Journal of Physics: Conference Series **228** (2010) 012020 doi:10.1088/1742-6596/228/1/012020

Multitechnique investigation of Ta_2O_5 films on SiO_2 substrates: comparison of optical, chemical and morphological properties.

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Abstract. Ta_2O_5 mechanical losses seem to be the main cause of mirror thermal noise, limiting current interferometric gravitational wave detectors sensitivity in the 50-300 Hz frequency range. Work is in progress for the identification of these relaxation processes probably related with lattice defects and impurities that are distributed both in the mirror bulk and at the surface, in order to introduce step by step the suitable modifications in the samples until a stable "optimum performance" is obtained both from the optical and the thermo-mechanical point of view. Here we present our first results of a multitechnique characterization of Ta_2O_5 films deposited on SiO_2 substrates. Optical, chemical and morphological properties have been investigated by means of Spectroscopic Ellipsometry, X-ray Photoelectron Spectroscopy and Atomic Force Microscopy. Measurements carried out on pure bulk Ta_2O_5 samples will be also reported for comparison.

1. Introduction

The sensitivity of current interferometric gravitational wave detectors is limited in the 50-300 Hz frequency range by the mirror thermal noise. More precisely, the dielectric coating deposited on the mirror surface was found to induce a significant degradation of the high quality factor, Q ($10^6 \div 10^9$ at room temperature) of the silica substrates [1–3]. A stack of Ta_2O_5 and SiO_2 layers is presently used to obtain the required optical performances, and there is evidence that losses in the Ta_2O_5 are the major source of noise [4–8]. Several attempts have been made for improving the global (substrate + coating) quality factor of the mirrors. A good approach is to optimize the dimensions of each layer [9, 10]; this approach may be considered not alternative but complementary to other strategies aiming to improve the performances of the layers by modifying their structure and/or composition: in this sense experiments have been performed introducing a dopant in the Ta_2O_5 layers, leading to interesting results [8, 11].
Any strategy aimed at modifying the structure of the layers, either internal or at the interface surface between layers, requires a preliminary and accurate knowledge of the physical-chemical properties of the Ta_2O_5/SiO_2 repeat unit.

In this paper, we will present our first results obtained on as-received Ta_2O_5/SiO_2 films. Optical, chemical and morphological properties have been investigated by means of spectroscopic ellipsometry (SE), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). XPS measurements carried out on pure bulk Ta_2O_5 samples will be also reported for comparison. Measurements of quality factor obtained using a new kind of nodal suspension (GeNS, see ref. [12]) will be also reported.
Our work in progress is aimed to characterize defects/non-idealities both at the surface (using AFM, XPS and SE) and in the bulk (mainly through the application of SE) of the Ta_2O_5 layers, and to relate them, if possible, to the mechanical response of the samples.

2. Experimental

2.1. Materials

Ta_2O_5 films (200 nm nominal thickness) were deposited on Corning 7980® substrates by Double Ion Beam sputtering (ATFilms) and used without any further cleaning procedure. Ta_2O_5 powder (Aldrich, 99.99% trace metal basis, particle size < 5 μm) was used as-received.

2.2. Methods

Standard SE measurements were performed on a recently upgraded rotating compensator ellipsometer (M-2000, J.A. Woollam Co. Inc.). The instrument allows simultaneous measurements at 674 different wavelengths in the range 245-1700 nm. Principles of SE are described at length in several books [13–15]. In brief, the output of ellipsometry is the complex reflection coefficient $\rho = \frac{r_p}{r_s} = \tan\Psi \exp(i\Delta)$, where r_p and r_s are the Fresnel reflection coefficients for p- and s-polarization, respectively. Analysis of ellipsometric spectra allows to gather information on the optical and morphological properties of films with thickness ranging from some micrometers down to monolayer level [16].
XPS analysis was carried out with a PHI ESCA 5600 MultiTechnique apparatus. The system consists of an X-ray Al-monocromatised source ($h\nu = 1486.6$ eV) and a spherical capacitor electron energy analyser, used at a constant pass energy of 5.85 eV. In the standard configuration the analyser axis formed an angle (take-off angle) of 68° with the sample surface. The binding energy (BE) scale was calibrated setting the adventitious C 1s level at 284.8 eV.
Tapping mode AFM measurements were performed using a Multimode/Nanoscope IV system (Digital Instruments) and Si cantilevers (OMCL-AC160 TS, Olympus).
Mechanical quality factor measurements were performed exciting a resonant mode of the sample and measuring the ring down. The damping envelope is an exponential decay whose rate is

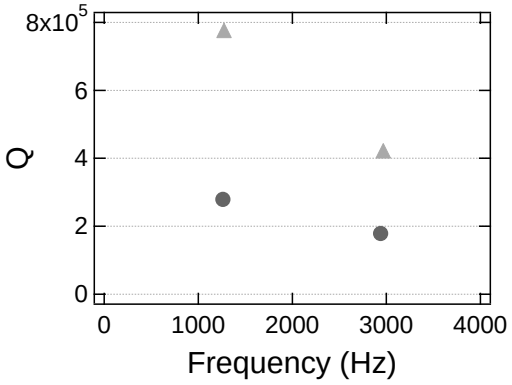

Figure 1. Maximum Q values obtained using GeNS [12] on 50 mm diameter/0.5 mm thickness Corning disks: bare substrates (triangles) and 200 nm thick Ta_2O_5 film covered ones (full circles).

inversely proportional to the quality factor at the frequency of the excitation. All the mechanical characterization were performed using GeNS [12], a new kind of nodal suspension designed to minimize the effect of the external losses due to the experimental apparatus on the measurement of Q. Figure 1 shows the maximum quality factor of the first and second butterfly mode measured on 200 nm thick Ta_2O_5 film on Corning glass compared with the value of bare Corning substrate (disks diameter = 50 mm, disks thickness = 0.5 mm). It is possible to observe how the presence of the film reduces the mechanical quality of a factor ≈2.5.

3. Results and discussion

3.1. Spectroscopic Ellipsometry

Information on optical properties and thickness of thin films can be derived by comparing the experimental data with simulations based on realistic optical models of the system under investigation [14, 15, 17]. A good knowledge of the optical response of the substrate is hence of utmost importance. Figure 2 (panels (a) and (b)) shows typical $\cos\Delta$ and $\tan\Psi$ experimental

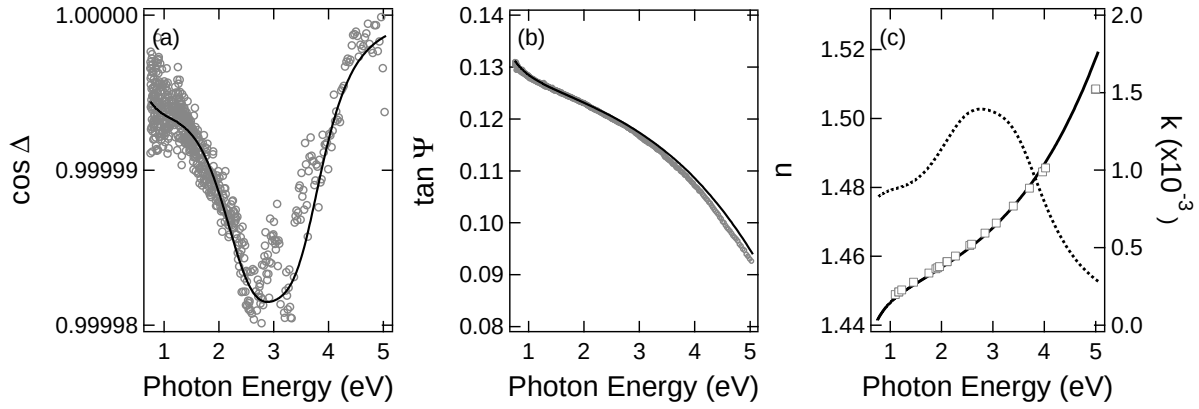

Figure 2. Panels (a) and (b): typical $\cos\Delta$ and $\tan\Psi$ experimental (grey markers) and generated (black curves) patterns collected on Corning 7980® bare substrates at 60° of incidence. Data range of panel (a) has been properly scaled to emphasize the very small dip in the $\cos\Delta$ pattern. Panel (c): refractive index (n, full line) and extinction coefficient (k, dotted line) obtained for the Corning 7980® substrate. A very low (k of the order of 10^{-3}) absorption over the whole spectral range was assumed (see text). Refractive index provided by Corning Inc. company [19] (grey open squares) is reported for comparison.

patterns (grey markers) collected on Corning 7980® bare substrates at 60° of incidence. Measurements were performed following the *index matching* method described in ref. [18] to suppress backside reflections occurring when dealing with transparent substrates. The use of adhesive tape (Scotch Magic® or similar) applied to the back surface of soda-lime glass was proved being effective over the full measured spectral range [18].

The best fit (black solid curves in panels (a) and (b) of figure 2) of the experimental data required the simulation of a very weak absorption to reproduce the very small dip visible in panel (a). A model was adopted which takes effectively into account the effect of inclusions (i.e. trapped air bubbles, traces of metal coming from the melting procedure, solid impurities from the raw material), the very low surface roughness of the samples (order of $0.1 \div 0.2$ nm, evaluated by AFM) and even some possible non-idealities of the transfer function of the instrument. The resulting optical properties are reported in panel (c) of figure 2, compared to the refractive index provided by Corning Inc. company [19].

Figure 3 shows typical $\cos\Delta$ and $\tan\Psi$ experimental patterns (collected at 60° of incidence) measured on Ta_2O_5 films together with simulated data obtained using a four-phases-model (surface roughness/dense Ta_2O_5 film/lower density Ta_2O_5/Corning substrate). The best fit was

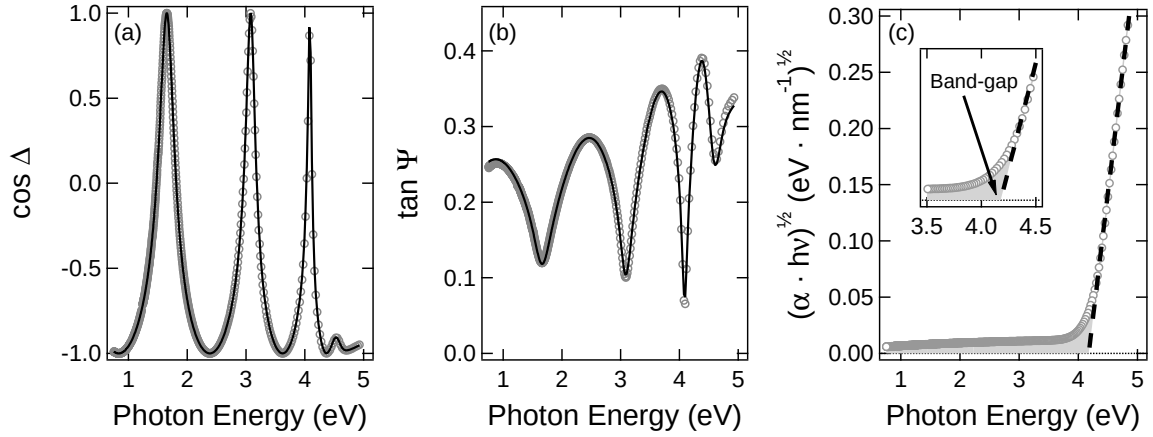

Figure 3. Panels (a) and (b): typical $\cos\Delta$ and $\tan\Psi$ experimental (grey markers) and generated (black curves) patterns, collected at 60° of incidence on Ta_2O_5 films. The best fit was obtained through the four-phases-model described in the text. Panel (c): Tauc plot (see text). Ta_2O_5 layers show a low but significant absorption (grey area) in the energy region below the band-gap, a behavior symptomatic of non-stoichiometric Ta_2O_5 [21].

obtained with a surface roughness layer (50% voids and 50% material) thickness of (1.6 ± 0.2) nm and a total thickness of the Ta_2O_5 layer of (195.6 ± 0.2) nm, in good agreement with the nominal thickness. Ellipsometric surface roughness was confirmed by AFM measurements on several zones of the samples. To properly describe the optical response of the Ta_2O_5 layer, it was necessary to take into account a small fraction of voids (approximately 1.5%) in a 20 nm-thick region next to the Corning substrate; this "low density" layer could be related to faults in the growth process.

The optical properties of the Ta_2O_5 layer were obtained through a Cody-Lorentz model with Urbach tail absorption in the region below the band-gap energy [20]. This model was shown to well describe the optical behavior of amorphous materials in the region around the band-gap energy. A low intensity Drude absorption was also added, in order to take into account the absorptions in the low energy range. Since stoichiometric Ta_2O_5 should be non-absorbing and non-dispersive [21] at energies below the band-gap, our ellipsometric characterization seems to indicate the presence in the film of species of low stoichiometry. This unexpected behavior could be emphasized by looking at the so called Tauc plot [21, 22] (panel (c) of figure 3), in which the quantity $(\alpha \cdot h\nu)^{1/2}$ is plotted against the photon energy $h\nu$. α is the absorption coefficient, $\alpha = 4\pi\, k/\lambda$, where k is the extinction coefficient of Ta_2O_5 obtained from the best fit of the SE data. The energy gap of the material (approximately 4.2 eV) can be obtained through a linear fit of the high energy part of the plot, as sketched in the figure (dashed line). A significant absorption tail is present in the energy region below the band-gap (grey area).

3.2. X-ray Photoelectron Spectroscopy

In order to evaluate the stoichiometry/chemical properties of our samples, XPS measurements were performed. Figure 4 (panels (a) and (b)) shows typical spectra obtained on the Ta 4f and O 1s regions. For each Ta 4f doublet, a 1.91 eV energy splitting and a 4:3 intensity ratio between

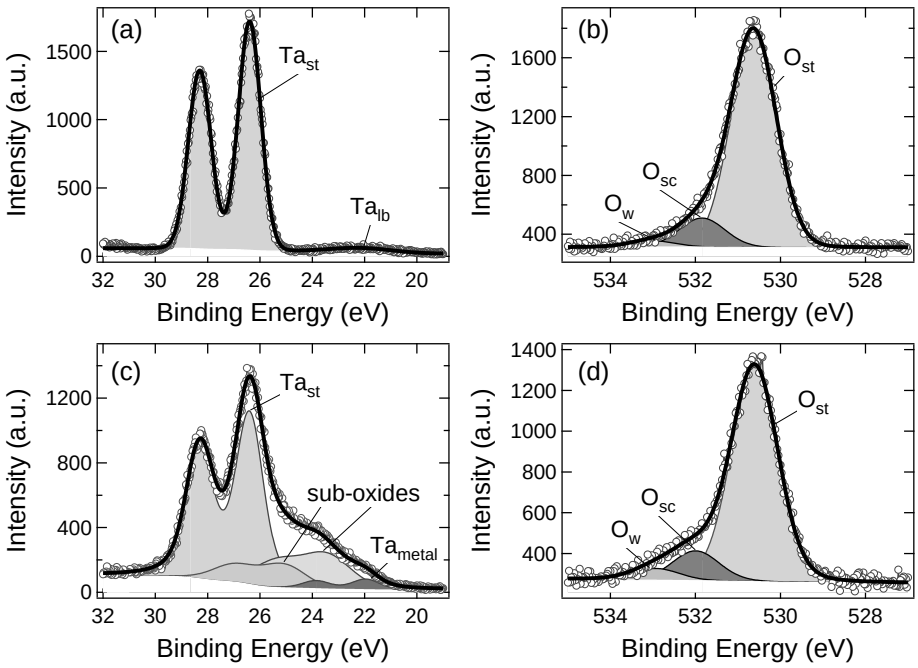

Figure 4. Panels (a) and (b): Ta 4f and O 1s experimental (grey markers) and generated (black lines) data collected on Ta_2O_5 films. For comparison, data collected in the Ta 4f region of a sputtered Ta_2O_5 film and O 1s region of ultra-pure Ta_2O_5 powder (panel (c)and (d) respectively) are reported.

the 7/2 and 5/2 components were applied.

Analysis of the Ta 4f region points out the presence of an intense doublet with the 7/2 component at 26.4 eV (Ta_{st}), typical of the stoichiometric form Ta_2O_5 [23, 24]. A hardly visible peak centered at around 22 eV is also present (Ta_{lb}). Metallic Ta and sub-oxides can be identified in this low binding energy region (see panel (c) of figure 4), looking at the Ta 4f spectra collected on a sputtered sample (12 seconds, 3 KeV Ar^+), confirming the indication obtained by the ellipsometric characterization.

Concerning the O 1s region, at least three different species should be considered in order to obtain a good fit of the experimental data: the first, O_{st}, intense, centered at around 530.6 eV, is ascribable to oxygen of the stoichiometric Ta_2O_5 [23]; the second one, O_{sc}, at higher binding energy (around 532 eV), is usually attributed to surface contaminations [24]; the third, O_w, centered at 533 eV is likely related to water contaminations [23]. However, a similar interpretation scheme does not take into account oxygen species of the sub-oxides. Moreover, the same species, with the same O_{st}/O_{sc} intensities ratio, can be observed in the data collected on ultra-pure Ta_2O_5 powder, a sample with an higher surface-to-volume ratio (panel (d) of figure 4). In addition, on sputtered samples the O_{sc} species is still present (although decreased in intensity), despite all the carbon contaminations were removed. Further investigations are needed to clearly identify this O_{sc} oxygen; nevertheless, the results of these first XPS measurements seem to indicate that both O_{st} and O_{sc} are bound to Ta atoms and they are peculiar of Ta_2O_5 material. If confirmed, the possibility of thermally activated transitions between these two different species could be considered as a candidate source of mechanical losses in this material.

4. Conclusions and Perspectives

In this paper, we have presented the first results of the characterization of Ta_2O_5/SiO_2 films through SE, XPS and AFM. We have implemented an experimental protocol capable to detect and characterize defects/non-idealities in these films; in order to confirm the results here reported, our protocol has to be tested on a statistically relevant number of samples. Our studies will be focused on understanding the origin of these defects and on finding their possible implication on the degradation of the quality factor of gravitational wave detectors mirrors.

Acknowledgments

This research has been supported by Istituto Nazionale di Fisica Nucleare - Italy, MIUR PRIN 2007T7AC3L and Fondazione Carige. MP acknowledges the experimental support of M. Neri and G. Pizzigoni in this first stage of the work.

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