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Methane plasma-based ion implantation of metallic and galvanically oxidized tantalum

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ABSTRACT

Tantalum and oxidized tantalum exhibit distinct differences when treated with plasma-based ion implantation of methane with −20 kV. The implantation profiles of carbon are similar, but carbides are formed in the case of tantalum, as verified with X-ray diffraction and X-ray photoelectron spectrometry in combination with depth profiling, whereas there is no detectable carbide in the tantalum oxide film. The distributions of the co-implanted hydrogen also vary in that the intensity in depth profiling with secondary ion mass spectrometry does steadily decrease in the oxidized Ta, while in the metallic Ta it shows a short indentation below the surface and then decreases only very slowly.

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1. Introduction

While tantalum exhibits some superior properties like biocompatibility and good corrosion resistance it shows a poor tribological performance. This can be improved by implantation [1] or deposition of a diamond-like carbon (DLC) layer. Plasma-based ion implantation (PBII) with hydrocarbon gases is a suitable method for implanting carbon into materials and thus forming a gradient transition layer towards the surface. This is one method (apart from metallic interlayers [2] or mechanical surface treatments like peening [3]) to increase the adhesion between the substrate and a diamond-like carbon (DLC) film on top; well-adhering DLC-films improve the tribological properties [4]. Adhesion is almost always problematic with non-carbide formers, e.g. Cu [5], oxides [6,7] and non-conducting samples like polymers [8]. The limited conductivity sometimes also poses a problem for implantation due to charging or reduction of the applied potential.

Only few experiments by PBII are concerned with oxides; on the basis of our earlier work on metals, including some typical carbide formers (Ti and Ta [9]), the investigations were extended to oxides, namely Ta_2O_5. Fabrication of Ta_2O_5 is possible by several methods [10], including anodic oxidation of Ta [11] which was chosen here. Generally, tantalum pentoxide combines a high dielectric constant with excellent chemical stability, interesting optical properties and biocompatibility [12].

2. Experimental

Both metallic and oxidized rolled tantalum foils were used as substrates. For the latter, tantalum samples were electrochemically anodized, thus forming an amorphous film of Ta_2O_5 with a thickness of about 250 nm. Both types of samples were subjected to plasma-based ion implantation in a methane plasma (pressure 1 Pa) at a voltage of −20 kV at process times of 2 h and a pulse duration of 10 µs with a repetition rate of 1 kHz. The particular feature of this experiment was that no external plasma excitation source, such as DC or RF, was applied, the plasma was ignited by the high voltage pulse itself; the apparatus used was described in detail elsewhere [9].

The samples were analyzed for phase composition by glancing angle X-ray diffraction (GXRD) with Cu Kα excitation at an angle of 0.5°. The chemical composition and chemical state of the samples was evaluated using X-ray photoelectron spectrometry (XPS) under Mg Kα X-ray irradiation combined with 2 keV argon ion sputter etching. Additional depth profiles were recorded by secondary ion mass spectrometry (SIMS). The SIMS measurements were performed with 8 keV oxygen primary ions, detecting positively charged secondary ions out of the inner 60 µm (diameter) of a $175 \times 175\ \mu m^2$ crater; the ion current was 15 nA. The end crater depths and thus the time/depth conversion factors were measured by profilometry (Dektak D8000). The pressure inside the sample chamber during the SIMS measurements was 3×10^{-8} Pa.

Further structure information of the samples was obtained by Raman spectrometry with an excitation wavelength of 633 nm (HeNe laser).

3. Results and discussion

Glancing incidence X-ray diffraction showed some Ta reflexes and one small broad reflex of the carbide phase indicating that the implanted

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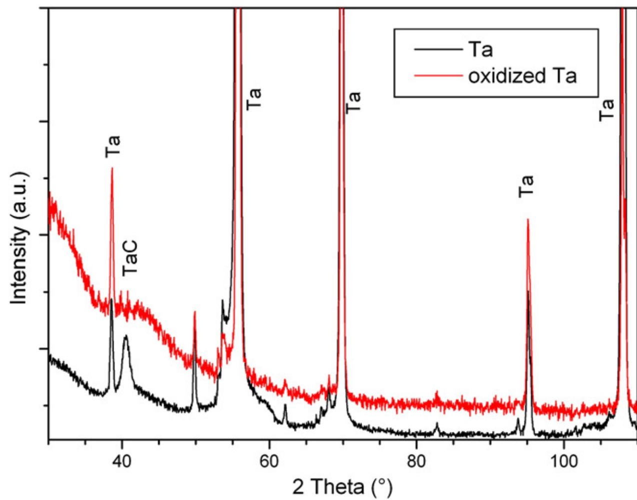

Fig. 1. X-ray diffractograms of Ta and oxidized Ta, treated by methane PBII.

carbon reacted with tantalum to carbide grains of small size, Fig. 1. With the oxidized sample there is no reflex at this position; the oxide does not give any additional reflexes because of its amorphous structure. Because of the small film thickness the reflexes of Ta from the underlying substrate also appear.

This is corroborated by the XPS results, with the signals of C1s, O1s and Ta4f shown in Figs. 2 and 3. There is some oxygen at the surface of the Ta sample and also some carbon that can be assigned to C–C bonds, which then shifts to Ta–C bonds (281.9 eV) below the surface and is recognizable up to about 11 min sputtering time. The Ta4f signal (with its two components $4f_{7/2}$ and $4f_{5/2}$) starts from the Ta_2O_5 position at the oxidized surface (26.5 eV for $4f_{7/2}$); from the Ta–C bonds at 23.0 eV the signal shifts to Ta (21.6 eV) within the first ten minutes of sputtering. The oxidized Ta exhibits a peak in the O1s spectrum assignable to Ta_2O_5 at all times as the oxide was not completely removed within the 30 min of Ar sputtering. The C1s starts in the same way as with the Ta sample, i.e. with C–C bonds at the surface, but then there is no immediate shift to a strong Ta–C bond. The Ta4f spectrum shows the initial Ta_2O_5 but then an additional signal that can be attributed to a lower oxidation state [13]. This, however, might be due to the sputtering process that removes the oxygen preferentially.

As Ta is an avid carbide former, the implanted carbon is used accordingly within the pure Ta; within the oxide though the implanted carbon does not have any opportunity to form bonds with the Ta as Ta–O bonds are favoured energetically. According to concentration values gained from the XPS measurements the maximum value for carbon is about 40 at.% near the surfaces of both samples (the concentrations do not account for the hydrogen).

The presence of amorphous carbon on top of the samples is also confirmed by Raman measurements, Fig. 4; for both samples they exhibit asymmetric slopes between 1000 and 1800 cm^{-1}, characteristic for amorphous carbon, consisting of two Gaussian distributions corresponding to the D-band (1350 cm^{-1}) and G-band (1530 cm^{-1}).

In the SIMS depth profiles, Figs. 5 and 6, the matrix signals (^{180}Ta, ^{181}Ta, ^{16}O, ^{18}O) as well as the implantation elements are recorded (as single atoms, ^{1}H, ^{12}C, and as molecule $^{12}C^{1}H$). It has to be noted that there is also a contribution of the primary ions to the ^{16}O-signal. At the beginning of the depth profiles it takes some fifty nm until the matrix signals are stable, due to the implantation of the primary ions in the SIMS measurement but also because of the changing C and H levels in the surface. The carbon signal in the metallic tantalum sample decreases almost exponentially after an initially high signal and a small local maximum at 200 s. In the oxide sample there is first a slight slope followed by a steeper one. In the Ta_2O_5 sample it takes nearly 60 nm to decrease to 10% of the C peak value and 100 nm to reach the background level of C, while in Ta it takes 40 and 100 nm, respectively. The expected ion range obtained from TRIM simulations [14] of 15 keV carbon ions into Ta_2O_5 is nearly two times the value as the one for Ta (431 Å and 222 Å, respectively). The reason that this is not strictly observed is twofold: on the one hand the sputtering yield has to be considered; the surface is simultaneously sputtered by the impinging plasma particles. TRIM simulations yield with 1.36 a nearly twice as large value for Ta_2O_5 as for Ta (0.71). Differences in sputtering yield, e.g. due to crystal orientations, can produce significant variations in depth distribution of implanted carbon [15,16]. The observed difference in sputtering yields during the SIMS measurements is not that high, because the surface to be sputtered also contains oxygen due to the primary ions. On the other

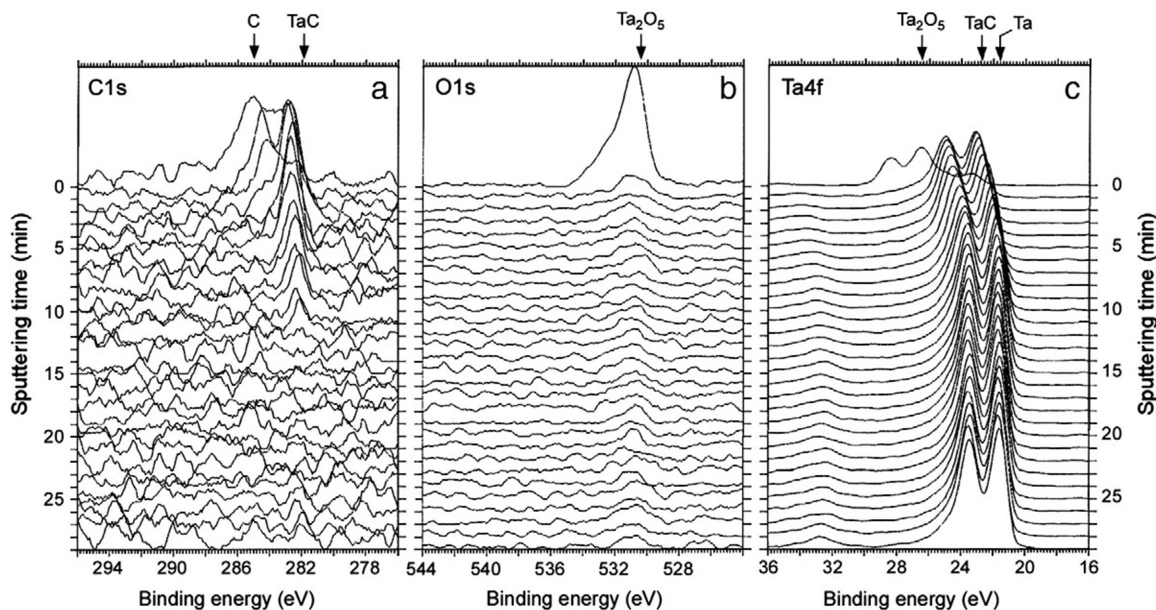

Fig. 2. XPS spectra of Ta, treated by methane PBII, at different sputter etching times a) C1s b) O1s c) Ta4f.

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