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Influence of modulation frequency on the synthesis of thin films in pulsed magnetron sputtering processes

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The research on the influence of modulation frequency on the properties of films synthesized using a unique pulsed power supply combined with a standard unbalanced circular magnetron was conducted in the process of pulsed magnetron sputtering (PMS). It was shown that by using different levels of modulation, the composition of plasma (measured by optical emission spectroscopy, OES) as well as film growth rate and morphology (observed with scanning electron microscope, SEM), can be changed. The impact of modulation is related to the used materials and gases and can vary significantly. It was concluded that modulation frequency can greatly influence the synthesis of materials and can be used as an additional parameter in PMS. Specific relations between modulation frequency and synthesized material require further investigation.

Keywords: *pulsed magnetron sputtering; pulse plasma, modulation frequency; metallic films, ceramic films*

1. Introduction

Magnetron sputtering is one of the most often used methods for synthesis of thin metallic and ceramic layers among available plasma surface engineering techniques. Typical structures made by conventional plasma assisted physical vapor deposition (PAPVD) techniques exhibit a porous and columnar structure. Morphology of these structures has been described by Thornton model [1]. Among them, the most desired is a fine grained and compact morphology of transition zone (T zone). Columnar growth of thin films can be disrupted by changing supply power characteristics [2]. This is possible to achieve by using plasma surface technique [3–5]. DC pulsed power supply DPS [6] used in the experiment is characterized by a unique ability to change the constant and uniform application of power with a so called internal frequency ($f_w = 125$ kHz) and modulation frequency (f_{mod}) used to group discharges of f_w (Fig. 1), while keeping overall power constant. Due to the fact that the process efficiency and layers properties are related directly to synthesis conditions, it can be expected that the changes in f_{mod} are important to the synthesis process.

In this research, it has been assumed that by using frequency modulation to change single package power over 50 times between $f_{mod} = 10$ Hz and 1000 Hz, and keeping overall power constant, important differences in synthesis conditions and thin film properties depending on modulation will appear. It was expected that the differences in plasma composition and energy delivered to the sample will allow to modify the properties of obtained thin films. It should expand the PMS technique and create a wider range of materials by the means different from impulse plasma deposition (IPD) or high-power impulse magnetron sputtering (HIPIMS) [7].

In this paper, the process of plasma generation related to modulation frequency is described and influence on the properties of obtained metallic and ceramic films is studied.

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2. Experimental

The experiments were conducted using a PMS system employing a standard unbalanced circular 50 mm magnetron with a degree of unbalance g = 1.12 (Group V) [8]. The vacuum system consisted of a rotary and a diffusion pump. Before synthesis, a (1 0 0) silicon substrate was placed on a metallic substrate holder and the atmosphere was evacuated to the base pressure of 5×10^{-3} Pa. During synthesis in a non-reactive process, Ar gas was used, whereas in reactive processes a mixture of Ar and N_2 gases was employed. The exception was Cu–N synthesis, when only N_2 was used. Gas purity was 99.999 %. Power was supplied by a DPS power supply of internal frequency $f_w = 125$ kHz and chosen modulation frequencies $f_{mod} = 10$ Hz, 250 Hz, 1000 Hz. Materials were synthesized using the parameters shown in Table 1.

Temperature measurements were carried out using a thermocouple in a fixed position at the back of the sample holder. Morphology analysis was conducted with a scanning electron microscope SEM (ZEISS Ultra Plus), analysis of current and voltage was done using an Agilent MSO8064A oscilloscope. Plasma composition was studied using optical emission spectroscopy (OES).

3. Results and discussion

3.1. Current-voltage characteristics

Modulation frequency as a technological parameter used in thin film synthesis employing PMS techniques allows to control plasma generation conditions thereby allowing modification of obtained films by changing the way of material delivery to the substrate. Measurements made with an oscilloscope revealed the internal structure of modulation of the discharge generating signal (Fig. 1) and allowed to calculate plasma generation parameters. The internal structure of the discharge signal is shown in Fig. 1, right column.

Using the characteristics shown in Fig. 1, generation time of pulse packages was defined and fill factor was calculated (Fig. 2) using equation 1:

$$k_w = \frac{\tau}{t} \qquad (1)$$

where τ is discharge time and t is period time.

Periodic generation of pulses with a set modulation frequency results in significant changes in plasma lifetime (discharge time) and fill factor. Change in generation time (5×10^{-3} s to 19×10^{-5} s) shown in Table 2 and proportional change in the fill factor (5 % to 19 %) translate to over 26 times increased plasma lifetime and nearly 4 times increase in the fill factor.

Using equation 2 taken from the literature [9], the work per single discharge package was calculated:

$$P_{Pulse} = \int_0^t V(t)\, I(t)\, dt \qquad (2)$$

where t is discharge time.

Both the values were plotted in Fig. 2 with fill factor to package power ratio added.

Considering the calculations based on Fig. 2, it was revealed that, though there are significant changes in discharge duration and the fill factor value, their ratio is almost constant. It means that the power set on the power supply is constant and does not fluctuate.

Additionally, during synthesis of Cu–N layers, temperature of the substrate was measured (Table 3). Temperature values clearly correlate with the calculated power for pulse packages, reaching maximum at $f_{mod} = 10$ Hz and then falling off.

3.2. Growth rate and morphology

Metallic films obtained using the PMS method with different values of f_{mod} are characterized by changes in their growth rates which depend on used target material and f_{mod} value. Aluminum layers (Fig. 3a, Fig. 3b, Fig. 3c) show a linear correlation between f_{mod} and growth rate. Conversely, copper layers (Fig. 3d, Fig. 3e, Fig. 3f) exhibit the highest rate of growth at the lowest f_{mod}. Titanium layers (Fig. 3g and Fig. 3h) seem to be less influenced and show similar levels of growth rate. The most interesting results have been found for molybdenum which exhibits a bell-like curve relation with a maximum at $f_{mod} = 250$ Hz.

Table 1. Process parameters.

Material	Power [W]	Pressure [Pa]	Target-substrate distance [mm]
Mo Al Cu Ti	1000	1 Pa (Ar)	100
CuN	500	1 Pa (N_2)	
AlN	1500	1 Pa ($Ar + N_2$)	

Table 2. Parameters of discharge time, period time and fill factor.

f_{mod} [Hz]	Discharge time [s]	Period time [s]	Fill factor [%]
10	5×10^{-3}	10^{-1}	5
250	36×10^{-5}	4×10^{-3}	9
1000	19×10^{-5}	10^{-3}	19

Table 3. Substrate temperature in Cu-N synthesis.

f_{mod} [Hz]	Top temperature 150 Watt to 500 Watt [°C]
10	31 – 70
250	30 – 57
1000	28 – 60

The using different values of f_{mod} resulted in differences between morphologies of obtained films. $Al_{10\,Hz}$ (Fig. 3a), $Cu_{250\,Hz}$ (Fig. 3e) and all titanium layers show a columnar structure. However $Cu_{10\,Hz}$ (Fig. 3d), $Cu_{1000\,Hz}$ (Fig. 3f) and all molybdenum layers have changed to a finer structure.

Al–N layers (Fig. 4a, Fig. 4b, Fig. 4c) show a changing morphology and growth rate that depends on the used f_{mod}. Al–$N_{10\,Hz}$ (Fig. 4a) demonstrates the lowest growth rate and a dual morphology: initially the film grows in a finer structure which later changes to clearly columnar in nature. Al–$N_{250\,Hz}$ (Fig. 4b) is a fully columnar structure that grows faster than its 10 Hz counterpart. Further increase in f_{mod} caused additional increase in the growth rate but the film preserved the columnar morphology. Cu–N (Fig. 4d, Fig. 4e) samples compared with Cu samples show a high increase in the growth rate for low frequencies modulation (Cu–$N_{10\,Hz}$ (Fig. 4e)) and a columnar structure. At f_{mod} increased to 1000 Hz, Cu–$N_{1000\,Hz}$ growth rate was lowered but the film retained its columnar structure.

Analyzing Fig. 5 and Fig. 6, it can be seen how large is the influence of f_{mod} on the growth rate and morphology and how important is this parameter for synthesizing thin films by PMS technique. The parameter can be used to extend the control over material design. The film of $Ti_{250\,Hz}$ delaminated shortly after removal from the vacuum chamber and was not investigated.

3.3. Emission optical spectroscopy

OES measurements were carried out to study the influence of f_{mod} on plasma composition and to characterize the synthesis environment. Results are shown below. It was expected to reveal differences in plasma composition depending on modulation frequency relating to different amounts of power provided by the power supply unit. Plasma composition, as one of the most important factors influencing synthesized material parameters, is one of the most desirable elements to control the synthesis process.

Differences between plasma composition depending on the used f_{mod} value and target material visible in the OES derived graphs (Fig. 7) [10], enable better understanding of the influence

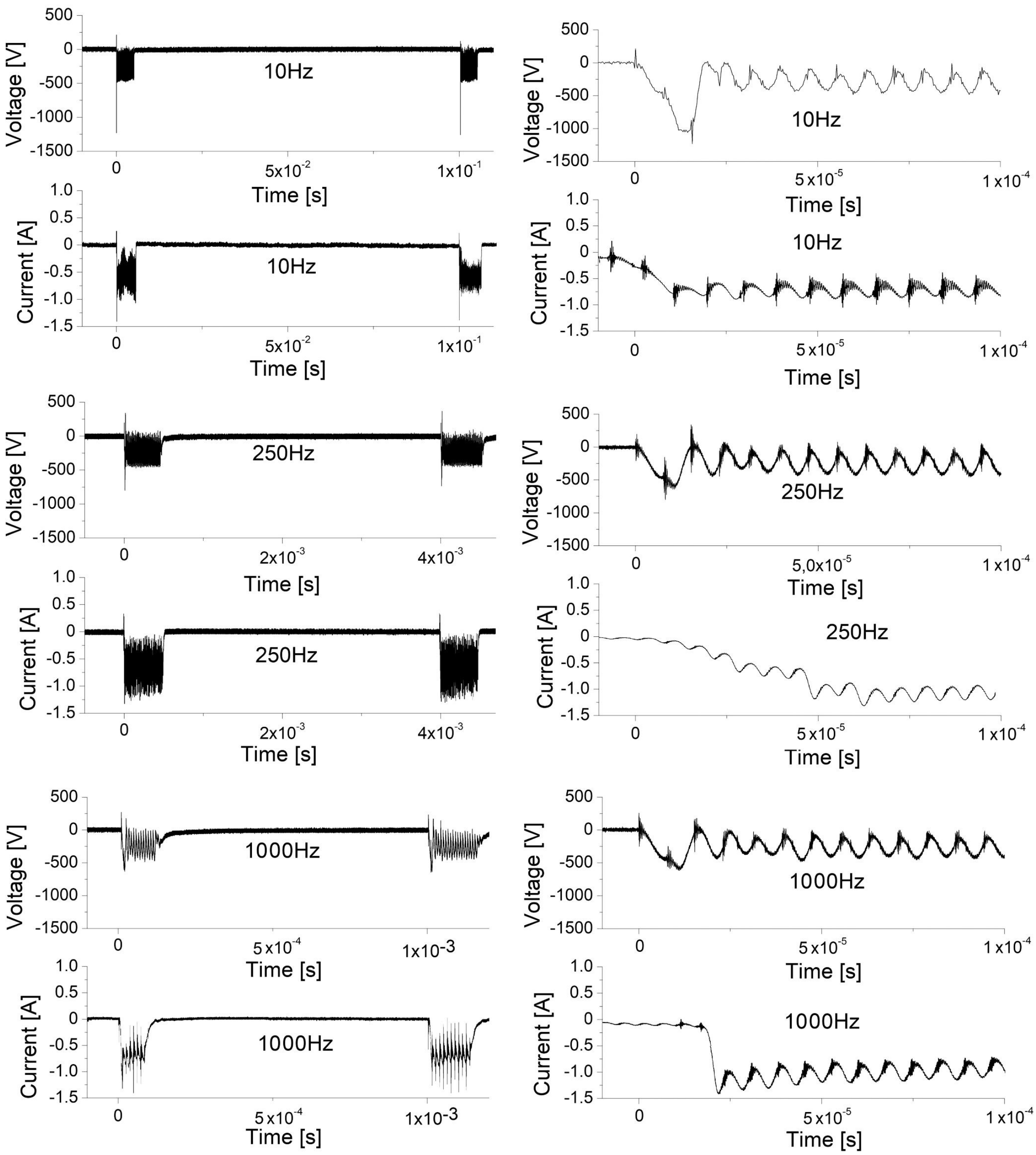

Fig. 1. Voltage and amperage characteristics for the modulation frequencies used in the experiments (10 Hz, 250 Hz, 1000 Hz) (left), and internal structure of a single packet of plasma generation signal (right).

of modulation frequency on material synthesis. The studied materials were shown to share similarities and differences. Both aluminum and titanium exhibit the maximum intensity at $f_{mod} = 250$ Hz, but their minima occur at 10 Hz and 1000 Hz, respectively. For copper, the maximum is observed at $f_{mod} = 10$ Hz. Molybdenum shows a less clear dependency on f_{mod}, but its minimum occurs at 1000 Hz. Selected spectra lines were extracted, the weakest signal was normalized to unity and then combined for better illustration (Fig. 6). Description tags (e.g. $Al_{250\ Hz}$) indicate location of maximum for a particular metal at a given value of f_{mod}.

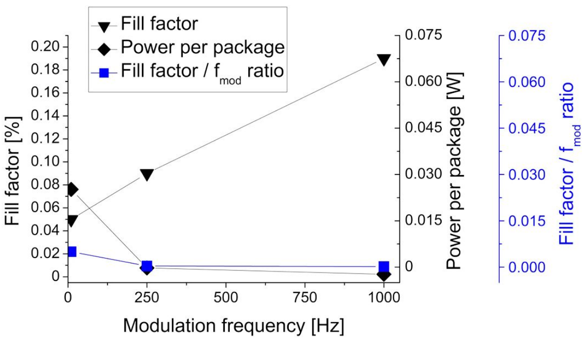

Fig. 2. Correlation of fill factor (% of time used for sputtering), single discharge package power (power in W spent on a single sputter packet) and their ratio (dimensionless).

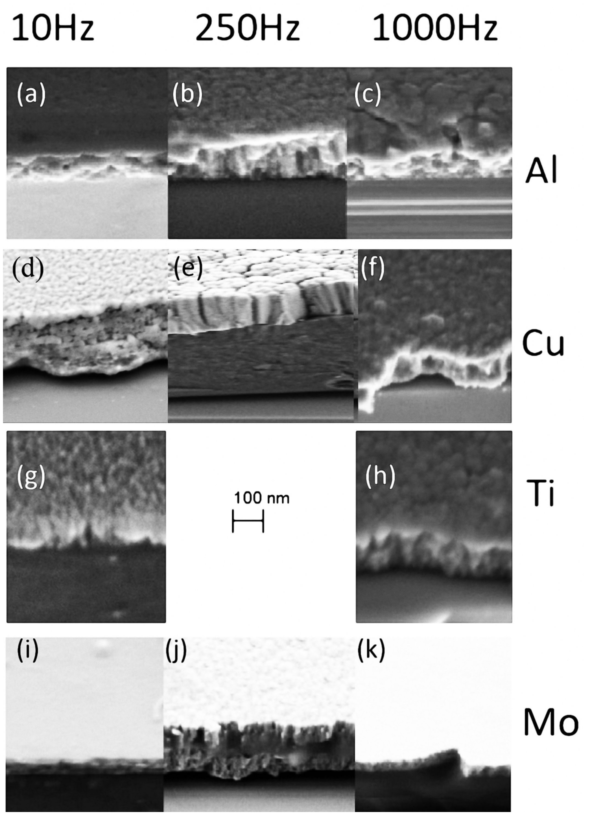

Fig. 3. Cross-section view of metallic layers obtained at different modulation frequencies.

Switching to reactive mode by adding nitrogen has not changed the OES spectra and Al–N plasma behaved in the same fashion as Al–Ar, as far as relative levels are concerned (Fig. 8).

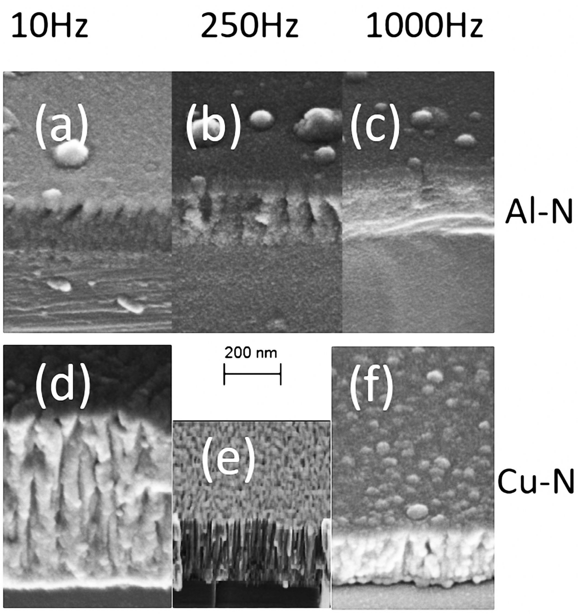

Fig. 4. Cross-section views of nitride films obtained at different modulation frequencies.

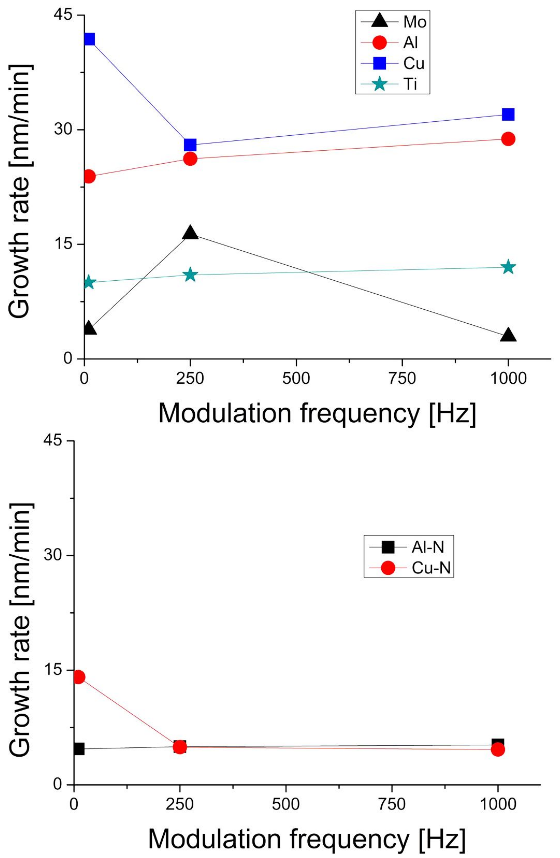

Fig. 5. Growth rate of metallic (upper) and nitride films (lower).

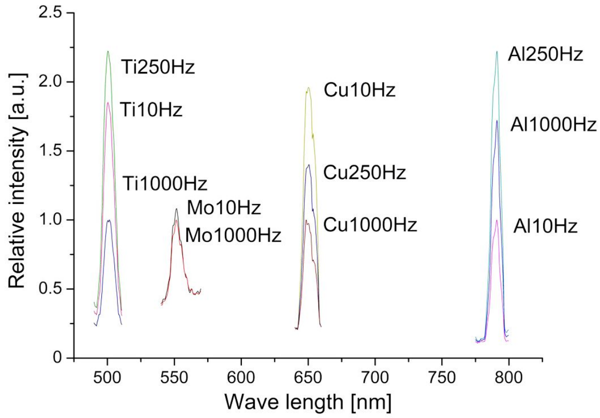

Fig. 6. Extracted representative peaks for metallic processes.

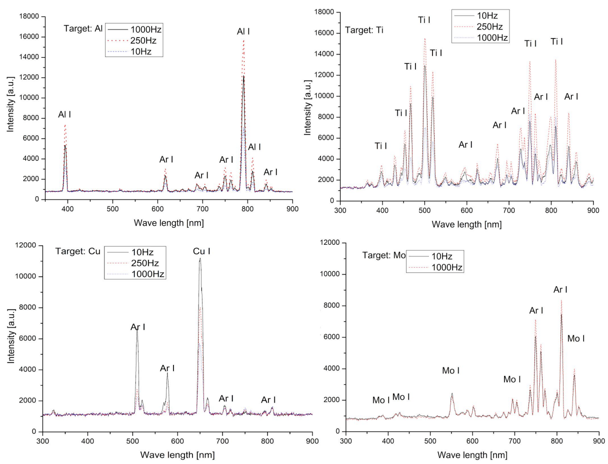

Fig. 7. Emission spectra recorded for nonreactive processes.

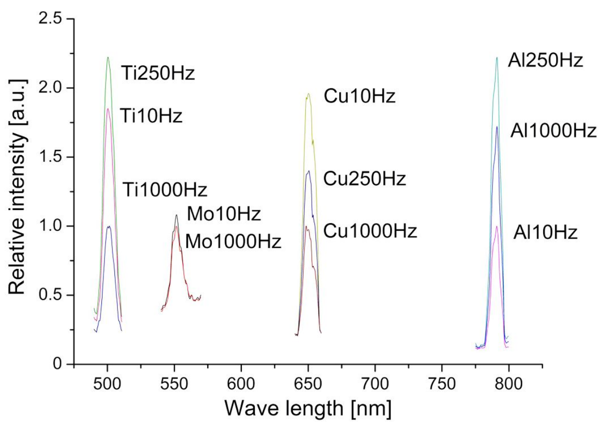

Fig. 8. Emission spectra recorded for reactive Al–N synthesis.

4. Conclusions

Modulation frequency, which is one of parameters of PMS process, allows for significant changes to be made in morphology and growth rate of thin films synthesized using this technique through the modification of plasma composition and the manner of how the energy is delivered to the substrate. Plasma composition is directly related to the modulation frequency and as such allows for better control of the synthesis process which leads to extending material design possibilities as has been reported for Cu–N films [11]. Obtained structures were either clearly columnar or exhibited a more fine-grained structure.

Growth rate as a function of modulation frequency f_{mod} was different for every material. In most extreme cases of Cu and Mo, the difference was about 50 % and over 500 %, respectively. Relation between the sputtering yield Y and f_{mod} is currently not elucidated just like the connection between voltage and amperage characteristics (Fig. 1) and OES spectra (Fig. 7 and Fig. 8). Furthermore, correctly chosen f_{mod} allows for obtaining a huge increase in effective sputtering yield for materials with a relatively low yield (Ar^+ at 600 eV) in comparison to materials with a higher yield ($Y_{Cu} = 2.3$, $Y_{Al} = 2.7$, $Y_{Mo} = 0.9$) [12] (Fig. 5).

Acknowledgements

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