



Order, disorder and mixing: The atomic structure of amorphous mixtures of titania and tantalum



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ABSTRACT

The atomic structure of mixtures of titania (TiO₂) and tantalum (Ta₂O₅) ion-beam sputtered amorphous thin film coatings at various post-deposition annealing temperatures have been studied using Ta L_{III} and Ti K edge Extended X-ray Absorption Fine Structure (EXAFS). The results indicate that post-deposition annealing produces subtle changes in the short range order (<1 nm) for samples which remain amorphous. We also show that titania–tantalum mixtures maintain a structure similar to that of pure tantalum, with the titanium atoms preferring to sit at the second shell distance, which is similar to the Ta–Ta distance seen in the pure tantalum structure. A discussion is also included on interpretation of the general trends identified in the EXAFS data and how this relates to previous and ongoing studies of the structure and mechanical loss measurements of titania–tantalum coatings.

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1. Introduction

Thin film coatings of amorphous heavy metal oxides such as amorphous tantalum pentoxide (a-Ta₂O₅), otherwise known as tantalum, are commonly used as high-refractive-index materials in many high-precision optical applications. Tantalum is known for its low optical absorption and relatively high index contrast with silica [1] making the material extremely useful in optical atomic clocks [2], ring laser gyroscopes [3], frequency combs [4,5], and high-precision interferometers such as the Laser Interferometer Gravitational-wave Observatory (LIGO) [6]. However, in many of these cases, the tantalum layers are a limiting source of Brownian thermal noise, which is directly related to the mechanical loss (internal friction) of the material [7].

Previous research has shown that variations in mixing with other materials and post-deposition annealing can noticeably change both the optical and mechanical properties of ion beam sputtered (IBS) tantalum thin films [8–10]. It is speculated that these changes come about due to increased oxygen bonding and increased constraints on the so-called two-level-systems responsible for mechanical loss [11,12].

In order to fully understand why these manufacturing conditions alter the thin film properties, and to inform studies that aim to further improve their performance, it has become necessary to understand the nature of the changes at the level of their atomic structures.

Changes in the atomic structure of amorphous tantalum due to annealing may include reduction of oxygen deficiencies and increased local order [13]. Recently, studies using Transmission Electron Microscopy have probed the short range order of tantalum [14] and shown a correlation between short range order and mechanical loss [15] in titania and tantalum mixtures. These atomic structure investigations have demonstrated that a detailed understanding of the structural changes on the nano-scale may reveal the origins of the mechanical loss, and help inform various atomic modeling efforts. Additionally, a previous report using Ta L_{III} EXAFS measurements gives detailed information on the local structure of pure tantalum annealed at various temperatures [16].

The work presented here builds upon this previous research by using Ta L_{III} and Ti K EXAFS to analyze the short range order of mixtures of titania and tantalum ion-beam sputtered thin films, with titania concentrations of 14%, 52%, and 68% by cation percentage. Data from pure tantalum and pure titania samples are also given for comparison.

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2. Experimental setup

The samples in our study are single-layer 500 nm-thick IBS thin film coatings of amorphous tantalum mixed with titania ($a\text{-Ti:Ta}_2\text{O}_5$) deposited by the Australian Centre for Precision Optics (ACPO, Lindfield, Australia) on 1 in. diameter fused silica substrates. After deposition, the samples were annealed for 24 h in air at 300 °C and 600 °C, some were also left unannealed in their as-deposited (AD) state. A pure unannealed IBS titania sample was also measured and was deposited by MLD Technologies (Mountain View, California).

Samples were measured using Electron Energy Loss Spectroscopy (EELS) to have titania cation concentrations of 0, 14 ± 3 , 52 ± 10 and $68 \pm 1\%$. Some of the samples were back-thinned to reduce the substrate thickness from 6.35 mm to ~ 0.1 mm, allowing for some EXAFS data to be taken in transmission. In this article, we will refer to samples using their titania cation concentration and annealing temperature, therefore, the 52% titania sample that was annealed to 300 °C will be referred to as the 52% Ti 300 °C sample.

The samples were characterized at beamline 4–3 at the Stanford Synchrotron Radiation Lightsource (SSRL), which is a dedicated X-ray Absorption Spectroscopy (XAS) beamline. A standard experimental setup was used, which allowed for simultaneous collection of the data in both fluorescence and transmission modes. The Ta L_{III} absorption edge has an energy of 9881 eV, and spectra were collected over an energy range of 9700 eV to 11020 eV. Additionally, EXAFS spectra were taken on the Ti K absorption edge, which has an energy of 4966 eV, and data were collected over an energy range of 4735 eV to 5900 eV. The data from the samples were studied in both fluorescence and transmission, and it was determined that self-absorption in fluorescence mode was negligible. Ultimately, fluorescence data for the samples were analyzed, as it had a higher signal-to-noise ratio (SNR).

3. Data analysis procedure

Analysis of the EXAFS absorption data was done similarly to that described in recent work by Bassiri et al. [16]. As is standard for EXAFS data, the information on the nearest neighbor distribution is given by the oscillatory part of the absorption coefficient above an absorption edge. The raw EXAFS data is converted from energy space to k -space, and is normally represented as the function $\chi(k)$, which can be Fourier transformed to give a distribution in real space, R -space, denoted as $\chi(R)$.

The EXAFS background subtraction and data extraction was done using the Athena data analysis package [17]. Fourier transformation to R -space was done using a k^3 weighting and Hanning windowing over the k -range of 3 to 14 \AA^{-1} for the Ta L_{III} edge and 3 to 10 \AA^{-1} for Ti K edge.

IFEFFIT [18] was used for fitting to the $\chi(R)$ data, with three free parameters per path and an additional parameter for the absorption energy. The data were fit using a ΔR between 1 and 4 Å for both the Ta L_{III} and Ti K edges. For the Δk ranges, 3 to 14 \AA^{-1} and 3 to 10 \AA^{-1} were used for Ta L_{III} and Ti K edges respectively. Only single scattering paths were used in the fits, as no significant multiple-scattering paths were identified.

Theoretical standards were generated by performing *ab initio* calculations of EXAFS spectra from single-atom scattering using the standard EXAFS formula [19], with the fit parameters given in Table 1. The MSRD, σ_r^2 , measures the mean-square-relative-displacement in the bond distance. In some fits, σ_r^2 was subject to additional constraints, such as

requiring that the MSRD of scatterers be equal to those of closer ones (shown as the dash ‘-’ in Table 2). The absorption energy, E_0 , is a fit to the true energy of the absorption edge, to make up for variation in calibration and energy shift due to bonding conditions. E_0 is only fit once per spectra. The number of scatterers at a distance R_i is probed by the parameter $N_i S_0^2$. Ideally, the value on N_i would give the number of atoms at this distance, but difficulties arise in separation from the value of S_0^2 . While the value of S_0^2 is generally between 0.8 and 1.0, additional systematic errors that arise when fitting to amorphous samples, and large correlations between the value of N_i and other parameters lead to real uncertainties sometimes greater than 15% [20,21]. In the tables found in Sections 4, we give both $N S_0^2$ and $N(S_0^2 = 0.8)$ with the associated errors from the IFEFFIT fit, however, these numbers should not be regarded as an exact measurement, given the limitations described here.

4. Results and analysis

4.1. Model fitting to Ta L_{III} Edge

Fig. 1 shows the resulting best fit to data taken on the Ta L_{III} edge of the 14% Ti AD sample. The Fourier Transform of $\chi(k)$ spectra, $\chi(R)$, is a representation of nearest neighbor distributions. The peaks are usually shifted by 0.3–0.4 Å to lower R values due to a phase shift of the electron wave function in the scattering process. From this figure, one can see which features within the $\chi(R)$ plots are associated with which atoms in the fit model. The atomic shell model was chosen based on that from Bassiri et al. [16] as this model might be expected to fit at least the data from the 14% Ti samples, and any deviations could be attributed to the addition of titanium. In the Bassiri model, the first shell is a split shell of oxygen atoms (O1 and O2) located roughly 1.9 Å from the central tantalum atom, the second shell is composed of a tantalum atom (Ta1), and the third shell is another oxygen atom (O3). Finally, a fourth-shell tantalum atom (Ta2) is visible at roughly the position one would expect from a 180-degree Ta–O–Ta bond, at ~ 3.9 Å.

Due to constraints on the allowable number of fit parameters, only one titanium atom could be fitted, and the ~ 3 Å location was the only position where a titanium atom would fit to the data. This may be taken as a strong indication that this is the true location of titanium within the Bassiri model. This also seems to indicate that the titanium atoms prefer a radial distance similar to those of the Ta1 atoms.

Looking at the values of $N S_0^2$, given in Table 2, we can draw some conclusions on the effects of the addition of titanium atoms into the tantalum. In agreement with the Bassiri model, the sum of the $N(S_0^2 = 0.8)$ values of first-shell oxygen atoms surrounding the central tantalum atoms was 4–5, and this did not change significantly with the addition of titanium atoms into the material. The partial crystallization of the 68% Ti 600 °C sample did, however lead to an increase in first-shell oxygen atoms, with the sum being 5.31(54), much larger than in any other sample.

The value of $N S_0^2$ of the second-shell tantalum atoms has a large uncertainty associated with it, due to the influence of the nearby oxygen and titanium scatterers in the $\chi(R)$ plots, but the number appears to be unaffected by the concentration of titanium atoms, aside from the possible difference between pure tantalum annealed at 300 °C and any other sample. This would appear to indicate that while the titanium atoms prefer the Ta1 position, they do not replace the Ta1 atoms. This can be seen more clearly in Fig. 2, where the number of Ta atoms (from the last column of Table 2) at the 3.1 Å position is plotted against the number of Ti atoms at the same position for various annealing temperatures. The values for the 68% Ti samples are not included due to the large uncertainty in their fit values. However, it is not clear what the mechanism for this is: such an increase in metal atoms within the vicinity of the central tantalum atom would be expected to change the oxygen coordination and atomic distances, which is an effect that we do not see. In this particular case it is not possible to fully differentiate between

Table 1
Description of fit parameters in fitting EXAFS data to *ab-initio* models.

Fit parameter	Description
$N S_0^2$	Total scattering amplitude
R_i	Distance to scatterer
σ_r^2	Mean square relative displacement (MSRD)
E_0	Absorption energy

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