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Preparation and characterization of osmium films on quartz substrate by magnetron sputtering method

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ABSTRACT

Micron-thick osmium films were deposited on quartz substrates with a pulsed −200 V bias using magnetron sputtering method. Application of ~100 nm Ti buffer layer resulted in successful deposition of as thick as ~3 μm Os films. Structure and morphology of the films were studied in terms of X-ray diffraction, scanning electron microscopy and atomic force microscopy, and their dependence on the duty-ratio was revealed. The mechanical properties of the films, namely, the Young's modulus and the hardness, were studied and discussed in comparison with the measurement of Os bulk sample. The Os film was found to be ~40% harder than the bulk sample due to the internal stress and the refined grains. The thickness-dependent resistivity was determined to be $\rho = 13.0 + 1.74/t$ (μΩcm), where t is the film thickness in micron.

1. Introduction

Osmium (Os) is a special noble metal in the applications of catalysis, fuel cells, electronics, and sensors [1,2]. Os has an as high as 3033 ± 30 °C melting point and a good electrical conductivity (8.1 μΩcm) [2]. At ambient temperature, Os is stable, but easily reacts with atomic oxygen (AO), forming OsO_4 *via* $Os + 4O \rightarrow OsO_4$ with a reactions rate of ~3×10^{-26} cm^3 per AO [3]. OsO_4 is volatile, thus Os films have been suggested as a candidate of materials for fabrication of sensors detecting AO in the environment of low earth orbit (LEO, 200–700 km) [3]. However, osmium and rhenium (Re) are the known densest natural elements, with a very low compressibility and a high bulk modulus comparable with that of diamond. Therefore, it is not easy to prepare micron thick Os film on an insulating substrate, such as quartz and ceramics, because the generated high internal stress would make Os films crack or peel during deposition, although the deposition technique and the deposition parameters play a very important role in controlling the residual stresses.

Due to the high melting point, atomic layer deposition (ALD) [1], chemical vapor deposition (CVD) [4–7], microwave-assisted chemical decomposition [8], sol–gel method [9,10], electrodeposition [11–12], and other chemical techniques have been used for deposition of Os films. These chemical methods are capable of preparing submicron Os films, but possess a common problem that the film purity is quite low. The remains such as C and O [4–12] are unfavorable for fabrication of AO sensors. Furthermore, these chemical technologies cannot be applied for deposition of Os films with a thickness meeting the requirements of AO detection in LEO environment. Physical vapor deposition technology, such as electron beam evaporation and magnetron sputtering, enables high-rate deposition of Os films [13], but cracking and peeling are the problems that have to be avoided in fabrication of AO detectors. Li *et al.* [14] had used magnetron sputtering to prepare Os–Ru films on W substrate under a DC negative bias. They found that the films poorly bonded with the substrate, even for the submicron thick films. Therefore, preparation of micron thick Os films with high quality is the key issue for the application of AO detection in LEO environment.

In this study, magnetron sputtering was used to deposit Os films on quartz substrates for the application of AO detection in LEO environment. To improve the film adhesion, a Ti buffer layer was grown on the substrate before deposition of Os films and a pulsed negative bias was applied during film deposition. Using X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM), we characterized the morphology and structure of the Os films deposited at different duty-ratios of pulsed negative bias. Using a nanoindenter, we studied the mechanical properties of Os films in comparison with Os bulk material. In addition, the dependence of the resistivity on the film thickness was determined.

2. Experimental methods

The deposition of Os films was carried out on a JGP-450 magnetron sputtering system, in which there are three sputtering guns in parallel arrangement for deposition of different materials. 1.5-mm thick fused quartz, which is polished on both sides, was cut into a size of

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30 mm × 20 mm for Os film deposition. The substrates were successively cleaned in acetone, ethanol, deionized water and finally dried through nitrogen stream, and then rapidly loaded into the vacuum chamber. The target for deposition of Os films was prepared by powder metallurgy protected in pure Ar ambient using 99.99% Os powder. The target purity for deposition of the Ti buffer layer is 99.99%. The Ti buffer layer and Os films were deposited at 550 °C using 99.999% Ar as the working gas under the pressures of 0.5 and 1.8 Pa, respectively. Before deposition, the base pressure was pumped to be better than 5×10^{-4} Pa using a turbo-molecular pump backed by rotary pump. Prior to the film deposition, the Ti and Os targets were pre-sputtered for 10 min to remove any surface contamination. Ti and Os targets were driven by an 80 W radio-frequency and a 120 W DC powers, respectively. The deposition time for the Ti buffer layer was 15 min, and the Os films with different thickness were deposited by controlling the deposition time. During the deposition of Ti buffer layers and Os films, a pulsed −200 V bias with a 35 kHz repeating frequency was applied to the sample holder. To study the role of the pulsed negative bias, the duty-ratio was set to 0%, 5%, 10%, 15% and 20%, respectively. After deposition, the samples were slowly cooled to 400 °C in a ~2 °C/min rate. After preservation for 1 h at 400 °C, the temperature was decreased below 100 °C in an average cooling rate of ~1.5 °C/min.

The Os films were analyzed by XRD on Bruker D8 DISCOVER using a Cu K_α radiation aligned by a göbel mirror, which provides a ~0.03° divergence for the X-ray beam. Coupled scan in ω–2θ mode is used for collection of XRD patterns with 0.02° intervals. MTS Nano-Indenter XP was used to characterize the hardness and elastic modulus of the films with different thickness. AFM (Benyuan CSPM5000) and SEM (Hitachi S-4800) were used to observe the surface and cross-sectional morphology of Os films. The film compositions were determined by X-ray energy dispersive (EDX) spectroscopy. The film thickness was basically determined by the weighting method and checked by the cross-sectional SEM observation. The measurement of Os film resistance was performed on a RTS-9 four-probe testing instrument and 12 points were measured for each sample, and then the deviation in the film resistivity was determined.

3. Results and discussion

3.1. Morphology and structure of the Os films

Fig. 1 shows the typical in-plane and cross-sectional SEM images of the Os film grown on the quartz substrate, which was deposited at a pulsed −200 V bias with a 15% duty-ratio. The Os film exhibits a smooth surface and a dense column structure with ~3.3 μm thickness. Between the Os film and the quartz substrate, there is a ~100 nm Ti buffer layer, with which the Os film is well adhered to the quartz substrate without cracking or peeling. EDX analysis showed that Os is the only element that could be detected above noise level, indicating the high purity of the Os films, as shown in the inset of Fig. 1(a). The above results revealed that high-quality micron-thick Os films have been successfully deposited on the quartz substrate using magnetron sputtering method under the pulsed negative bias.

To study the role of biasing pulses in the deposition of Os films, the duty-ratio of the pulsed negative bias was set to 0, 5, 10, 15, and 20%, respectively. Fig. 2 shows the AFM images, which are in accordance with the in-plane SEM observation, of Os films deposited at different duty-ratios. The Os films deposited at low duty-ratios of the pulsed negative bias exhibit island-like morphology. With the increase in the duty-ratio, the island-like morphology gradually disappers, indicating enhancement of ion bombardment producing the smooth surface. Fig. 2(f) depicts the dependence of the surface roughness on the duty-ratio of the pulsed negative bias. Of the films deposited at the duty-ratios below 5%, the surface roughness is ~3.7 nm. With increasing the duty-ratio from 10% to 20%, the surface roughness linearly decreases from ~1.5 nm to a value less than 1 nm, which can be ascribed to the smoothing effect of ion bombardment. Measurement showed that the deposition rate is not obviously changed when increasing the duty-ratio from 0% to 20%.

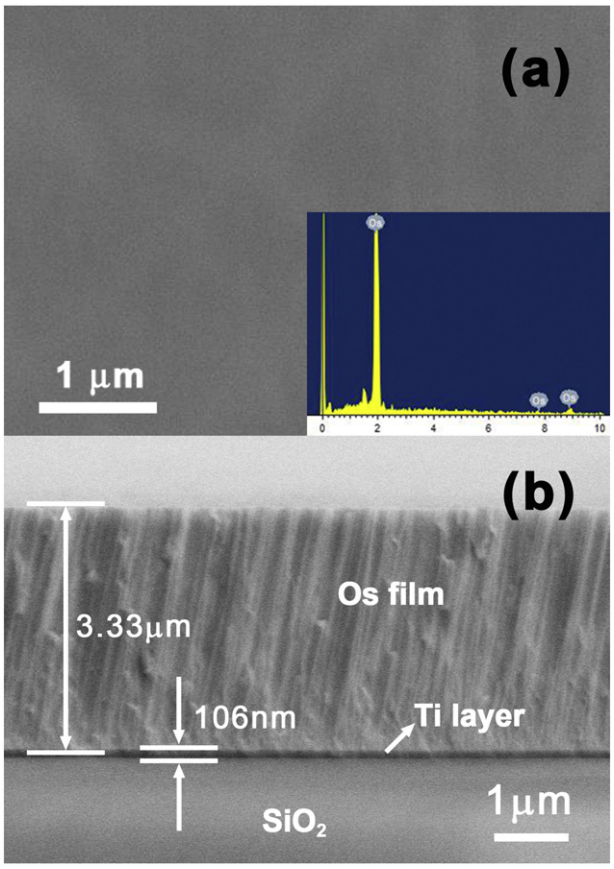

Fig. 1. Typical in-plane (a) and cross-sectional (b) SEM image of Os film on quartz substrate. The inset is the EDX spectrum of the Os film.

Fig. 3 shows the XRD patterns of Os films deposited at the given duty-ratios in the same deposition time. For comparison, a standard PDF card (87-0716 for a hexagonal phase with $P6_3/mmc$ space group) is also present. Compared to the standard intensities of Os powder, the Os films are textured mainly in the (001) or (100) direction. For the films deposited at the duty-ratios below 15%, the film growth prefers to the (001) direction. For the film deposited at the duty-ratio of 20%, the preferential orientation changes to be (100). Similar change in preferential orientation was also observed by Li *et al.* [14] in the deposition of Os–Ru films when increasing bias power, being consistent with our conclusions. The dependence of preferential orientation on ion bombardment is a complicated problem related to the nucleation thermodynamics. In short, ion bombardment usually promotes formation of nuclei due to creation of defects, and then increasing the density of critical nuclei, but reducing their sizes. The change in grain size affects the stability of the critical nuclei, which is related to the surface free energy of grains and dominates the preferential orientation of grains. We must emphasize here that the critical size of grains in the nucleation stage differs from the grain size in the film because of the coalescence between grains during growth. In general, the grain size increases with the increase in film thickness when the film thickness is lower than a certain value.

The grain sizes in the films deposited at different duty-ratios were estimated by Scherrer method using the full width at half maximum (FWHM) of the diffraction peaks. We found that the duty-ratio has no significant effect on the grain size, except for the (100) textured film deposited at 20% duty-ratio, as shown in Fig. 4. The grain sizes in the (001) textured films deposited at different duty-ratios are approximately