Mechanisms of nitrogen incorporation into Ta-N films deposited by direct current and high-power impulse magnetron sputtering

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Abstract: The mechanisms of nitrogen incorporation into sputter-deposited thin films to form tailored nitrides are discussed. Two reactive species, N2+ and N are identified to be relevant for tantalum nitride film growth which opens up interesting possibilities with respect to steering the flux and energy of reactive species onto the film by applying a substrate bias. The results are interpreted with regard to principal differences and similarities of reactive direct current and high-power impulse magnetron sputtering.

Keywords: reactive magnetron sputtering, TaN, Ta3N5, HiPIMS, DCMS

1. Introduction

The Ta-N binary system has a remarkably rich phase diagram ranging from the solid solution Ta(N) to the highly nitrided Ta3N5 phase [Oka08][Li14]. Applications are equally wide-spread and some typical examples are TaN mechanical coatings [Sah97] or diffusion barriers for microelectronics [Let01]. Lately, Ta3N5 has attracted interest for the bias-free photoelectrolysis of water [Ish04] in view of the energy transition towards renewable sources. For this last application, the semiconducting phase of the Ta-N system is well suited due its conduction and valence band edge positions with respect to the oxidation and reduction potential of the H2/H2O and the O2/H2O electrochemical couples.

The Ta/N2 system is not only interesting from an application point of view but also provides an interesting test system for reactive sputter deposition due to its δ-TaN phase that is stable even for large non-stoichiometric compositions.

Past studies on reactive sputtering focused mainly on the fate of the target surface and its poisoning that is interesting from a process point of view due to its strong correlation with the deposition rate. So far, little work concerned the interaction between the plasma and the film in the reactive mode. The metallic mode, on the other hand, has been comprehensively investigated in terms of morphological, structural and macroscopic characteristics such as density and surface roughness [Pet03] and the dependence of each parameter on the plasma state.

The transfer of knowledge to reactive sputtering is not readily possible as the incorporation of non-target species into a film follows a completely different physics: 1) The precursor is typically a diatomic gas that is inert in its standard state and needs to undergo physical transformations to be able to be chemically react with the growing film. 2) The reactive species do not have the same kinetic distribution as the target species which gain their initial energy upon sputtering from the target. The typical gas temperature in a sputtering reactor does not exceed room temperature by much so that for the reactive species any acceleration potential is the dominant mechanism to gain energy. 3) The incorporation of reactive species in the film can follow more than one pathway.

The aim of this work is to elucidate the pathways from gaseous N2 to nitrogen incorporated into a Ta-N film using optical emission spectroscopy (OES), Rutherford backscattering spectrometry (RBS) and nuclear reaction analysis (NRA). The results are discussed in the light of nitrogen incorporation mechanisms proposed in literature, their individual contribution to film growth and different sputtering modes such as direct current (DC) and high-power impulse magnetron sputtering (HiPIMS).

2. Mechanisms of nitrogen incorporation

The dinitrogen molecule N2 is chemically inert with a strong triple bond of 9.75 eV [Iti06]. As it is also electrically neutral, it cannot gain energy from electric fields to supply the energy in a bond-breaking collision. It must therefore rely on energetic collision partners to undergo physical transformations before reacting with the growing film. In the frame of this study, direct mechanisms to produce the most abundant nitrogen species from electron impact collisions are considered. The exclusive consideration of electron collisions is justified by the low reactor pressure of 0.5 Pa which is typical for sputter deposition. Time-integrated optical emission spectroscopy (described below) evidences the presence of N2+ and N. Mass-spectrometric studies on reactive sputtering of titanium in an Ar/N2 atmosphere also revealed the presence of N+ [Pet94] in comparable conditions concerning reactor pressure (0.4 Pa instead of 0.5 Pa in this study) and the discharge power (between 66 W and 96 W compared to 80 W in this study). It was concluded, however, that its contribution to film growth is inferior to its neutral counterpart atomic nitrogen. The same applies to the exotic molecule TiN and its ion TiN+.

The presence of tantalum nitride molecules cannot be
verified by optical emission spectroscopy as optical transitions are unknown. Two pathways for nitrogen incorporation into the growing film are thus remaining:

1. The reaction of neutral N with Ta dangling bonds on the film surface.

2. Attraction of molecular nitrogen ions $N_2^+$ by a substrate bias either by a plasma-induced self-bias or an intentionally applied radio-frequency bias. The charged molecules can gain an energy equal to the sum of the plasma potential and the substrate bias before being neutralized right by charge exchange right in front of the film. If its kinetic energy exceeds the dissociation energy of $N_2$, dissociation takes place and two nitrogen atoms are incorporated in the film [Lan79].

The difference in net charge of the two species identified as being dominantly contributing to film growth has major implications for reactive sputtering. As the gas temperature typically does not exceed room temperature by much, the N radicals for mechanism (1) lack the energy to penetrate deeply into the growing film but can only react on surface sites. A high substrate bias on the other hand supplies the ionized molecule for mechanism (2) with energy that can easily reach several 100 eV which is sufficient to implant the nitrogen below the surface.

3. Experimental procedure

Thin films are deposited by direct current and high-power impulse magnetron sputtering using a reactor with a given procedure described elsewhere [Rud15] (Fig. 1) and using an average power of 80W. The $N_2$ concentration in the Ar/$N_2$ gas mixture $c_{N_2}$ injected into the reactor was varied between 2 and 30% and the total reactor pressure was kept constant at 0.5 Pa. During deposition the substrate holder rotated about the reactor axis at a velocity of 20°/s in order to achieve a homogeneous film.

The film composition was analyzed using Rutherford backscattering spectrometry (RBS) for sampling Ta by $^{73}$Ta(α,α)$^{73}$Ta at 1800 keV and Nuclear reaction analysis (NRA) for sampling N by $^4$N(d,α)$^7$C at 1450 keV. Oxygen was sampled as well but found to be negligible.

Time-integrated optical emission spectroscopy (OES) on the magnetized region of the plasma is conducted to determine abundant species in the plasma. An 0.5 m focal length Acton Research spectrometer is used with an intensified CCD camera cooled down to -70° C. The collimator has a diameter of 0.5 cm and is oriented perpendicularly to the target surface normal.

Optical ultraviolet/visible (UV/VIS) transmission/reflectance spectra were taken using an integrating sphere for both transmission and reflectance measurements. The wavelength is scanned by a monochromator with a 2 nm slit width between 300 and 1000 nm. The absorption coefficient $\alpha$ is then calculated using the following expression with the sample thickness $t_s$, the sample transmission and reflectance $T_s$ and $R_s$ and the transmission of the substrate $T_{sub}$:

$$\alpha = \frac{1}{t_s} \ln \left( \frac{T_s}{T_{sub}} \right) \left( 1 - R_s \right)$$

Eq. (1)

![Fig. 2. Setup of collimator and sputtering target for the time-integrated optical emission spectroscopy (OES). The distances x and d were kept constant for this study at 20 mm and 160 mm respectively.](image2)

Fig. 3. Direct electron impact cross sections for the total dissociation of $N_2$ and the production of $N_2^+$ and $N^+$ [Iti06].
4. Optical emission spectroscopy

As stated above, the time-integrated optical emission spectroscopy revealed the presence of N and N$_2^+$ in the both the DC and HiPIMS discharge. The reason for the absent emission signals from N$^+$ lies in the small cross section for dissociative ionization with a maximum at a high energy of 120 eV for the direct production from N$_2$ (Fig. 3). Compared to that, the production of both, N$_2^+$ and N by electron impact with N$_2$ are more favorable with larger cross sections by an order of magnitude and maxima at smaller energies of 50 and 100 eV respectively [Ito06]. As a result, the direct production of N$_2^+$ and N is dominant while N$^+$ is negligible with respect to film growth.

5. First results from thin film characteristics

Rutherford backscattering spectrometry (RBS) and nuclear reaction analysis (NRA) reveal the N/Ta atomic fraction in the films as a function of cN$_2$ (Fig. 4). Both, the direct current and high-power impulse magnetron sputtering exhibit a transition region with a steadily increasing nitrogen molar fraction in the film with increasing cN$_2$. At a certain cN$_2$ value, films from each of the two sputter modes saturate in nitrogen from which point on, the fraction remains constant. For both modes, the saturation point may occur at different cN$_2$ but coincides earliest for values of cN$_2$ $\geq$ 20 %.

In the transition region, the HiPIMS mode shows its superior performance in incorporating nitrogen into the films compared to the DC mode. This can be explained by the high energy tail of the electron distribution function during the pulse as well as a higher electron density in the magnetized region in front of the target. Both effects are characteristic for the HiPIMS mode [Ehi01].

The nitrogen incorporated into the films shows up directly in the optical absorption spectrum as shown for the HiPIMS films in Fig. 5. While the films up to a concentration of cN$_2$ of 10% do not show an absorption edge within the spectrum investigated, the films deposited with a cN$_2$ of 12% clearly show a transmission window indicating the presence of a band gap. The absorption edge shifts towards the blue spectrum with increasing nitrogen incorporation before saturating for the films deposited at a cN$_2$ of 20% and 30%. The saturated films exhibit an E$^{04}$ band gap of approximately 2 eV, corresponding to that of ideal crystalline Ta$_3$N$_5$. Grazing incidence x-ray diffraction (not shown) does not show at a crystalline Ta3N5 phase, though.

Fig. 4 and 5 show a correlation between the nitrogen incorporated in the film derived from RBS/NRA measurements and the spectral characteristic. Hence, as a side effect, of the transmission/reflectance measurements, they give a good indication for the nitrogen molar fraction in the film and can thus be used as a simple screening tool.

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Fig. 4. Nitrogen molar fraction incorporated in the films deposited by DC magnetron sputtering and HiPIMS. A border between the transition region and the saturation region is schematically indicated where both sputter modes enter saturation.

Fig. 5. Absorption coefficient derived from UV/VIS transmission/reflectance measurements according to equation (1). The films exhibit a blue shift of the absorption edge with increasing nitrogen molar fraction in the film.

6. Preliminary conclusion and outlook

The discussion shows that the incorporation of N$_2^+$ and N are the principle species for nitrogen incorporation during sputter deposition. The amount of nitrogen incorporated into films of Ta-N can be easily monitored by transmission/reflectance measurements, thus avoiding costly techniques such as RBS/NRA.

Experiments are currently under way to investigate the influence of the substrate bias, which may be used to influence the flux of N$_2^+$ while leaving the flux of N unchanged. This will give interesting insights into the dominance between N$_2^+$ and N under varying process
conditions such as the peak current density in the high-
power impulse magnetron sputtering mode.

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