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Medium range structural order in amorphous tantala spatially resolved with changes to atomic structure by thermal annealing

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ABSTRACT

Amorphous tantala (a-Ta_2O_5) is an important technological material that has wide ranging applications in electronics, optics and the biomedical industry. It is used as the high refractive index layers in the multi-layer dielectric mirror coatings in the latest generation of gravitational wave interferometers, as well as other precision interferometers. One of the current limitations in sensitivity of gravitational wave detectors is Brownian thermal noise that arises from the tantala mirror coatings. Measurements have shown differences in mechanical loss of the mirror coatings, which is directly related to Brownian thermal noise, in response to thermal annealing. We utilise scanning electron diffraction to perform a modified version of Fluctuation Electron Microscopy (FEM) on Ion Beam Sputtered (IBS) amorphous tantala coatings, definitively showing an increase in the medium range order (MRO), as determined from the variance between the diffraction patterns in the scan, due to thermal annealing at increasing temperatures. Moreover, we employ Virtual Dark-Field Imaging (VDFi) to spatially resolve the FEM signal, enabling investigation of the persistence of the fragments responsible for the medium range order, as well as the extent of the ordering over nm length scales, and show ordered patches larger than 5 nm in the highest temperature annealed sample. These structural changes directly correlate with the observed changes in mechanical loss.

1. Introduction

Ion-beam sputtered amorphous tantala (a-Ta_2O_5) is often the material of choice for the high refractive index layer of highly reflective thin film coatings and find widespread applications that range from optical atomic clocks [1], ring laser gyroscopes [2], frequency comb techniques [3] and high-precision interferometers such as the Laser Interferometer Gravitational-wave Observatory (LIGO) [4]. Amorphous tantala also has applications that include insulating films with high dielectric constant for electronics [5] and corrosion resistant coatings for biomedical applications [6].

However, the performance of the coatings must be improved to make them a viable option for future upgrades to ultra-high precision gravitational wave interferometers, which are currently expected to be limited, at their most sensitive frequencies, by thermal noise arising from the coatings. To do so, it is necessary to understand changes in the atomic structure that occur during manufacturing and post-processing. Previous studies have shown that doping and annealing of the thin films cause considerable changes to the macroscopic properties such as optical absorption, scattering and mechanical loss [7–9]. Mechanical loss is equivalent to internal friction and is defined as the reciprocal of the mechanical Q factor, a quantity that describes the level of damping in an oscillator; a higher Q value indicates a lower rate of energy loss per oscillation with respect to the energy that is stored within the oscillator. This measure of mechanical stability and its relationship to Brownian thermal noise is quantified through the fluctuation dissipation theorem by Callen and Greene [10]. In general, only small changes are observed in the atomic structure of the coatings of the same material prepared by different methods when studied by electron diffraction reduced density function (RDF) analysis (which appear to be only sensitive to short range order, principally around the 1st and 2nd nearest neighbours, and up to a maximum of about 1 nm, and consequently cannot distinguish between atomistic models that contain or do not contain nanoscale order) [11–13]. A previous study using this technique has however demonstrated a correlation between mechanical loss and the concentrations of titania in titania-doped tantala [14]. Extended X-ray

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Absorption Fine Structure (EXAFS) shows more extensive order to perhaps the 3rd or 4th nearest neighbour and is chemically sensitive to the ordering about specific atoms, although this still does not reveal any order beyond 1 nm. Our recent work has shown that this provides further insights into the behaviour on annealing [15]. The previous electron diffraction studies have shown the atomic structure to be homogeneous at volumes probed with electron beams of 50 nm in lateral extent up to a 600 °C heat treatment, whereas in the present study the atomic structure is shown to be heterogeneous over volumes probed with an electron beam of 2 nm in lateral extent. It has been suggested previously, that this apparent homogeneity of the coating atomic structure is a consequence of the scale at which the structure has been examined; the inherent averaging over volumes containing hundreds of millions to hundreds of billions of atoms averages out any local structural differences in the materials. It is then expected for there to be a peak in the heterogeneity of the atomic structure at a scale determined by the volume of the material probed, coinciding with the maximum variance in structural order. In this work, the volume of material probed contains in the order of thousands of atoms, and proper variation in the ordering of the structure at the medium range can be quantified.

Fluctuation Electron Microscopy (FEM) is a diffraction and/or imaging technique that quantifies medium range order (MRO) in the roughly 1 to 3 nm range. The original formulation of FEM Gibson and Treacy [17] examines the MRO by measuring spatially resolved diffracted intensity fluctuations from nano-volumes in the sample material through the normalised variance,

$$V(k,Q)=\frac{\left\langle I^2(\mathbf{r},k,Q)\right\rangle}{\langle I(\mathbf{r},k,Q)\rangle^2}-1, \tag{1}$$

where $I(\mathbf{r}, k, Q)$ is the diffracted intensity as a function of position $\mathbf{r}$ on the sample, scattering vector k, probe size Q, and $\langle\ldots\rangle$ indicates averaging over $\mathbf{r}$. The technique is sensitive to three- and four-body correlations [16], and the fluctuations are maximally sensitive when the electron probe size is of comparable length scale to the MRO structural ordering being probed. So the extent of MRO is quantified through the magnitude of the variance of the diffracted intensity, as a function of scattering vector over a length scale determined by the size of probe used. Originally proposed by Gibson and Treacy [17], the technique was initially carried out using dark-field imaging in the TEM, although an equivalent experiment can be carried out using scanning diffraction [18]. This latter experimental approach has distinct advantages, especially on modern scanning transmission electron microscopes, where probes well below 1 nm in diameter can be routinely produced, provided the diffraction patterns can be acquired reasonably quickly (which is now possible due to advances in imaging detectors).

Atomistic models have shown that the variance displays clear trends as a function of the size and volume fraction of the ordered regions [19, 20] and, to date, the technique has been employed to show variation in the nanoscale order of amorphous silicon [21–26] and amorphous germanium [16, 18, 27] thin films, phase change chalcogenide materials [28–30], and a selection of amorphous metals [31, 32]. In these experiments, qualitative differences in FEM variance were observed and attributed to fundamental physical phenomena such as differences in film deposition condition [23], the existence and thermal ripening of subcritical nuclei that precede crystallisation [29, 30], and the effect of alloying on crystallisation kinetics [33]. Quantitative FEM analysis has thus far proven challenging, but with recent developments such as variable resolution FEM, information about the extent of the nanometre-scale ordering can be extracted [26, 34]. Nevertheless, a number of recent studies have been successful in relating the scattering covariance and angular correlations in FEM data to structural information [13, 35, 36].

In recent work, we used scanning nano-diffraction FEM to collect data, in a similar way to that described by Voyles and Muller [16], and demonstrated the existence of MRO in a-Ta_2O_5 [37]. In the version of FEM applied in the present work, we depart from the standard formalism in Eq. (1), and by assuming noise-free kinematic coherent diffraction to be Gaussian distributed, compute the variance of standardised correlation coefficients obtained from a normalised cross-correlation of a Gaussian filter with the raw diffraction data,

$$V(\gamma,k,Q)=\left\{\langle\gamma^2(\mathrm{I}(\mathbf{r},x,y,Q),\mathrm{t})\rangle-\langle\gamma(\mathrm{I}(\mathbf{r},x,y,Q),\mathrm{t})\rangle^2\right\}_k. \tag{2}$$

where γ, the correlation coefficient is obtained from:

$$\gamma(x,y)=\frac{\sum_{x,y}\left(I(x,y)-\bar{I}_{u,v}\right)\left(t(x-u,y-v)-\bar{t}\right)}{\sqrt{\sum_{x,y}\left(I(x,y)-\bar{I}_{u,v}\right)^2\left(t(x-u,y-v)-\bar{t}\right)^2}}. \tag{3}$$

In Eq. (3), t is the Gaussian filter, $\langle\ldots\rangle$ indicates averaging over $\mathbf{r}$, and I is as in Eq. (1) with the exception that here the variance is computed on a pixel by pixel basis (x, y) through the diffraction pattern stack resulting in a variance map which is thereafter azimuthally averaged (represented by $\{\ldots\}_k$) to obtain the variance as a function of scattering vector k. Eq. (2) is a standard expression for variance which can be found in any statistical reference manual and is easily recognised by the mnemonic "mean of the square minus square of the mean"; it differs in form from Eq. (1) by the change of variable and the normalisation factor in the denominator; we normalise our data through Eq. (2) prior to computing the variance. Whilst the Gaussian filtering was initially intended to mitigate noise, it became apparent that a change of variable in the variance calculations from intensity to a normalised score of the intensities structural significance simultaneously removed noise, background and standardised the datasets. In Eq. (3), $I(x,y)$ denotes the intensity value of the diffraction pattern at the point (x,y), $\bar{I}_{u,v}$ is the mean value of $I(x,y)$ within the area of the Gaussian filter t at the point (x,y), and $\bar{t}$ is the mean value of the Gaussian filter. The denominator in Eq. (3) contains the variance of the zero mean diffraction pattern function $I(x,y)-\bar{I}_{x,y}$ and the zero mean Gaussian filter function $t-\bar{t}$ at the point (x,y). The 2-D normalised cross correlation is used here as a standardised means to evaluate the significance of the raw diffracted intensity at each point in the diffraction pattern, and is scored upon the similarity of the local distribution of intensity around each point to our model diffraction maxima centred on that point. Our model diffraction maximum is a 7×7 pixel rotationally symmetric normalised Gaussian filter with a two pixel standard deviation, obtained by fitting a 2-D Gaussian function to a sharp Bragg spot in a diffraction pattern from the same sample series, which had crystallised after a 800 °C heat treatment. Using this approach, the absolute magnitude of the scattered intensity is irrelevant and instead, it is the shape of the intensity distribution around each pixel that becomes relevant, allowing coherent diffraction with poor SNR to emerge from the background. The resulting normalised correlation map is then a standardised transform of the diffraction pattern into a map of the diffracted intensity's structural significance, where scores range in value between −1 (maximally anti-correlated), zero (uncorrelated) and 1 (maximally correlated). Only positive scores are deemed structurally significant as we assume coherent diffraction to be approximately Gaussian, whereas the diffuse background and single pixel events are not Gaussian distributed. We thus remove the negatively scored intensity contributions from calculations which anti-correlate with our model Gaussian filter, and we assume that much of the noise and diffuse background in the system will result in this negative range of scored intensities. As a result of this normalisation, $\gamma(x,y)$ is invariant to brightness or contrast variations in the diffraction patterns (including from diffuse inelastic scattering), which are related to the values of the mean and the standard deviation; this has the effect of standardisation of the data-sets and preservation of real diffraction spots deemed structurally significant through positive correlation, whilst rejecting single pixel noise or X-ray events. Intuitively, this approach seems well suited to the study of