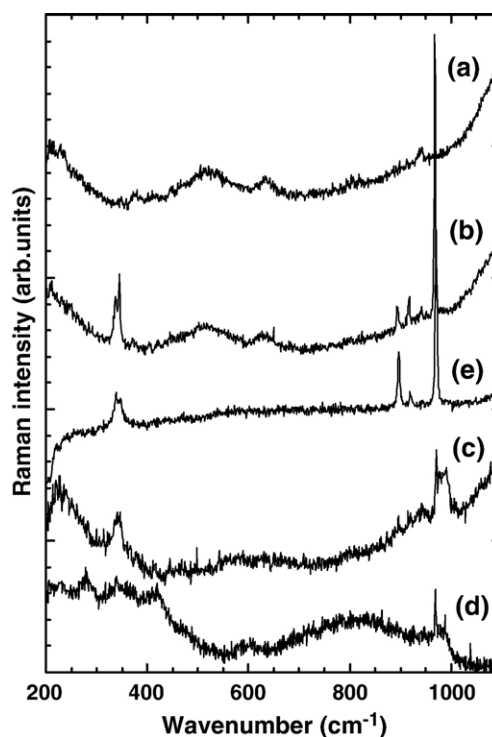


Fig. 3. Micro-Raman spectra of (a) pure amorphous TaO_x thin film, shown in Fig. 2 (a); (b) the island in mixed Ta–Re oxide film with Re content 20% (see Fig. 2(b)); (c) the dendritic structure in mixed Ta–Re oxide film with Re content 62% (see Fig. 2 (c)); (d) the homogeneous mixed Ta–Re oxide film with Re content 70% (see Fig. 2 (d)); (e) microcrystals grown on quartz by evaporation of ReO_3 powder at 220 $^\circ\text{C}$.

islands growing inside the amorphous TaO_x films (Fig. 3(b)) is a clear indication of their close chemical similarity. It is interesting to note that co-sputtering of Re and Ta in oxidizing atmosphere leads to the same crystal structure for rhenium compound as evaporation in air of ReO₃ powders.

Such behaviour could be tentatively attributed to the strong reactivity of rhenium in the gas phase with oxygen and other chemical species (water, carbon dioxide, aromatic hydrocarbons, etc.) present on the trace level in the chamber [25]. The ReO₄⁻ and, to a lesser extent, ReO₃⁻ negative ions are the most abundant rhenium oxide anions in the gas-phase [25]. The surface-assisted reactions in the oxidizing environment promote the formation of stable groups based on Re⁷⁺ in tetrahedral coordination, acting as seeds for the growth of solid phases with the same basic symmetry. On the contrary, octahedral coordination results more stable in reducing environments, generating rhenium (+4 to +6) oxide phases with octahedral structure. Obviously an extensive series of measurements, at variable temperatures and controlled atmosphere, is necessary to gain a better understanding of such phenomena, after the preliminary observations reported in the present work.

Upon increasing Re concentration, some structural transformations occur, as revealed by micro-Raman spectroscopy. For 62% Re, a dendritic-like network covers most of the film (Fig. 2(c)). The corresponding Raman spectrum is reported in Fig. 3(c): it appears changed with respect to those of the islands in lower Re-concentration films. Two bands occur at about 340 and 980–990 cm⁻¹, being always broader than the very sharp peaks previously observed. This fact suggests a much smaller size (growth of nanocrystals) and/or a more disordered structural configuration for the rhenium-containing domains.

Finally, a strongly changed Raman spectrum appears in the films with a Re concentration of 70%, as shown in Fig. 3(d), corresponding to the film micro image of Fig. 2(d). It consists of a low frequency broad contribution with maxima at 225, 277, 345 and 420 cm⁻¹, another very broad band centred at about 800 cm⁻¹ and a high frequency feature with a maximum at 980 cm⁻¹. Different intensities appear in correspondence with different regions in the films, and the best signal is associated to darker islands, as the one shown in Fig. 2(d), even if the basic broad spectral shape does not change. It is evident that a new structure is formed for such a composition, and it is weakly Raman active. The occurrence of a very broad band centred at about 800 cm⁻¹ can suggest even the presence of octahedrally coordinated rhenium atoms, randomly distributed inside the tantalum oxide matrix. In this case the existence of a homogeneous mixed oxide can be proposed. It is interesting also to note that such film appears changed in colour and is more sensitive to light. In fact the Raman spectra appear noisier because they were collected at a lower laser power, to avoid crystallization of the amorphous structure. The key role for the peculiar changes of structural and optical properties of the film at such composition could be attributed to the change of rhenium valence and coordination inside the solid phases; however, further investigations seem to be necessary to explain the observed transformations.

4. Conclusions

The co-sputtering of Ta and Re in a reactive oxidizing atmosphere leads to interesting combination of crystalline and amorphous phases as a function of the metal mixing ratio.

For low Re content (20%) most of the film retains the same amorphous structure as the pure tantalum oxide films, as demonstrated both by XRD and by micro-Raman investigations. Only few regions, growing in their density versus the Re concentration, exhibit well crystallized structure, tentatively assigned to HReO₄, which is also found in films obtained by evaporation of pure ReO₃ powders. For a composition corresponding to 62% Re, a dendritic-like growth of a separate solid phase is found on the surface; a more disordered or nanocrystalline character of such layer can be proposed. Finally, for a 70% content of rhenium, a weakly Raman active, homogeneous mixture is obtained, with different optical properties.

Taking into account the properties of protonic conduction of the tantalum oxide matrix [15], and the possible different structures of the microcrystalline, nanocrystalline or amorphous clusters of embedded rhenium-based compounds, surely containing protons, it appears quite interesting to continue the investigations on the possible interactions between the different solid phases. Structural and electrical measurements are planned, to investigate the possible applications of such films, for electrochromism and for insertion in liquid crystal cells, where they can, in principle, modify the electrooptical response.

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