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# Local structure of Ta-Re mixed oxide thin films studied by x-ray absorption spectroscopy

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## ABSTRACT

Mixed Ta-Re oxide thin films were synthesised for the first time by dc magnetron co-sputtering. Local environment around tantalum and rhenium atoms was studied by the Ta and Re  $L_3$ -edges x-ray absorption spectroscopy in pure  $Ta_2O_5$  and mixed Ta-Re oxide thin films (Ta:Re= 50:50, 38:62, 20:80 as determined from the ratio of the Ta-to-Re absorption edges). It was found that rhenium atoms are four-fold coordinated by oxygen atoms with  $R(Re-O)=1.74\pm 0.01$  Å and the mean square relative displacement (MSRD)  $\sigma^2=0.0012\pm 0.0005$  Å<sup>2</sup>. In pure  $Ta_2O_5$  thin film, tantalum ions are coordinated by six oxygen atoms at  $R(Ta-O)=2.02\pm 0.01$  Å with the MSRD  $\sigma^2=0.010\pm 0.001$  Å<sup>2</sup>. The addition of rhenium ions shortens the Ta-O distance by about 0.02-0.03 Å and makes the Ta-O distances distribution slightly broader with the MSRD  $\sigma^2\approx 0.013\pm 0.001$  Å<sup>2</sup>. The high frequency contribution in the Ta  $L_3$ -edge EXAFS signals, which is responsible in its Fourier transform for the peak beyond the first coordination shell, is due to the multiple-scattering effects within distorted  $[TaO_6]$  octahedron.

**Keywords:**  $Ta_2O_5$ , thin film, Ta-Re oxide films, EXAFS, XANES

## 1. INTRODUCTION

Tantalum oxide ( $Ta_2O_5$ ) is important technological material with a wide range of possible applications. Recently, the  $Ta_2O_5$  thin films were suggested as alternative dielectrics to silicon dioxide for memory and logic devices [1,2,3]. Besides, they may also work as a proton and Li ion conductor in electrochromic devices [4,5]. The catalytic properties of silica-supported tantalum oxide were also studied [6]. The optimisation of useful properties can be achieved by  $Ta_2O_5$  mixing with other metal oxides [7,8]. For example, an addition of  $Y_2O_3$  or  $WO_3$  allows to improve the insulating properties of tantalum oxide, while maintaining high dielectric constant [7].

Physical properties of tantalum oxide depend crucially on its atomic structure [9]. For many practical applications, an amorphous tantalum oxide (a- $Ta_2O_5$ ) is used. Since only short range order exists in a- $Ta_2O_5$ , it is important to know precisely the local environment around tantalum (or impurity) atoms. Among different experimental techniques, x-ray absorption spectroscopy (XAS) is the only direct structural tool, which is able to provide with such information. Recently XAS was used to study tantalum oxide films prepared by two different approaches: (i) chemical vapor deposition (CVD) method using  $Ta(OC_2H_5)_5$  and  $O_2$  gas mixture [10] and (ii) reactive sputtering from a Ta metal target in pure  $O_2$  atmosphere [11].

Only the first coordination shell around tantalum atoms was analysed in  $Ta_2O_5$  films made by CVD [10]. The analysis was performed in a short interval of wave vectors  $k=5-10$  Å<sup>-1</sup> within Gaussian model [10]. It was found that for as-deposited amorphous films, tantalum atoms are coordinated by  $N=6.1\pm 0.7$  oxygen atoms, located at a distance  $R(Ta-O)=2.05\pm 0.02$  Å with the mean square relative displacement (MSRD) or Debye-Waller factor  $\sigma^2=0.0054\pm 0.001$  Å<sup>2</sup> [10]. An annealing of the films in oxygen plasma at 400°C or in dry  $O_2$  or  $N_2$  at 750°C does not modify significantly the local structure around tantalum atoms: the values of the structural parameters (N, R and  $\sigma^2$ ) remain close within the

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fitting errors in spite of the Ta<sub>2</sub>O<sub>5</sub> films crystallisation, occurring at 750°C [10]. This result can be partially explained by the short interval and low signal-to-noise ratio of the EXAFS signals in [10].

The local environment of tantalum atoms in sputtered tantalum oxide films was found to be slightly different [11]. Also in this case, only the first coordination shell was analysed within Gaussian model [11]. The mean Ta-O distances were found to be much shorter  $R=1.93\pm 0.02$  Å, whereas the MSRD  $\sigma^2=0.009-0.013$  Å<sup>2</sup> was larger [11]. Besides, the obtained coordination numbers had quite large uncertainty, being equal to 4.48 or 6 depending on the model used in the fit of the Ta L<sub>3</sub>-edge EXAFS signals [11].

In spite of rhenium exists in a number of oxidation states and there are three anhydrous oxide forms - ReO<sub>2</sub>, ReO<sub>3</sub> and Re<sub>2</sub>O<sub>7</sub>, only one work exists to our knowledge on pure rhenium oxide thin films, prepared by dc magnetron sputtering [12]. Note that only reflectivity studies were conducted in [12]. The absorption features and the variation in the colour of these films from golden brown to red suggest that the films structure corresponds mainly to metallic-type ReO<sub>3</sub> phase with some oxygen non-stoichiometry [12].

Thus, it is clear that more studies are required to understand precisely the short range order in tantalum and rhenium oxide thin films. In this work, we have studied by x-ray absorption spectroscopy the local structure in pure Ta<sub>2</sub>O<sub>5</sub> and mixed Ta-Re oxide thin films.

## 2. EXPERIMENTAL AND DATA ANALYSIS

Ta<sub>2</sub>O<sub>5</sub> and mixed Ta-Re oxide thin films were deposited on silicon, glass and polyimide film substrates by dc magnetron sputtering of tantalum and rhenium metallic targets in a mixed argon-oxygen atmosphere. The argon partial pressure was set at 0.016-0.040 Pa, while the oxygen partial pressure at 0.053-0.107 Pa. The distance between the target and the substrate was 8.5 cm. The working pressure in a vacuum chamber during the sputtering process was 6.67 Pa. The films thickness was in the range of 400-1200 nm. The content of the rhenium ions was varied by changing the ratio of two targets areas, and it was estimated from the ratio of Ta-to-Re L<sub>3</sub> absorption edge jumps.

The Ta and Re L<sub>3</sub>-edge x-ray absorption spectra were measured at room temperature at the LURE DCI EXAFS-13 beamline (Orsay, France). A standard transmission scheme with a Si(311) double-crystal monochromator and two ion chambers was used. The absorption spectra were analysed by the EDA software package [13]. The theoretical backscattering amplitudes and phases, calculated by the ab initio FEFF6 code [14], were used in the analysis of the first coordination shells around Ta and Re ions. The calculations were performed for several clusters, having a structure of crystalline L-Ta<sub>2</sub>O<sub>5</sub>, TaO<sub>2</sub>, ReO<sub>3</sub> and ReO<sub>2</sub> and of regular octahedron [TaO<sub>6</sub>] with  $R(\text{Ta-O})=1.96$  Å and tetrahedron [ReO<sub>4</sub>] with  $R(\text{Re-O})=1.74$  Å. Complex exchange-correlation Hedin-Lundqvist potential was employed to account for inelastic losses [14]. To align experimental and theoretical EXAFS spectra in the best way, the position of the photoelectron energy origin  $E_0$  [13] in the experiment was chosen to match the theoretical one.

## 3. RESULTS AND DISCUSSION

Following conventional approach [15], one can divide the total x-ray absorption spectrum of an element into x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS).

Typical XANES signals at the Ta and Re L<sub>3</sub>-edges in mixed Ta-Re oxide thin films are shown in Fig. 1. In both cases, a strong resonance, the so-called "white line" (WL) [16], is located just above the absorption edge. At the Ta(Re) L<sub>3</sub>-edge, following the dipole transition rule  $\Delta l = \pm 1$ , a  $2p_{3/2}(\text{Ta/Re})$  core-electron is excited to an empty quasi-bound  $(5,\epsilon)d$  state in the continuum ( $\epsilon$ ) with  $5d(\text{Ta/Re})$  atomic character, and the final state is described as  $2p^5 5d^{n+1}$  ( $n$  is the number of  $5d$  electrons in the ground state) [14]. This transition gives an origin to the WL. The second possible channel  $2p_{3/2}(\text{Ta/Re}) \rightarrow (6, \epsilon)s$  was found to be smaller by a factor of  $\sim 50$  [17], therefore we have neglected it in the further analysis. Note that the final states  $(5,\epsilon)d$  and  $(6, \epsilon)s$  of the photoelectron are the relaxed excited states in the presence of the core-hole at  $2p(\text{Ta/Re})$  level screened by other electrons.

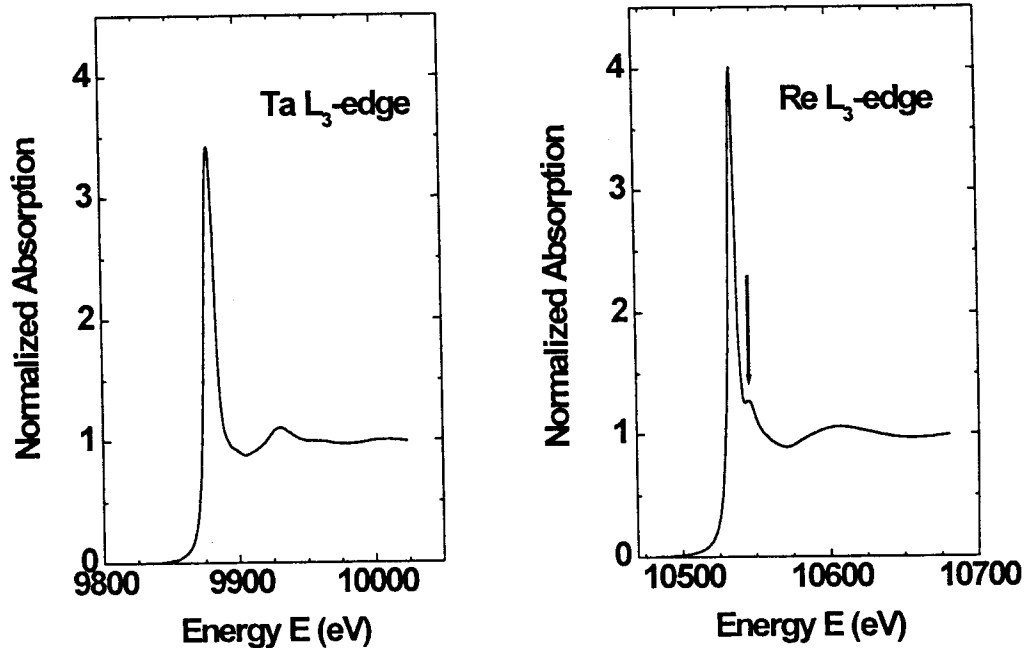


Figure 1: Experimental Ta and Re  $L_3$ -edge normalized XANES signals in mixed Ta-Re oxide thin film (Ta:Re=20:80). The main peaks, located just above the absorption edge at 9879 and 10535 eV, are the so-called "white lines". Note the presence of a feature, indicated by arrow, at the Re  $L_3$ -edge, which is typical for tetrahedral coordination of rhenium ions.

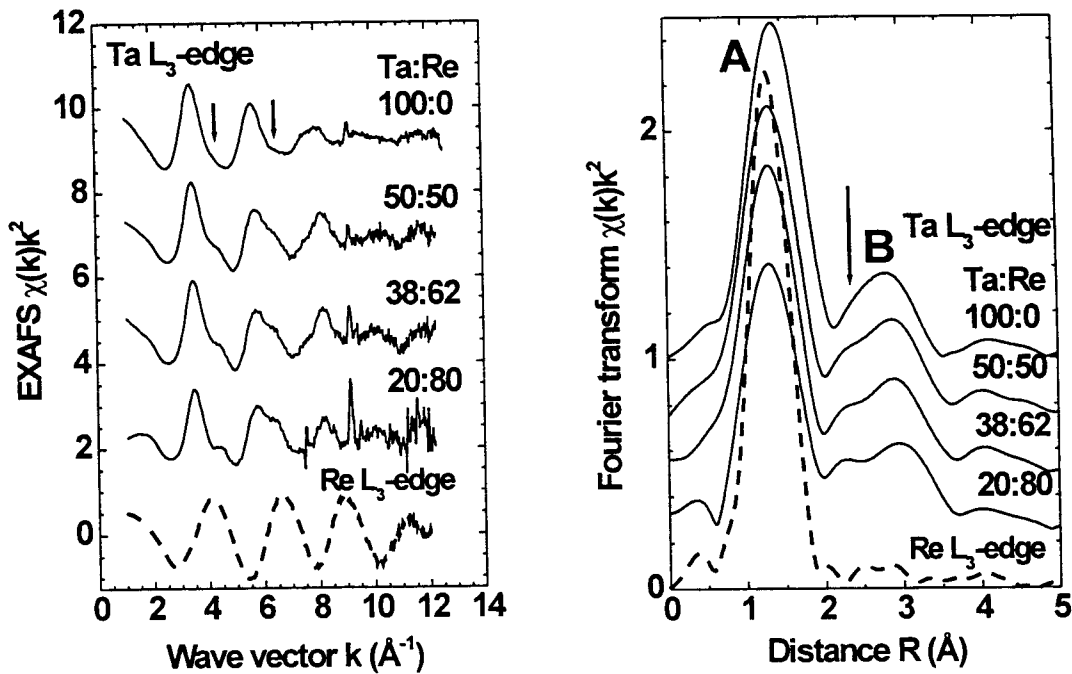


Figure 2: Experimental Ta and Re  $L_3$ -edge EXAFS  $\chi(k)k^2$  signals (left panel) and their Fourier transforms (FTs) (right panel) in mixed Ta-Re oxide thin films. The ratio of Ta:Re in the films was estimated from the ratio of their  $L_3$  absorption edge jumps. Note a variation of the EXAFS signals (and FTs) upon addition of Re ions, indicated by arrows. The two peaks, visible in FTs (right panel), are attributed to the first coordination shell (peak A) and to the multiple-scattering effects within the first shell (peak B).

The integral intensity of the WL (the WL area) is proportional to the squared radial matrix element times the number of empty 5d(Ta/Re) states. Therefore, high intensity of the WL is due to well localised character of the final state. There is a noticeable difference between the Ta and Re XANES signals expressed as a feature, located at the right-hand side of the WL at the Re  $L_3$ -edge (shown by arrow in Fig. 1). This feature can be used as an indication of tetrahedral coordination of rhenium ions in oxide materials. As we show further, the tetrahedral coordination of rhenium in the films is fully supported by the results of the EXAFS analysis.

The Ta and Re  $L_3$ -edge EXAFS  $\chi(k)k^2$  signals were extracted following conventional procedure [13] and are shown in Fig. 2 (left panel). Here one can recognise several differences between two edges: the Ta EXAFS has high frequency contribution (indicated by arrows in Fig. 2) and decreases at high wave vector values due to the static and thermal disorder, whereas the Re EXAFS represents single-frequency signal, having very small disorder induced damping. The Fourier transforms (FTs) of the EXAFS signals are shown in Fig. 2 (right panel). Only one narrow peak A, located at  $\sim 1.3$  Å and corresponding to the first coordination shell of rhenium atoms, is well visible in the FT of the Re EXAFS signal. In FTs of the Ta EXAFS signals, two peaks, A at  $\sim 1.35$  Å and B at  $\sim 2.7$  Å, are well visible and produce the dominant contribution into the total EXAFS signals. Note also that both peaks A and B vary depending on the chemical composition, i.e. rhenium content. To obtain structural information from the EXAFS signals, one needs to perform theoretical simulations. In this work, the local structure around Ta and Re ions was reconstructed from the EXAFS signals using multiple-scattering (MS) multi-shell fitting approach [15].

We found that the radial distribution function (RDF) around rhenium atoms can be well approximated by the Gaussian function. The results of the best-fit procedure suggest that rhenium atoms in mixed Ta-Re oxide films are always coordinated by four oxygen atoms, located at the distance  $R(\text{Re-O})=1.74\pm 0.01$  Å with the MSRD  $\sigma^2=0.0012\pm 0.0005$  Å<sup>2</sup>. Very small value of the MSRD means strong Re-O bonding and explains small damping of the Re EXAFS signals with an increase of the wave vector value. Note also that such coordination is typical for  $\text{Re}^{7+}$  ions in  $[\text{ReO}_4]$  complexes, existing in perhenates.

The analysis of the Ta  $L_3$ -edge EXAFS signal in pure  $\text{Ta}_2\text{O}_5$  thin film suggest that the first coordination shell (peak A in Fig. 2) around tantalum is composed of about six oxygen atoms, located at  $R(\text{Ta-O})=2.02\pm 0.01$  Å with the MSRD  $\sigma^2=0.010\pm 0.001$  Å<sup>2</sup>. The addition of rhenium ions shortens the Ta-O distance by 0.02-0.03 Å and makes the Ta-O distances distribution slightly broader with  $\sigma^2\approx 0.013\pm 0.001$  Å<sup>2</sup>. This means that addition of rhenium ions produces significant effect on the tantalum oxide network. One can suppose that a coexistence of Ta-O-Ta bridging bonds and Ta-O-Re bridging or Ta=O non-bridging bonds is responsible for a deformation of the  $[\text{TaO}_6]$  coordination polyhedra.

Finally, we will discuss the origin of the peak B at  $\sim 2.7$  Å in Fig. 2 (right panel). Note that this contribution is responsible for the high-frequency component in the EXAFS signals (indicated by arrows in Fig. 2 (left panel)). Since the peak B is present only in the FTs at the Ta edge, two contributions may be in principle responsible for its origin: (i) the second coordination shell composed of tantalum atoms and/or (ii) the multiple-scattering (MS) effects within  $[\text{TaO}_6]$  octahedron. The assumption of the second tantalum shell would mean the existence of short Ta-Ta interactions via octahedra edges. Such model match up badly with amorphous structure of the films, besides it is also not supported by our modelling procedure. The second model of the MS contribution was found to be consisted with our experimental data. In fact, the MS signals are always expected in the octahedral coordination [17,18]. Among different MS paths, which can be found in an octahedron [17,18], the two signals - the double-scattering signal in the triangular  $\text{Ta}_0\rightarrow\text{O}_1\rightarrow\text{O}_2\rightarrow\text{Ta}_0$  atomic chains ( $\text{Ta}_0$  is the absorbing atom and  $\text{O}_1/\text{O}_2$  are the two nearest neighbours) and the double/triple-scattering signals in the linear chains  $\text{O}_1\text{-Ta}_0\text{-O}_2$  ( $\angle\text{O}_1\text{Ta}_0\text{O}_2=180^\circ$ ), are the most important ones.

In Fig. 3 we show results of the best fit analysis of the EXAFS signals, related to the peaks A and B. The EXAFS signal from the peak B was singled out by the back-Fourier transform procedure in the interval  $R=1.9\text{-}3.5$  Å (see Fig. 2 (right panel)), whereas the EXAFS signal from the peak A was determined by subtracting the EXAFS signal of the peak B from the total one. Note that as a result of such procedure, the EXAFS signal of the peak A contains some contribution from peaks above  $R>3.5$  Å, that could lead to some discrepancy in the fitting procedure. Our model was based on the  $[\text{TaO}_6]$  octahedron, where two contributions were considered: the single-scattering contribution from six oxygen

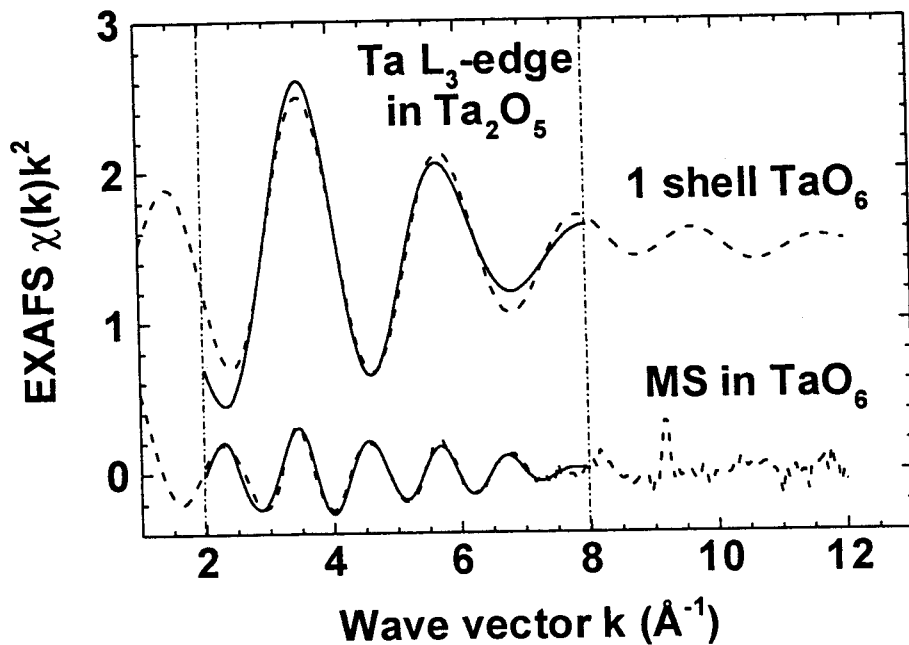


Figure 3: Best fit (solid curves) of the experimental (dashed curves) Ta L<sub>3</sub>-edge EXAFS  $\chi(k)k^2$  signals in pure Ta<sub>2</sub>O<sub>5</sub>. The model consists of the [TaO<sub>6</sub>] octahedron. Two vertical lines show the interval of the best fit. The single-scattering contribution from six oxygen atoms and the total multiple-scattering signal, generated within the [TaO<sub>6</sub>] octahedron, are shown separately.

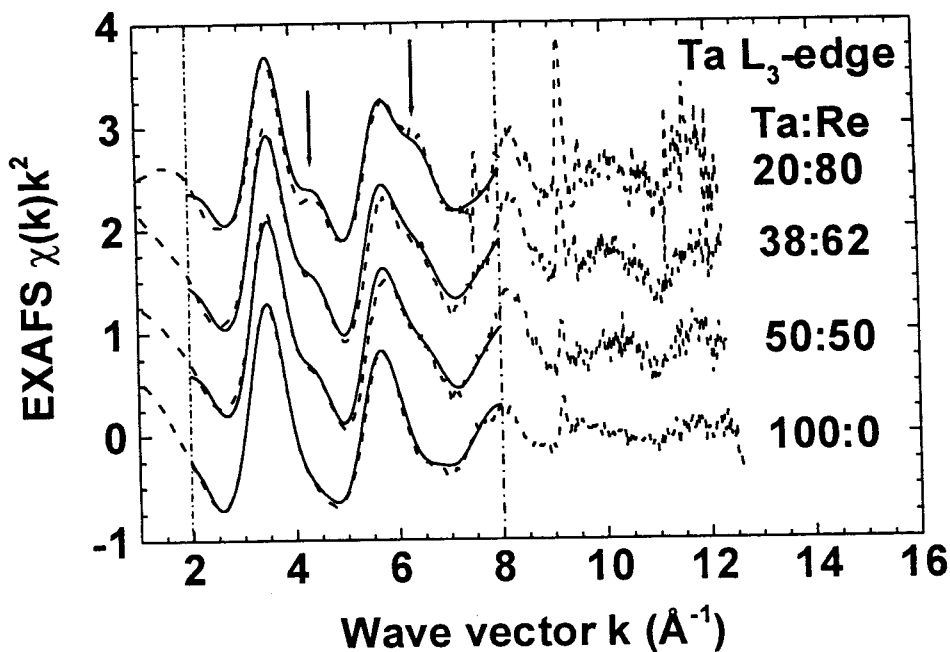


Figure 4: Best fit (solid curves) of the experimental (dashed curves) Ta L<sub>3</sub>-edge EXAFS  $\chi(k)k^2$  signals in pure Ta<sub>2</sub>O<sub>5</sub> and mixed Ta-Re oxide thin films. Note a variation of the EXAFS signals, indicated by two arrows, due to high-frequency multiple-scattering contribution from the [TaO<sub>6</sub>] octahedron of the first coordination shell.

atoms, responsible for the peak A in FTs, and the multiple-scattering signal, generated within the  $[\text{TaO}_6]$  octahedron and responsible for the peak B in FTs. The best fit was performed in the interval  $k=2-8 \text{ \AA}^{-1}$  within Gaussian approximation. The fit parameters were the paths lengths  $R$  and the MSRD values  $\sigma^2$ , whereas the paths degeneracies  $N$  were fixed. Some disagreement, observed for the first shell signal (upper curves in Fig. 3), can be attributed to influence of distant peaks above  $3.5 \text{ \AA}$  and to limitations of the Gaussian model, which is not able to account accurately for a distortion of the  $[\text{TaO}_6]$  octahedra. Anyway, we found very good agreement between high-frequency EXAFS component and the total MS signal, generated within the  $[\text{TaO}_6]$  octahedron (lower curves in Fig. 3).

The application of the same model to the experimental EXAFS signals from mixed Ta:Re oxide thin films is shown in Fig. 4. In this case, two contributions from peaks A and B were simultaneously included in the fit. This allows to exclude errors, which can be introduced by the Fourier filtering procedure. We obtained rather good overall agreement between the calculations and the experiments. The main changes in the MS contribution follow that for the first peak, i.e. a shortening of distances and an increase of disorder. Thus, the observed variations of the experimental EXAFS signals in Fig. 4 (indicated by arrows) are attributed to the interference effect between single-scattering and multiple-scattering contributions, which both vary upon addition of rhenium ions.

#### 4. CONCLUSIONS

Mixed Ta-Re oxide thin films were synthesised for the first time by dc magnetron co-sputtering. X-ray absorption spectroscopy was used to study the local environment around tantalum and rhenium atoms in pure  $\text{Ta}_2\text{O}_5$  and mixed Ta-Re oxide thin films (Ta:Re= 50:50, 38:62, 20:80 as determined from the ratio of the Ta-to-Re absorption edges). The thin films are amorphous, so that only the first coordination shell is observable around metal ions. The rhenium atoms are strongly bound to four oxygen atoms at  $1.74 \pm 0.01 \text{ \AA}$ . The tantalum ions in pure  $\text{Ta}_2\text{O}_5$  thin film are coordinated by six oxygen atoms, located at  $2.02 \pm 0.01 \text{ \AA}$ , with relatively large static/thermal disorder, given by the MSRD  $\sigma^2 = 0.010 \pm 0.001 \text{ \AA}^2$ . An addition of rhenium ions shortens the Ta-O distance by about  $0.02-0.03 \text{ \AA}$  and makes the Ta-O distances distribution slightly broader with the MSRD  $\sigma^2 \approx 0.013 \pm 0.001 \text{ \AA}^2$ . The high frequency contribution in the Ta  $L_3$ -edge EXAFS signals, which is responsible in the Fourier transform for the peak beyond the first coordination shell, is due to the multiple-scattering effects within distorted  $[\text{TaO}_6]$  octahedron.

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#### REFERENCES

1. P. Balk, "Dielectrics in microelectronics - problems and perspectives," *J. Non-Cryst. Solids* **187**, pp. 1-9, 1995.
2. S. Ezhilvalavan and T.Y. Tseng, "Preparation and properties of tantalum pentoxide ( $\text{Ta}_2\text{O}_5$ ) thin films for ultra large scale integrated circuits (ULSIs) applications - A review," *J. Mater. Sci.* **10**, pp. 9-31, 1999.
3. A.I. Kingon, J.-P. Maria, and S.K. Streiffer, "Alternative dielectrics to silicon dioxide for memory and logic devices," *Nature* **406**, pp. 1032-1038, 2000.
4. M.J. Duggan, T. Saito, and T. Niwa, "Ionic conductivity of tantalum oxide by rf sputtering," *Solid State Ionics* **62**, pp. 15-20, 1993.
5. Y. Sone, A. Kishimoto, and T. Kudo, "Amorphous tantalum oxide proton conductor derived from peroxo-polyacid and its application for EC device," *Solid State Ionics* **70/71**, pp. 316-320, 1994.
6. T. Ushikubo and K. Wada, "Preparation, characterization, and catalytic activities of silica-supported tantalum oxide for the vapor phase decomposition of methyl tert-butyl ether," *Appl. Catal. A* **124**, pp. 19-31, 1995.
7. H. Fujikawa and Y. Taga, "Effects of additive elements on electrical properties of tantalum oxide films," *J. Appl. Phys.* **75**, pp. 2538-2544, 1994.

8. P.S. Dobal, R.S. Katiyar, Y. Jiang, R. Guo, and A.S. Bhalla, "Structural transformation in  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  ceramics," *J. Phys. Chem. Sol.* **61**, pp. 1805-1808, 2000.
9. A.L. Gubskii and S.D. Khanin, "Influence of the short-range order on the energy spectrum of electrons in tantalum oxide," *Sov. Phys. Solid State* **31**, pp. 442-445, 1989.
10. H. Kimura, J. Mizuki, S. Kamiyama, and H. Suzuki, "Extended x-ray absorption fine structure analysis of difference in local structure of tantalum oxide capacitor films produced by various annealing methods," *Appl. Phys. Lett.* **66**, pp. 2209-2211, 1995.
11. D. Lützenkirchen-Hecht and R. Frahm, "Structural investigations of sputter deposited thin films: reflection mode EXAFS, specular and non specular X-ray scattering," *Physica B* **283**, pp. 108-113, 2000.
12. M.G. Krishna and A.K. Bhattacharya, "Growth of rhenium oxide thin films," *Solid State Commun.* **116**, pp.637-641, 2000.
13. A. Kuzmin, "EDA: EXAFS data analysis software package," *Physica B* **208/209**, pp. 175-176, 1995; "Reconstruction of the radial distribution function from EXAFS: new trends and comparative analysis of different methods," *J. Physique IV (France)* **7**, pp. C2-213-C2-214, 1997; *EDA: EXAFS Data Analysis Software Package, User's Manual*, Riga, 2001 (available at <http://www.dragon.lv/eda>).
14. A.L. Ankudinov, B. Ravel, J.J. Rehr, and S.D. Conradson, "Real-space multiple-scattering calculation and interpretation of x-ray-absorption near-edge structure," *Phys. Rev. B* **58**, pp. 7565-7576, 1998.
15. V.L. Aksenov, A.Y. Kuzmin, J. Purans, and S.I. Tyutyunnikov, "EXAFS spectroscopy at synchrotron-radiation beams," *Phys. Part. Nucl.* **32**, pp. 675-707, 2001.
16. A. Kuzmin and J. Purans, "The influence of the focusing effect on the x-ray absorption fine structure above all the tungsten L edges in non-stoichiometric tungsten oxides," *J. Phys.: Condensed Matter* **5**, pp. 9423-9430, 1993.
17. A. Kuzmin, J. Purans, M. Benfatto, and C. R. Natoli, "X-ray absorption study of rhenium  $L_3$  and  $L_1$  edges in  $\text{ReO}_3$ : Multiple-scattering approach," *Phys. Rev. B* **47**, pp. 2480-2486, 1993.
18. A. Kuzmin and R. Grisenti, "Evaluation of multiple-scattering contribution in EXAFS for  $\text{MeO}_4$  and  $\text{MeO}_6$  clusters," *Phil. Mag. B* **70**, pp. 1161-1176, 1994.