Acta Agrophysica, 2002, 80, 17-24

SPECTROSCOPIC STUDY OF REACTIVE SPUTTERING OF TITANIUM IN THE LINEAR MAGNETRON

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A b s t r a c t. This paper presents the results of investigations, performed by means of optical emission spectroscopy, for the linear magnetron discharge with titanium target in various argon-nitrogen mixtures. Emission intensities of titanium lines, Ti I, as well as Ar I, Ar II, N_2, N_2^+ and TiN spectra versus nitrogen contents in the gas mixture have been examined. The N_2 concentration was varied from zero to about 40% in the mixture. The effect of target poisoning was clearly revealed in the emission spectra. At constant discharge current equal to 0,3 A and the total pressure about 3 Pa the critical gas flow for the transition from the metallic to the reactive modes has corresponded to about 3% N_2 in Ar/N_2 mixture.

K e y w o r d s: linear magnetron, emission spectroscopy, TiN, sputtering poisoning.

INTRODUCTION

Many problems important for technological applications of gas discharges have been resolved by investigation of plasma emission spectra. For magnetron sputtering deposition of compound films like TiN, the reproducible conditions at the target are of the highest importance. Spectroscopic study of the plasma formed near the target surface is suitable for gaining information on mechanisms of reactive sputtering and the coverage of the target surface with reaction products (target poisoning). Intensities of spectral lines of the target material may further be used for a control and adjustment of the reactive gas flow, to monitor coating properties or for end point monitoring in target presputtering [1].

Most widely used in technology are planar magnetrons and a great number of papers deal with this subject. The present work has been undertaken to study a specific magnetron device equipped with a rod-shaped cathode. This type of cathode was proposed by Miernik [2]. In the linear magnetron an interval of a straight line is the drift path of secondary electrons, that makes this source distinct from standard planar magnetrons. A great advantage of the linear magnetron is a

simple construction, small transversal size of the cathode and possibilities of changes of the track length which enable its application for special purposes.

The attention of the present work is focused on study titanium cathode poisoning by nitrogen in a mixture with argon and it extends the previous study on TiN films deposition using the linear magnetron system [3,4].

EXPERIMENTAL

The experimental device was about 70-l sputtering chamber, equipped with the cathode, throttle valves and fourteen quartz windows (9 cm diameter) located along with the cathode. The cathode was 40 cm in length and 2 cm in diameter. Figure 1. shows a schematic diagram of the magnetron cathode. A d.c. power supply was used to bias the cathode. In each experiment, the current was maintained at a constant value of 0.3 A. Discharge atmosphere was a mixture of argon and nitrogen. The contribution of N_2 was varied from 0 to 40%. The argon pressure was constant and equal to 2 Pa. Argon and nitrogen flows were adjusted using ERG controllers. A voltage of the discharge was 600 V for pure argon and decreased with addition of nitrogen.

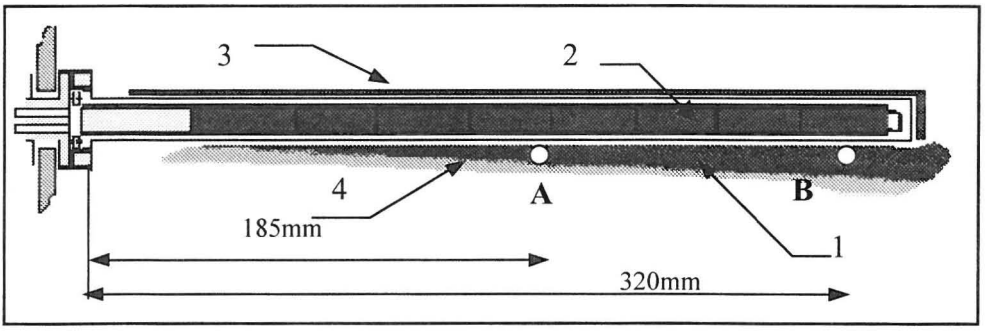

Fig. 1. The cathode of the linear magnetron and positions of OES measurement. (1) plasma zone; (2) magnetic system; (3) shield; (4) cathode (target); (A), (B) optical viewports.

Optical measurements were performed for the space located at positions about 185 mm (position A) and 320 mm (position B) from the beginning of the cathode (see Fig. 1). The light emitted in the vicinity of the target surface was focused by the optical lens and directed to the entrance of a monochromator Jobin-Yvon Triax 320, equipped with a 1200-groove/mm grating. The optical signal was measured using a photomultiplier tube (Hamamatsu R 636). The monochromator was driven by PC software (Jobin Yvon Spectramax ^{TM}).

RESULTS AND DISCUSSION

At conditions of clean cathode and the pure argon atmosphere, the emission spectra of the magnetron discharge composed of lines of Ti I, Ar I, Ar II and H. In the $Ar+N_2$ reactive atmosphere, numerous strong bands of N_2 (the $C^3\Pi$ - $B^3\Pi$ system) and N_2^+ (the $B^2\Sigma^+$ - $X^2\Sigma^+$ system) appeared additionally as well as weak bandheads of TiN lying at 613.9 and 619.9 nm (the $A^2\Pi$ - $X^2\Sigma^+$ system). No N I, N II or Ti II lines were found in the spectra.

Figure 2. shows the variations of Ti I and TiN intensities with increasing and decreasing the N_2 amount, (x_{N2}), in the N_2+Ar mixture. As x_{N2} increased up to about 4 % the Ti I and TiN intensities were changed in the opposite manner. The Ti I intensity decreased while TiN increased suddenly between x_{N2} from 2 and 4%. For x_{N2} higher than 4% the intensities of both Ti I and TiN decreased continuously.

Emission intensity of the X species in the plasma is not directly proportional to the total X concentration. However for Ti and TiN one can assume excitation due to inelastic electron collisions and deexcitation by radiative processes and thus the emission intensity at any location (z) in the discharge, originating from electronic transition is given by

$$I_X(z) = k\, N_X(z)\, n_e\, C_{exc}(X, U, s) \qquad (1)$$

where: $N_X(x)$ - the total X concentration, n_e – electron density, C_{exc} – electron excitation rate of the X species, which depends on the excitation cross-section (U) and on the electron energy distribution (s); k- geometry constant.

Excepting k, all the factors depend on discharge conditions such as current, pressure and gas composition. If argon pressure and the discharge current are kept constant, as in the case of that studies, optical emission intensity becomes directly proportional to the concentration of X species as long as amount of added reactive gas (N_2) is not considerable, because C_{exc} can be treated as constant. The behaviour of the Ti I and TiN intensities may thus be linked to target nitriding and explained as it has previously been reported for a planar magnetrons [e.g., 5-7]. The lowering emission intensity of Ti I indicates a decrease in the target sputtering efficiency due to the chemisorption and physisorption of nitrogen on the target and to the target bombardment by nitrogen ions (poisoning). According to [6] dissociative chemisorption of N_2 as well as surface reactions of nitrogen ions or excited nitrogen falling on the target give titanium nitride layers. The first stage of nitriding ($x_{N2} < 2\%$) concerns only the top layer of the target and only a small loss in sputtering efficiency is observed. Almost all the reactive gas is gettered on the sputtered titanium.

The magnetron works in so called metallic mode. This situation prevails until x_{N2} reaches a value above 2% where the condensation areas of titanium are no longer sufficient for continuous getter nitrogen. Then, nitrogen is consumed by the target as it is described above. The magnetron starts to work in reactive mode. The sputter rate of Ti from TiN is lower than that from a pure titanium target. This fact

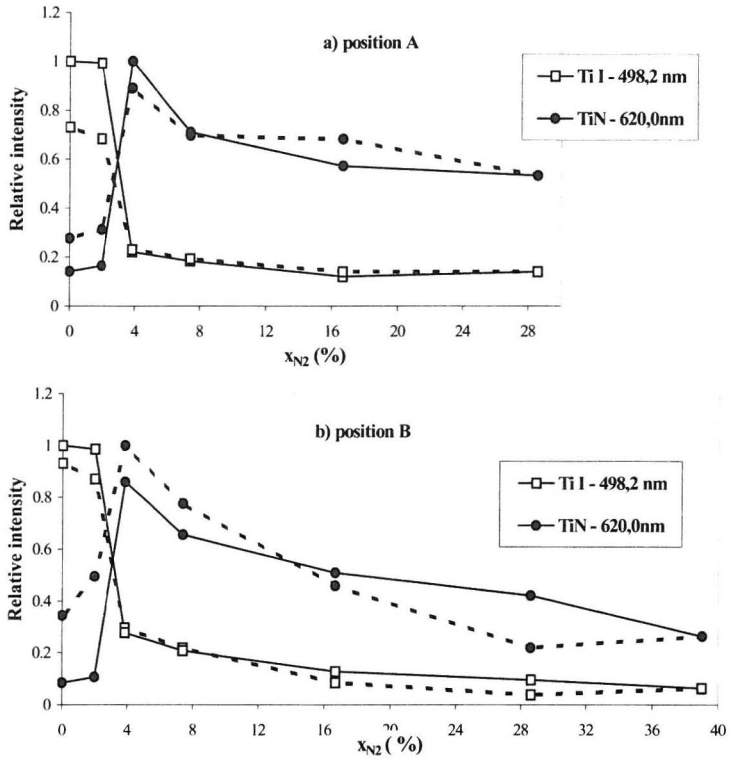

Fig. 2. Variations of Ti I and TiN intensities in position A (a) and B (b) with increasing (solid line) and decreasing (dotted line) nitrogen content in the $Ar+N_2$ mixture. Intensities are normalized to 1 at the maximum value.

was responsible for a rapid decrease of the titanium emission line intensity which was simultaneously observed with equally rapid increase of the TiN intensity (Fig. 2.). According to [6] the TiN emission originating from the TiN molecules formed on the target. Most of them is sputtered as nitrogen and titanium atoms, but a part is appeared in the gas phase as the TiN molecules. As it was mentioned earlier the TiN spectrum was weak in comparison with Ti I intensities, nevertheless

the observed changes in intensity were evident and well corresponded to changes in target sputtering efficiency. For x_{N2} higher than 4% the Ti I and TiN intensities decreased due to the fact that on the one hand the target tends to be completely nitrided and on the other hand the discharge atmosphere is getting more and more rich in nitrogen which has lower sputtering yield than argon. Expected changes of the electron excitation rate (C_{exc}) and electron density with N_2 content in the mixture can also be responsible, to a some extent, for a decrease in emission intensity of Ti and TiN spectrum.

When x_{N2} was reduced (Fig. 2. dotted line) the reverse transition from a covered target (reactive mode) to a metallic target surface was not achieved, but very clear growth in the intensity of Ti I and decrease in the TiN intensity at the same critical value of x_{N2} ~ 4% was observed. Consequently, our results do not show a classical hysteresis loop observed usually for reactive sputtering. Nevertheless it could be possible to observe of avalanche transition from metallic to reactive mode. It is probably because we work at relatively low discharge current and due to apparatus limitations of the present arrangement.

Figure 3. shows behaviour of emission originating from the discharge gas versus nitrogen content. In the case of excited argon (Ar I, Ar II) and nitrogen (N_2, N_2^+) species, different excitation and recombination processes may be involved in their steady state concentrations. However worth of note is a hysteresis observed for N_2 (Fig. 3.). Simultaneously intensities of ArI and Ar II lines were lower during transition from nitrided to pure target surface than during the reverse process. It well explains that it was hard under our experimental procedure to obtain the target surface free from nitrogen starting from a completely covered surface.

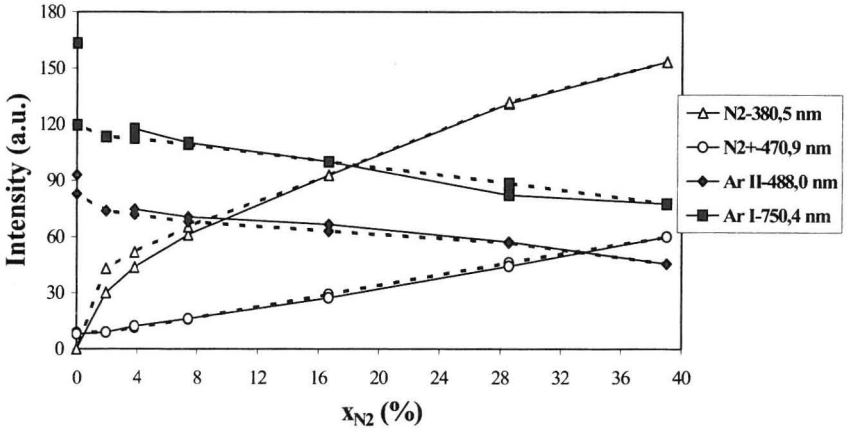

Fig. 3. Changes in emission intensities of argon and nitrogen species with increasing (solid line) and decreasing (dotted line) nitrogen content in the Ar+N_2 mixture. The results for the position B.

One of the characteristic features of a planar magnetron discharge there is inhomogeneity of the current density across the cathode. As a result the metal sputtering rate and consequently, the degree of target coverage by reactive gas are site-dependent. The evidences of inhomogeneity of the linear magnetron discharge have been found previously [3,4]. The plasma is not uniform along the target's length according to the configuration of the magnetic field. Figure 4. presents plots of the intensity ratios (I_B/I_A) for spectra obtained from viewports A and B (see also Fig. 1.) as a function of the nitrogen content.

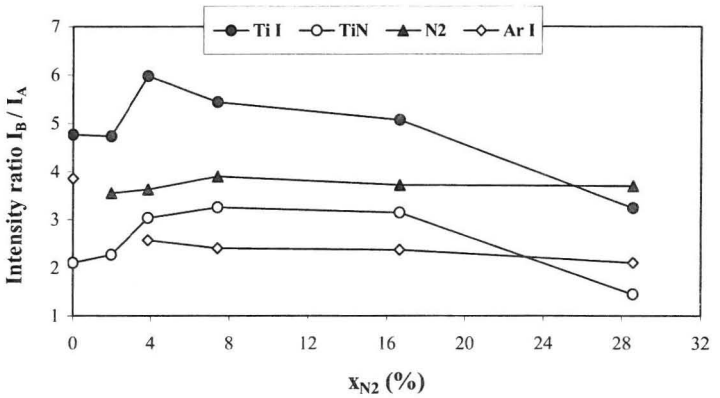

Fig. 4. Intensity ratios for spectra obtained from viewports A and B versus nitrogen amount in the $Ar+N_2$ mixture.

The I_B/I_A dependence for Ti I indicates that at the same nitrogen amount the sputtering efficiency in the position B, $R_s(B)$ was much higher than in the position A, $R_s(A)$. The difference between $R_s(B)$ and $R_s(A)$ was the highest at the $x_{N2} \sim 4\%$ and decreased with x_{N2}. For TiN, values of I_B/I_A were about two times lower than those for Ti I. On the other side the I_B/I_A relations with x_{N2} were similar. It can support argument for a common origin of the Ti and TiN species. The dependence for N_2 and Ar are similar but different from those for Ti I and TiN.

FINAL REMARKS

For the first time in the present study evidences for finding the critical nitrogen flow responsible for transition between metallic and reactive mode in the linear magnetron have been successfully reported using the optical emission spectroscopy as a tool. The Ti I and TiN can be used for control and monitoring the

reactive sputtering process as well other physical phenomena occurring in the linear magnetron.

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BADANIA SPEKTRALNE REAKTYWNEGO ROZPYLANIA TYTANU W MAGNETRONIE LINIOWYM

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S t r e s z c z e n i e. Praca przedstawia rezultaty badań spektralnych magnetronowego urządzenia rozpylającego, wyposażonego w tytanową katodę w mieszaninach argonowo-azotowych. Prześledzono zmiany intensywności emisji linii Em titanu, Ti I, a także Ar I, Ar II, pasma N_2, N_2^+ i TiN w funkcji ilości dostarczanego gazu reaktywnego (N_2). Stężenie N_2 było zmieniane od 0 do ok. 40% max. Dla stałej wartości prądu wyładowania 0,3 A i ciśnienia około 0,3 Pa gwałtowne zmiany w intensywności wszystkich obserwowanych widm, wskazujące na przechodzenie ze stanu metalicznego do zatrutego, wystąpiły już przy zawartości azotu około 3%.

S ł o w a k l u c z o w e: magnetron liniowy, spektroskopia emisyjna, TiN, rozpylanie tytanu.