Reduced density function analysis of titanium dioxide doped tantalum pentoxide

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Abstract. Future advanced gravitational wave detectors will need to be constructed using ultra low loss materials to achieve the desired sensitivity levels. Coating thermal noise which is related to mechanical loss has been determined to be a limiting factor for the sensitivity of these detectors and must be reduced. To achieve this goal, work is on going to identify the causes of coating mechanical loss. Recent experiments suggest this is micro-structural in origin, thus determining the structural features of coatings via appropriate modelling is of interest. It will be shown that through Transmission Electron Microscopy and reduced density function analysis, the local structural changes due to doping of coating materials can be identified. Furthermore by using this data as an empirical constraint for combined reverse Monte Carlo and Density Functional Theory simulations the trends seen in the data can be replicated in the modelling.

1. Introduction

Einstein’s general theory of relativity (GR) predicts the existence of wave-like distortions in space-time responsible for the transmission of gravitational information, which propagate at the speed of light [1]. These Gravitational Waves (GWs), when detectable will provide a new and unique way of studying some of the most exotic and violent objects in our Universe.

Current GW detectors are based on Michelson-type laser interferometers. The principle of laser interferometer GW detectors is that a GW would slightly change the arm length of the interferometer, which would alter the interference pattern created by the recombination of the two beams [2]. Due to the extremely small expected effects of GW signals from astrophysical sources, detectors must be carefully constructed to minimise any noise sources affecting their detection capabilities [3]. For the next generation of GW detectors, research suggests that thermal noise present in the mirror coatings will be a limiting factor within the most sensitive operational frequency range [4].

Two forms of thermal noise which are of concern for GW detectors are Brownian thermal noise [4] and thermoelastic noise [5]. Brownian thermal noise arises due to random thermal motion of atoms, and thermoelastic noise results from the statistical fluctuations in temperature of the materials coupling to displacements of the material surface via coupling through the thermal expansion coefficient. Although thermal noise can be difficult to measure directly at the frequencies of interest,
its effects can be determined through the measurement of mechanical loss, to which it is directly related [4].

The current material of choice for the high refractive index layers in multilayer mirror coatings is tantala (Ta$_2$O$_5$) due to its optical properties and relatively low loss at room temperature. The optical properties of tantala can be improved by heat-treating the coating up to 600°C [6] without unduly affecting the loss at room temperature [7]. However, heat-treatment has also been shown to increase the loss at low temperature [7], which is of interest for possible future cryogenic detectors [8]. Furthermore, it has previously been shown that the room temperature loss of tantala can be reduced by doping with titania (TiO$_2$) and that this effect peaks at ~30 cation % Ti [7]. It is not currently understood why titania reduces loss at room temperature nor why heat-treatment increases it at low temperature. Through work on silica, which shares similar low temperature loss properties with tantala, it has been postulated that observed loss peaks at low temperature may be due to specific structural features [9,10].

2. Method

The coatings studied in this work were deposited using dual ion beam assisted sputtering by LMA (Lyon, France) and were deposited onto 1 inch diameter by ¼ inch thick fused silica substrates held at a temperature of 90°C. Coated substrates were then heat-treated in air at 600°C for 24 hours to relax internal stresses and to allow the structure to equilibrate [11].

Specimens were prepared for Transmission Electron Microscopy (TEM) using a standard cross sectional method based on mechanical thinning, dimpling and ion beam thinning. The primary experimental constraint for the modelling process was electron diffraction data, which was recorded on a FEI Tecnai T20 TEM operated at 200 keV with a beam convergence semi-angle ($\alpha$) of 1.89 mrad. To ensure accurate calibration of the TEM diffraction data, diffraction patterns were recorded from a single crystal silicon specimen under exactly identical conditions just prior to recording the electron diffraction data from the glasses. The typical experimental discrepancy in the lattice parameters is below 1%, and given an accurate calibration, the value $dq$ is also calculated. This value $dq$ is a measure of the $q$ resolution of the CCD under the experimental conditions (where $q$, the diffraction vector, is defined as $q = 4\pi\sin(\theta)/\lambda$) and is typically of the order of 0.2 Å$^{-1}$pixel$^{-1}$.

The diffraction data is then used to calculate the Reduced Density Function (RDF), which is a statistical representation of where the nearest neighbours (NNs) lie in real space [12]. This is done by radially averaging the diffraction pattern, removing the intensity from individually scattering atoms and Fourier transforming the result. RDFs can be directly interpretable; quantities such as peak height, width and position provide information about the NN relationships in the structure.

The modelling process consists of using a Reverse Monte Carlo (RMC) simulation to create a structure which matches the experimental RDF [13]; Electron Energy Loss Spectroscopy (EELS) and X-ray reflectometry are used to constrain the stoichiometry [13] and density [14], respectively. Density Functional Theory is then used to simulate a liquid quench procedure, in order to relax the structure to an energetically lower state [13] using the simulation software CASTEP [15]. Studies of the energy evolution with time have allowed for a reduction in simulation time compared to previous work [13] by reducing the equilibration time from 5 to 2ps per temperature step; the one possible cost of reducing the equilibration time in this way is to reduce the probability of slower processes such as tunnelling occurring. The model is then refined further using a second RMC step on a larger model, constructed from the DFT model, to ensure both an energetically stable configuration and an acceptable fit to the experimental RDF [13].
3. Results and Discussion

It is known from previous work on tantala that the first two peaks in the RDF correspond to the Ta-O and Ta-Ta NNs [13]. This is assumed to be similar for titania doped tantala, since Ti-O bonds have similar lengths to Ta-O bonds in published oxide crystal structures [16]. Thus, the first peak will also contain Ti-O bonds, and the second will also contain Ti-X NN information, where X can be Ta or Ti. Clear trends are observed as a result of the increase in Ti content. Firstly, the X-O peak increases in height, becomes narrower, and moves to slightly larger distances (figure 1), suggesting that that the addition of Ti increases the ordering in the first coordination shell, as well as slightly increasing bond lengths. Secondly, the X-X peak develops a prominent shoulder indicating an increase in abundance of a NN distance slightly shorter than the Ta...O distance responsible for the 2nd peak in pure Ta$_2$O$_5$

Preliminary modelling suggests that titanium preferentially bonds to the oxygen and tantalum, rather than forming separate Ti-rich clusters in the structure. This is seen in Figure 2 where the abundances of Ti-O and Ti-Ta are greater than Ti-Ti. This suggests that the titanium atoms are substituting for tantalum atoms in the structure and not changing it fundamentally. This is illustrated in Figure 3, which shows the typical Ta$_2$O$_2$ planar fragment, which is one of the key building blocks of amorphous Ta$_2$O$_5$ (see supplementary material to ref [13], http://dx.doi.org/10.1063/1.3535982), and its modification as a result of Ti addition to hybrid TaTiO$_2$ and pure Ti$_2$O$_2$ rings.

![Figure 1: Experimental RDFs of 20.4 cat. % Ti and 53.8 cat. % Ti TiO$_2$ doped Ta$_2$O$_5$ showing the appearance of a “shoulder” in the 2nd peak at high TiO$_2$ percentage](image)

![Figure 2: Partial RDFs for (a) a 20.4% TiO$_2$ doped sample and (b) a 53.8% TiO$_2$ doped sample](image)

Analysis of the partial RDFs resulting from the fitted models reveals that the noticeable shoulder on the 2nd peak in Figure 1 for the 53.8 cat. % Ti sample arises from the high abundance of Ti-Ta distances at this doping level. Thus, the hybrid TiTaO$_2$ ring structure is far more abundant than either of the other ring structures as is evident from the large Ti-Ta peak height in Figure 2b, and is probably preferred at this composition. This distance is also shorter than Ta-Ta or Ti-Ti distances, as can also be seen from Figure 2b, which could indicate some form of interactions between Ti and Ta in these
planar fragments. It should also be noted that the pure Ti2O2 ring structure does not appear to have a Ti-Ti link unlike the other two variations. This happens since the O-Ti-O typical bond angle is more acute than the O-Ta-O bond and as such the Ti atoms are further apart and outside the normal NN criteria used by ourselves or others of the sum of covalent radii plus a small percentage (e.g. 10%).

Figure 3: Three variations of the Ta2O5 crystalline building block found in TiO2 doped Ta2O5: a) The pure Ta-Ta case b) the hybrid Ti-Ta case and c) pure Ti-Ti case. The metal atoms are at the top and bottom of each structure, and the oxygen atoms at the side.

4. Conclusions
In conclusion, diffraction data from transmission electron microscopy combined with reduced density function analysis has been able to detect a significant structural change due to doping in an amorphous mixed tantalum titanium oxide. This detectable change allows the development of unique structural atomic models for each dopant percentage. Initial structural models for samples containing about 20 and 50 cation % titanium show a strong preference towards Ti-Ta bonding over Ta-Ta or Ti-Ti, suggesting that titanium substitutes for tantalum in the structure, modifying it subtly as it does so. Understanding these structural changes in detail is the first step to understanding the processes which causes mechanical loss and thermal noise, ultimately allowing the design of lower loss materials.

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