

Time-resolved optical emission spectroscopy of HiPIMS discharge during formation of thin TiO_xN_y films

Vitezslav Stranak, Rainer Hippler (November 2009)

Application Note

Introduction

Titanium oxide is well known as photocatalytic material since seventies years of last century. Photocatalytic activity altogether with other interesting features makes TiO₂ as promising coating material. The photocatalytic activity of TiO₂ can be improved by N doping. The thin TiO_xN_y films can be prepared by High Power Impulse Magnetron Sputtering (HiPIMS) of Ti target in atmosphere of working gases Ar, O₂ and N₂. The characteristic feature of HiPIMS is operation of magnetron in pulse mode with low repetition frequency ($f \sim 100$ Hz) and very short pulse width ($t_p/T \sim 10\text{-}200$ μs), i.e. operation with duty cycles $\leq 1\%$. Due to low duty cycle high power density is accumulated into the active part of the pulse. Hence, HiPIMS is suitable method for deposition of oxides in particular crystallographic phases with unique technological properties. However, time-resolved diagnostic has to be employed in such a case.

Experimental and diagnostic arrangement

Thin TiO_xN_y films were prepared by pulsed planar magnetron sputtering operated in HiPIMS conditions. The planar magnetron of type Vtech 75 by Gencoa (Gencoa, Liverpool, UK), equipped by Ti target, is employed as a sputtering source. The sputtering source is situated in a stainless-steel UHV chamber pumped out by a turbomolecular pump. Working pressure is adjusted by a throttle valve installed between the chamber and the pump. The flow rates of working gases are controlled by MKS flow controllers. Discharge was excited using a combination of dc power supply AE MDX500 (Advanced Energy, Fort Collins, USA) designated for continuous regime and a home-built power switch based on charging of large capacitors during idle part of the pulses.

Pulse-modulated discharge was investigated by means of optical emission spectroscopy. The measurements were performed by Shamrock SR-500-B1 spectrometer equipped with iStar ICCD detector iStar DH740i-18U-03 (both by Andor Technology, Belfast, Northern Ireland). The spectrometer was equipped with three gratings 300, 1200 and 2400 lines per millimetre. The optical fibre, connected with the spectrometer, was built directly in vacuum chamber. The range of scanned spectra were $\lambda = 200$ nm – 850 nm. The pulse generator Agilent 33120A provided triggering signal for ICCD detector as well as for controlling high power switch. The spectrograph and was controlled by Andor Solis software.

Time-resolved optical emission spectroscopy

The overview spectra of Ar/N₂+O₂ discharge, shown in Fig.1, consists of the atomic lines of Ar, Ar+, Ti, Ti+, O, molecular bands of NO γ system ($A^2\Sigma^+ \rightarrow X^2\Pi$), N₂ first and second positive systems ($B^3\Pi_g \rightarrow A^3\Sigma^+_u$, $C^3\Pi_u \rightarrow B^3\Pi_g$).

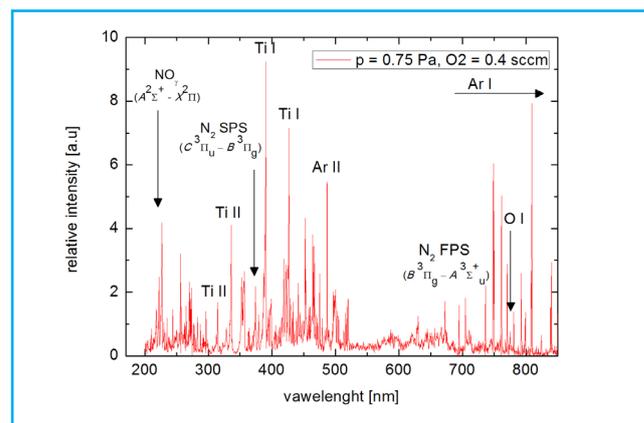
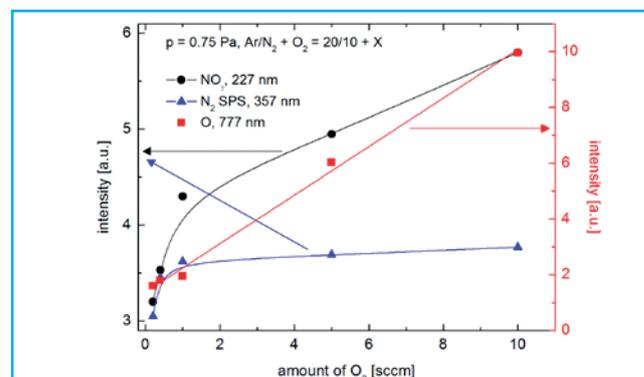


Fig.1. Overview of spectra measured in Ar discharge with O₂ and N₂ reactive admixtures. Experimental conditions: $p = 0.75$ Pa, $F_{Ar} = 20$ sccm, $F_{N_2} = 10$ sccm and $F_{O_2} = 0.4$ sccm. The spectra was recorded at $t_c = 50$ μs after discharge ignition.

The spectra and intensities of particular spectral lines are affected by the amount of reactive component O₂ added into the discharge. As expected the intensity of atomic oxygen line ($\lambda_{O} = 777$ nm) depends nearly linearly on the amount of added O₂ see Fig.2. Further we note that whereas the intensity of N₂ positive system ($\lambda_{N_2,SPS} = 357$ nm) is for higher O₂ component ($F_{O_2} < 0.5$ sccm) almost constant, the intensity of system NO γ ($\lambda_{NO\gamma} = 227$ nm) increases.

Fig.2. Plot of intensities of atomic line O and molecular bands of systems N₂



2nd positive and NO γ vs. amount of O₂ added in the discharge. Experimental conditions: $p = 0.75$ Pa, $F_{Ar} = 20$ sccm, $F_{N_2} = 10$ sccm and $F_{O_2} = 0.4$ sccm. The spectra were recorded at $t_c = 50$ μs after discharge ignition.

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The normalized intensities of atomic Ar⁺, (λ_{Ar+} = 487 nm), Ti (λ_{Ti} = 390 nm) and Ti⁺

(λ_{Ti+} = 335 nm) lines are presented in Fig.3, altogether with evolution of discharge current. The Ar⁺ starts to develop as first with comparison of Ti or Ti⁺ lines, respectively. Presence of Ar⁺ ions is necessary for initiation of target sputtering and discharge operation. Hence, time evolution of Ar⁺ line intensity qualitatively corresponds with trend of peak discharge current. Maxima value of Ar⁺ intensity is reached at t_o ~70 μs. After reaching its maxima the intensity linearly decreases up to the end of pulse width, i.e. t_o = 150 μs.

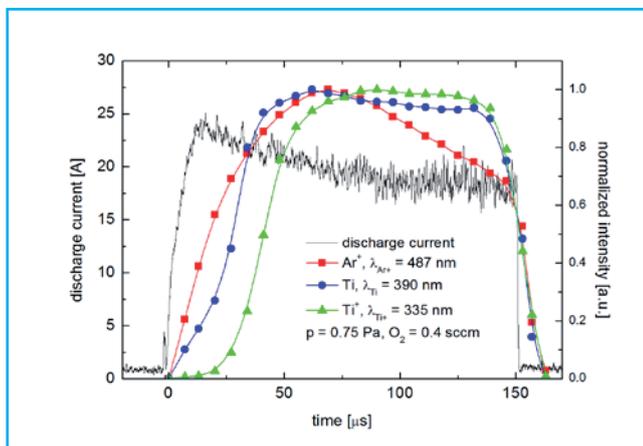


Fig.3. Time evolution of peak discharge current I_D (black line, left axis) and intensities of atomic spectral lines of Ar⁺ (λ_{Ar+} = 487 nm), Ti (λ_{Ti} = 390 nm) and Ti⁺ (λ_{Ti+} = 335 nm) during the pulse width (right axis). Experimental conditions: p = 0.75 Pa, F_{Ar} = 20 sccm, F_{N₂} = 10 sccm and F_{O₂} = 0.4 sccm.

When Ar⁺ ions are produced Ti atoms are subsequently sputtered as a result of ion bombarding of the cathode/target. It can be estimated from Fig.3 that normalized intensity of Ti line is delayed about 5-10 μs behind Ar⁺ at the beginning of the pulse width. Atomic Ti line reaches maxima at the same time as Ar⁺ and remains nearly constant. The ratio of measured relative intensities $I_{Ar+}/I_{Ti} \sim 0.6$ is more or less constant in the first half of the pulse width. This effect probably corresponds with re-sputtering of TiN film from target surface poisoned by nitrogen. After removing of nitride film from the target surface the ratio of intensities decreases due to higher sputtering yield from pure metallic target surface. However, the intensity of Ti line rapidly decreases (i.e. $I_{Ar+}/I_{Ti} > 1$) if higher amount of O₂ is added into the discharge due to lower sputtering yield of oxide films ($Y_{TiO} = 0.015$ for Ar⁺ ion energy of 300 eV).

The time development of the intensity of Ti⁺ line (λ_{Ti+} = 335 nm) is depicted in Fig.3, too. The Ti⁺ time evolution is delayed about 25 μs behind Ar⁺ and about 15 μs behind Ti line, respectively. The Ti⁺ line reaches intensity maxima at t_o ~75 μs. The positive Ti⁺ ions are created by ionization of sputtered Ti atoms in plasma volume. Due to lower ionization potential (E_{Ti} = 6.82 eV) Ti atoms are preferentially ionized if compared with Ar (E_{Ar} = 15.78 eV). The preferential ionization of titanium can explain the intensity decrease of Ar⁺ line while intensities of Ti and Ti⁺ remain constant.

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