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STRUCTURE AND ELECTRICAL RESISTIVITY DEPENDENCE OF MOLYBDENUM THIN FILMS DEPOSITED BY DC MODULATED PULSED MAGNETRON SPUTTERING

This work reports the results of a study of Mo thin films synthesis by DC Pulsed Magnetron Sputtering method (PMS), operating at pulse main frequency of 100 kHz and modulated by the additional modulation frequency, driving in the range of 5-1000 Hz (modulated Pulse Magnetron Sputtering – mPMS). We have studied the influence of mPMS on plasma chemical reactions and mechanisms of layer growth using optical emission spectroscopy technique. Our experiment showed strong influence of mPMS method, on the morphology (scanning electron microscopy), phase composition (X-ray diffractometry) and electric properties (4-point probes method) of nanocrystalline and amorphous Mo films. From the utilitarian point of view, low value of resistivity – 43,2 μΩcm of synthesized Mo films predestines them as back contacts for thin solar cells CIGS. Our results revealed that additional modulation frequency should be considered as an important factor for optimization of films synthesis by means of PMS-based methods.

Keywords: magnetron sputtering, modulated pulse magnetron sputtering, plasma&films characterization

1. Introduction

Magnetron sputtering (MS) is the most commonly used plasma surface engineering method of the films' synthesis. Undoubtedly, one of the biggest advantages of MS method is its potential for continuous development based on elementary assumption of sputtering the cathode within the magnetic field. The innovative variants of MS technology such as PMS [1] or the other new MS techniques such as: the GIMS (Gas Injection Magnetron Sputtering) [2-3], the HiPIMS (High Power Impulse Magnetron Sputtering) [4] are the examples of a progress. The scope of interest concerning mentioned techniques focuses particularly on optimization of the synthesis process, basing on the following factors: ionization state-of plasma, kinetics of layers growth, structure and morphology of layers, chemical and phase composition, etc.

In the presented experiment, the films were synthesized using the DC Pulse Magnetron Sputtering (PMS), in which a pulsed manner of plasma generation with the main frequency of power source of 100 kHz was applied. As a source of electric energy the DPS-type supplying system was applied, which enables controlling the power transmitted into the target material thanks to full resonance mode based on the sinusoidal energy converter, being described in details in [5]. The structural and technological uniqueness of DPS power supply consists mainly in adjusting conditions of plasma particles lifetime by means of modulated Pulse Magnetron Sputtering (mPMS) [6,7]. In our experiment, we deposited Mo thin films with different values of modulation frequency – (f_{mod}). We have expected, that various f_{mod} should influence the composition of plasma, the kinetics of films growth and morphology of films in accordance with electrical properties of deposited Mo condensates. We have anticipated that optimization of Mo films synthesis, based on mPMS method should be considered as a main factor, which will lead their structural, chemical and electrical properties to be more effective, e.g. putting them into use for ohmic contacts within (CIGS) solar cells.

2. Materials and methods

The Mo layers were synthesized by means of the mPMS method, inside the vacuum chamber equipped with a circular magnetron (Mo target diameter Φ = 50 mm, thickness t = 6 mm). The magnetron was powered by 10 kW DPS pulse power supply, operating in DC mode with 100 kHz frequency. Main frequency was modulated by additional frequency f_{mod} = 5, 10, 100, 250 or 1000 Hz, to achieve various sputtering condition. Fig. 1 illustrates how the power modulated by f_{mod} influences the duration of plasma impulses.

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The Mo layers were deposited on the monocrystalline silicon substrates <100> located parallel to the target with 120 mm distance and stayed at plasma potential during the sputtering. The pressure within the working chamber was evacuated to $< 5 \cdot 10^{-4}$ Pa and the process of synthesis was carried out in an argon atmosphere under the constant pressure equal to 0,65 Pa. No additional substrate heating was used during the processes.

In order to determine the Mo morphology and phase composition, scanning electron microscopy (SEM) and X-ray diffractometer emitting the Cu-Kα radiation were used. To study the state of plasma the optical emission spectroscopy (OES) technique was used. Optical signals, appearing in the discharge zone, were collected within a range of 250-450 nm through a transparent view port window and a fibre optic cable. To examine the Mo films resistivity and changes in their electrical conductance the 4-point probe method was applied [8].

3. Results and discussion

Voltage waveforms registered at cathode during using various f_{mod} were showed on Fig. 1. In each of presented pulse plasma duration waveforms, voltage amplitude reaches nearly 1400 V. According to the Paschen law [9], such voltage exceed the electrical power necessary to plasma generation, for steady-state glow discharge condition. Unlike, mPMS method takes advantage of using such a high power source of plasma excitation, e.g. reaching higher energy of plasma particles and ionization state indeed, what we have proved in previous work [10]. Modulation of plasmoids' (plasma packages) lifetimes takes place by means of change of f_{mod} parameter, indicating modification in periodical power impulses distribution. In accordance to plasma particles oscillating nature and theirs energy dependence on f_{mod} during the mPMS process, we noticed that variability of plasma flux distribution was the main reason of slightly different mechanisms of surface activation. We observed the results of application of the various f_{mod} in particular on plasma – chemical state and morphology of layers structure, which were presented on the following part of results.

In order to estimate qualitatively the influence of the discharge conditions on the plasma state and the films properties, the optical spectra of magnetron plasma was studied in wide range of f_{mod} = 5-1000 Hz (see Fig. 2). During the synthesis process, regardless of modulation frequency magnitude, the

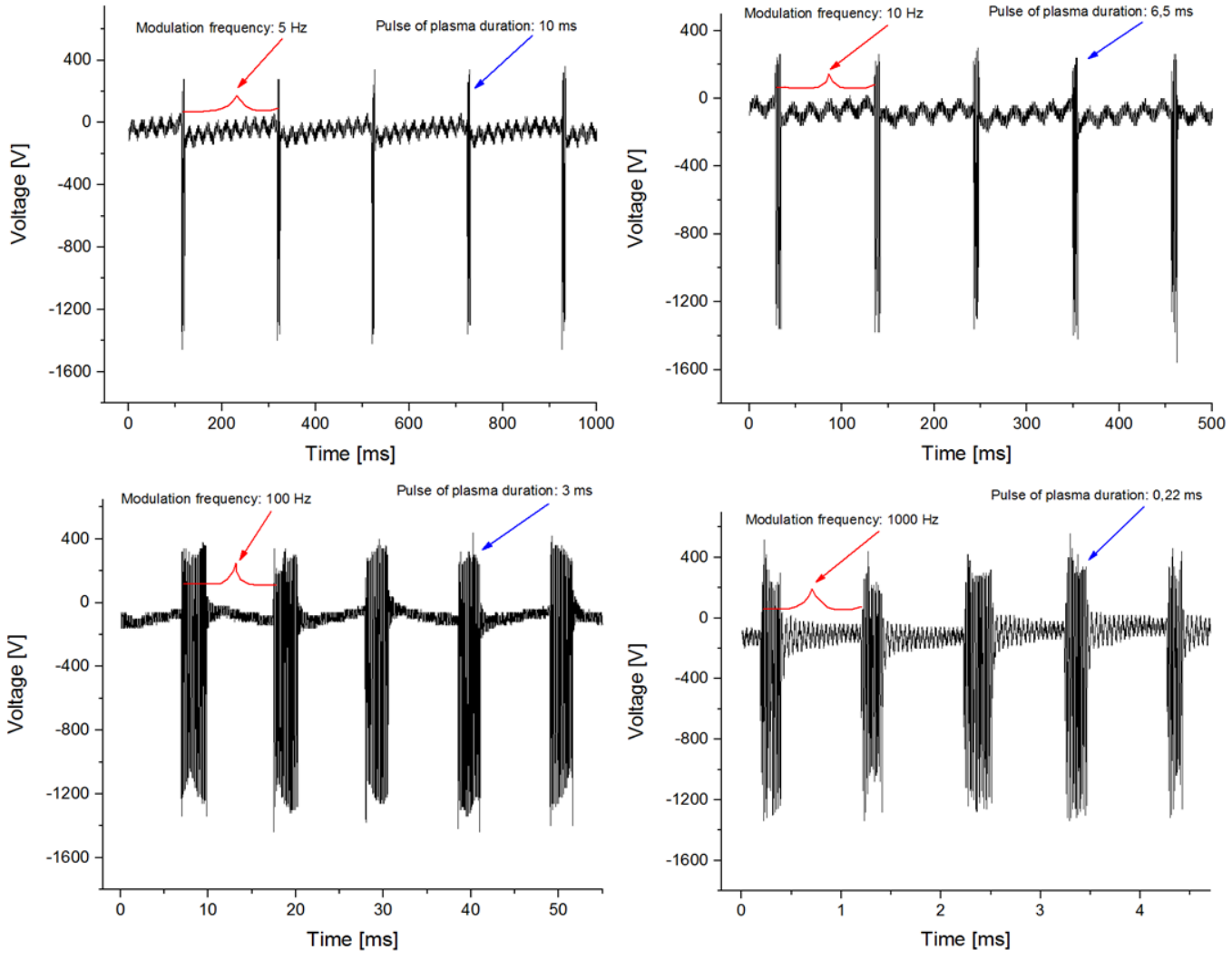

Fig. 1. Voltage waveforms of PMS process with different modulation frequencies (fmod) of: 5 Hz, 10 Hz, 100 Hz and 1000 Hz

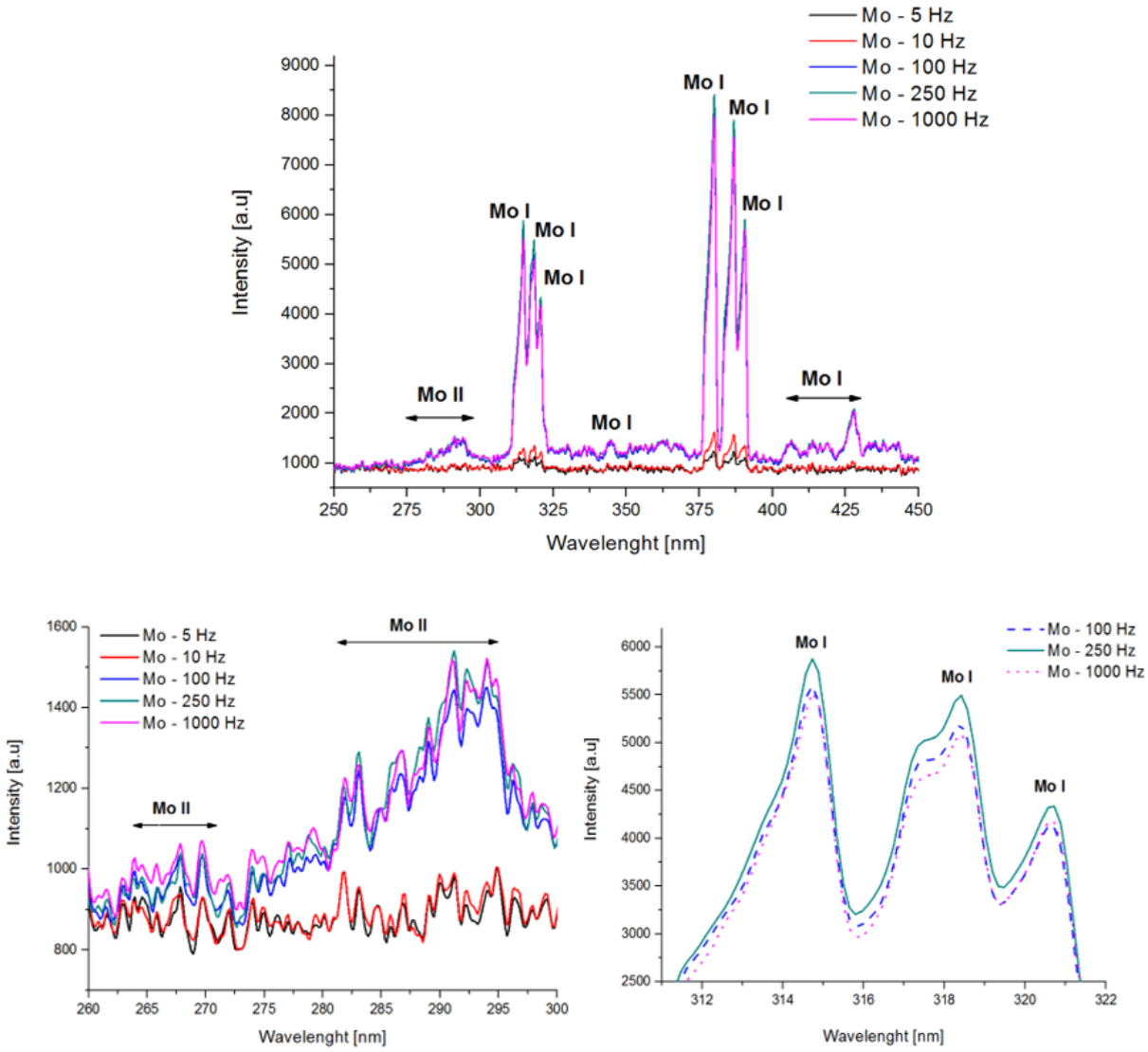

Fig. 2. Optical emission spectra from glow discharge during magnetron sputtering of Mo target

emission spectra within the scope of 250-450 nm were collected, because the most intense Mo spectral lines appear at the near – UV region [11]. Although the intensities of emission lines do not determine the number of species within plasma flux [12-13], the changes in relative populations of atoms and ions at different excitation and ionizations levels (in this case Mo I and Mo II) certainly might be considered as a qualitative factor of the recorded plasma spectra. The analysis of the emitted spectra reveals the presence of lines assigned for excited atoms (Mo I) and for ionized species (Mo II), originating from the sputtered target material. The most intense spectrum from Mo I was measured for the modulation frequencies of 100-250 Hz, which is in good agreement with increasing kinetics of layer growth (see Tab. 1). When the higher f_{mod} of power is applied, the decrease of excited atoms intensity as well as increase of ionized species population were simultaneously observed. It might be a result of the plasma thermalization process. This phenomena occurred when the relatively higher density of plasma particles (f_{mod} = 1000 Hz) tend to lose some part of their energy by inelastic collisions during the clusters formation. As a results the weaker

TABLE 1

Properties of Mo films as determined using different characterization techniques

Sample ID	Modulation frequency [Hz]	Resistivity [μΩcm]	Film thickness [nm]	Kinetic of film growth [nm/min]	Duration of deposition process [s]	Crystallite size [nm]	Strain [%]
Mo-1	5	461,4	60	6	600	—	—
Mo-2	10	384	80	10	480	—	—
Mo-3	100	43,2	120	40	180	11	1,91
Mo-4	250	49	140	48	175	9	1,78
Mo-5	1000	105,5	185	30	370	10	1,36

intensity of Mo I spectral lines and lower kinetic rate of film growth were obtained. Furthermore this interpretation proves, that molybdenum synthesis with the f_{mod} = 1000 Hz results in plasmo-chemical reactions occurrence directly in ionized flux (significant intensity of Mo II spectral lines).

The film thickness as well as the morphology of the films dependence on the modulation frequency were studied on the basis of SEM images (see Fig. 3). Using low f_{mod} = 5-10 Hz results with growth of relatively thin film (60-80 nm) without visible graininess. Extension of each time-off period between plasma pulses with decreasing f_{mod} parameter causes more effective dissipation of plasma thermal energy spreading in crystal lattice of substrate exposed to plasma activity. In our opinion, in this process, thermal activation of surface is slight so adatoms mobility on the substrate surface is strongly limited, which from the thermodynamic point of view significantly limits creation of nuclei with radius higher than the critical. SEM images, presenting the Mo-2 films surface, seems to confirm this. The surface is smooth, coherent and without any other features which means, that the low modulation frequencies effectively limits the long – range order structure being characteristic for the textured crystalline domains. In turn to the Mo-3 and Mo-4 films, the homogenous and nanocrystalline structure is characteristic, which clearly exhibits columnar structure, typical for deposition processes proceed in the low-temperature plasma. The obtained structure, typical for zone II, indicates an increase of homologous temperature (T_m) during the process using medium f_{mod} in comparison to low values of modulation frequency [14]. In this case, higher T_m contributes to more efficient adatoms mobility and at the same time the rate of crystallites growth (40-48 nm/min.), on the plane parallel to the substrate surface. Along with f_{mod} increase up to 1000 Hz, it can be observed, that the mechanism of layer growth is more complex. The structure of Mo-5 layer consists of two zones: fine – grained dense zone and columnar zone. Initially the nucleation process takes place on the surface, determining the nucleation of fine-grain structure, where fragmentation phenomenon disturbs the columnar growth of the layer. Columnar structure was expected here due the higher T_m in Mo-5 than Mo-3 and Mo-4 layers. Further, with the film growth, the change in structure for columnar is observed. This is an another result of plasma thermalization. This condition favors nucleation of phase in plasma flux. During the process of nucleating on plasma ions the Mo clusters are formed in plasma and then deposits onto substrate surface (in this case: previously created fined grain structure) [15]. Moreover, the Mo layer thickness reached for modulation frequencies of 100-1000 Hz suggests, that the plasma pulse shortening correlates with differences in morphology to originate from different growth mechanism, accompanying the synthesis during various f_{mod} parameter.

The interplanar lattice spacing $d_{(110)}$ was calculated using the Bragg's law and then was used to determine the crystallographic and mechanical properties of studied Mo films, according to the XRD measurements. The variation of the lattice spacing, i.e. the slight shift of (110) peak position in the direction normal to the plane of the films can be caused by compressive or tensile stress [16-17]. In general, stress intensity originated from crystalline domains is a result of change in lattice parameter (Δa) of the film. In the our experiment, the calculated lattice parameter for Mo films ranges from 3,190 to 3,207 Å, which is slightly higher when compared to the reference molybdenum

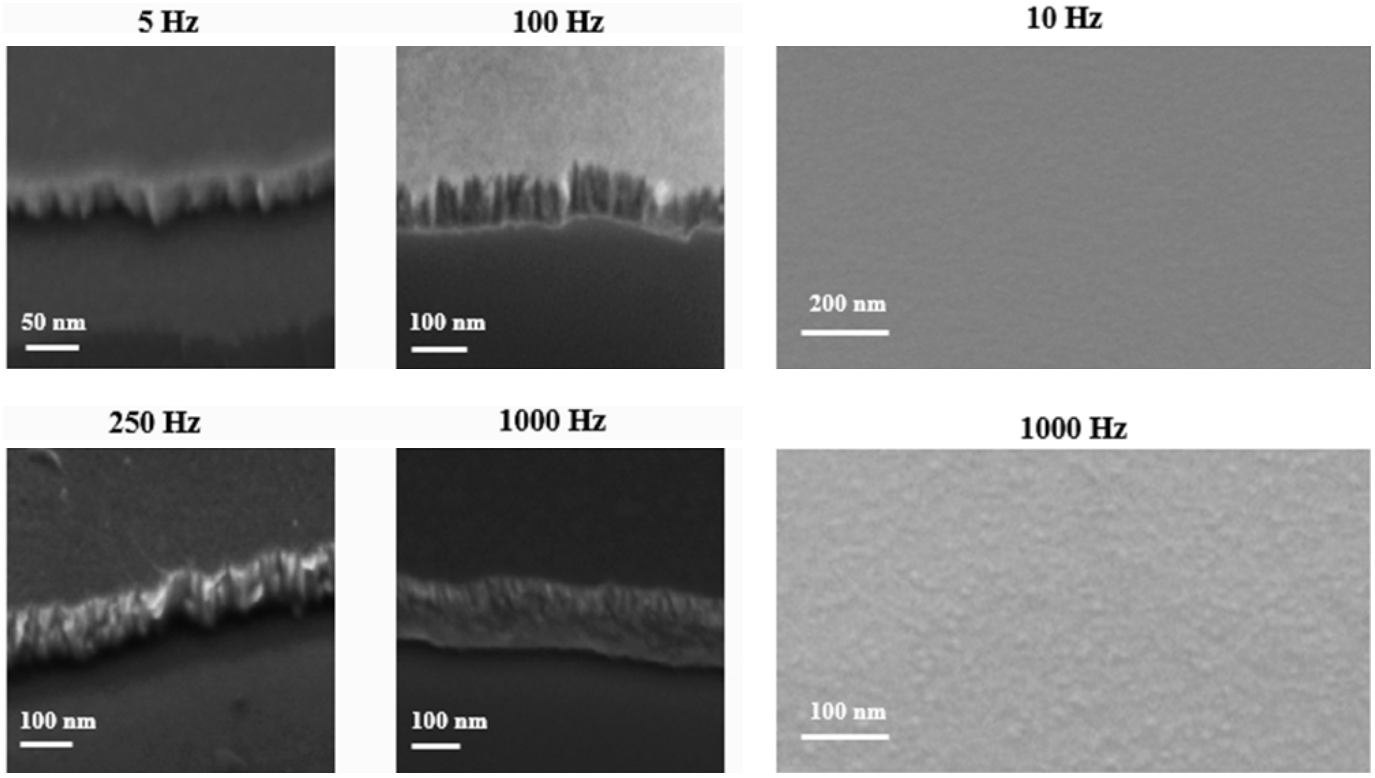

Fig. 3. Cross section and surface view of Mo layers obtained with different modulation frequencies (f_{mod}) of plasma generation – SEM

sheet (a_0 = 3,147 Å). According to the above, the strain of films was calculated by means of the following formula:

$$Strain(\%) = \frac{\Delta a}{a_0} * 100 \quad (1)$$

Calculated values of strain in the as-deposited Mo layers, which are also listed in table 1, did not exceed 2% and what is interesting, for the sputtering conditions only the tensile stress has been developed. One of the possible reasons for such effect may be defects and voids size distribution. We suppose that the interstitial Mo atoms diffuse to vacancies, simultaneously contributing the local tensile stress concentration (positive value of strain). In the case of this research, the lowest strain value amounting to 1,36% was reached for Mo-5 layer, which is possibly related to the morphology of the structure. It is highly probable, that due to intensely oscillating plasmoids phenomenon with f_{mod} = 1000 Hz, less limited stress relaxation effects might have occurred in crystalline Mo lattice film – more detailed description is presented in the following experimental part.

The variation of the full width at half maximum (FWHM) of the (110) peak with modulation frequencies was also measured. The average crystallite size of the molybdenum films may be calculated from the broadening of the corresponding (110) X-ray peaks using Scherrer formula [18]:

$$L_{hkl} = \frac{k\lambda}{\beta \cos\theta_{hkl}} \quad (2)$$

where L_{hkl} is the crystallite size, k is the Scherrer constant (considered 0,94 in our case), λ is the X-ray wavelength, β is the FWHM of the peak, corrected for instrument broadening (i.e., $\beta^2 = B^2 - b^2$ where B = experimental, b = instrumental) and θ_{hkl} is the Bragg angle. All results listed in Table 1 unequivocally emphasize the uniform and nanocrystalline Mo films structure, both with medium or high f_{mod}, where the average particle size reached ~10 nm.

For the f_{mod} from 5 to 10 Hz we did not notice at the XRD patterns any diffraction peaks deriving from any crystalline domains (Fig. 4). The thin Mo 1-2 films were distinguished by lack of the long – range order, which perfectly corresponds with the SEM and OES results indicating the existence of amorphous phase. In turn Mo-3, Mo-4 and Mo-5 films accordingly with f_{mod} = 100, 250 and 1000 Hz, we observed a main (110) peak assigned to crystalline Mo phase with a body centered cubic phase structure Im3m (JCPDS 42-1120). The diffraction data was adjusted to the Lorentzian function in order to determine the location of each 2θ peak. Intensity of Mo-3 and Mo-4 peaks (2θ = 39,73° and 2θ = 39,78° respectively) is higher than the Mo-5 peak (2θ = 39,95°). In this paper, the outcome of the applied middle modulated power (100-250 Hz) plays a significant role in the highest crystallinity of film, taking into account the uniform voltage of deposition, for each molybdenum condensate. In our opinion, the different distribution of plasma flux in processes Mo 1-5 has a strong influence on phase nucleation mechanism. Considering Mo 3-5 process, nucleation mechanism took place along highest planar packing density zones (minimum surface free energy), which may at the same time limit the random texture of nanocrystalline films. Process using the modulation frequencies from 100 to 1000 Hz provides the sufficient amount of energy to overcome the nucleation barrier and enables crystallites growth of Mo phase. We suppose, that during the deposition process with lower there is no sufficient energy to activate the substrate surface for nucleation, because of highly limited mobility of adatoms. In this case, implementation of modulation frequency acts a role of an activating factor, where surface activation proceeds by energy exchange between plasma species and surface atoms, as well as supporting nucleation and growth process.

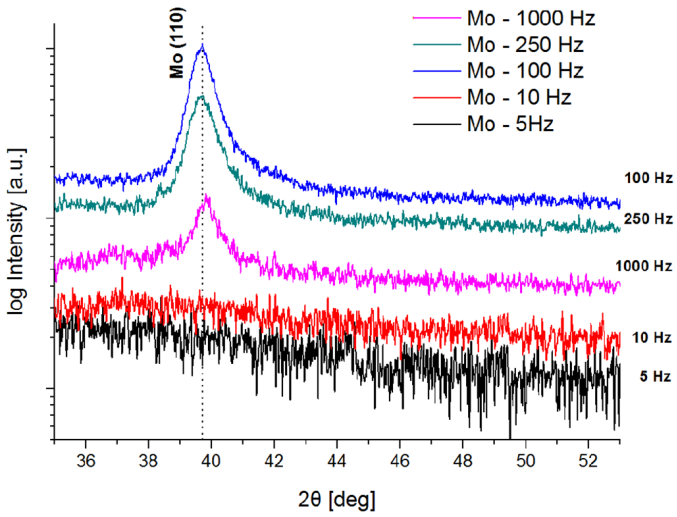

Fig. 4. X-ray diffraction spectra of different Mo thin films

The resistivity measurements and thickness of the metallic Mo films are presented in the Fig. 5 as a function of modulation frequencies. The resistivity of films varies between 43,2-461,4 μΩcm, which confirms their good electrical conductivity as for the metallic bond nature. The electrical resistivity of metals is determined by the scattering of electrons at all kinds of microstructural defects, such as point defects and grain boundaries [19]. In our study, the amorphous structure of Mo-1 and Mo-2 films is highly defected, so exhibits high tendency for electron scattering during the diffusion process within the electric field. From the utilitarian point of view, the special attention must be paid to the film deposited with f_{mod} = 100 Hz, which resistivity reaches the value near bulk molybdenum (ρ_{Mo} = 5,4 μΩcm) [20]. Such promising improvement of the electric conductivity is an indirect result of crystalline structure with thickness about 120 nm. However, it is worth mentioning, that the grain size itself does not solely determines the electrical properties of films, which also depend on the grain growth mechanism and their microstructure [21]. The decrease of resistivity to 43,2 μΩcm observed for the Mo-3 sample occurred due to more effective diffusion of carriers in the crystalline lattice. On the other hand, obtaining of thicker, but still nanocrystalline film by f_{mod} = 1000 Hz, caused a visible decrease in the electric conductivity. Explanation of such phenomenon can be found in larger contribution of grain boundaries textured perpendicular

to the electrons drift in the electric field, which also determines scattering of charged carriers.

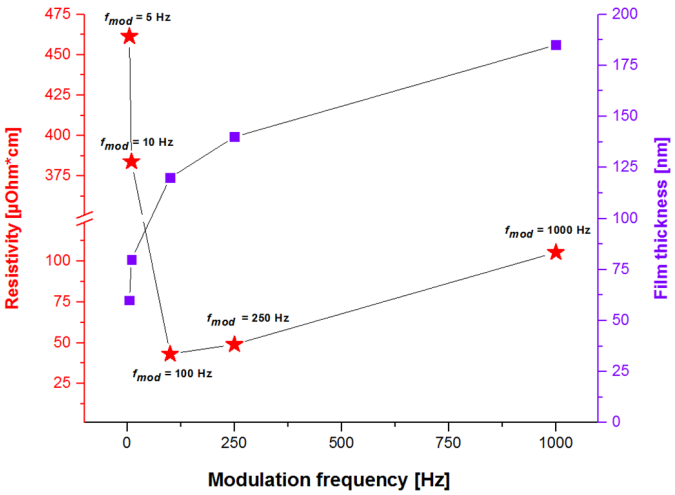

Fig. 5. Electrical resistivity, film thicknesses and f_{mod} for different Mo films

4. Conclusion

In the experiment described in this manuscript, the Mo films were synthesized by means of the DC modulated pulsed magnetron sputtering (mPMS) with various modulation frequency of plasma generation. The obtained results confirmed, that the changing conditions of plasma generation, resulting from the possibility of controlling its frequency and plasma lifetime, have a strong impact on quantity and activity of plasma particles and their interaction with the substrate. Described experiments confirm essence of various frequency plasma generation influence on microstructure, morphology and electrical properties within metallic Mo films.

The low modulation frequencies directly contributed to production of amorphous Mo films (60-80 nm) with relatively high resistivity value. In turn for f_{mod} = 100-1000 Hz, increased deposition rate of the Mo films resulting from the crystalline nucleation into the plasma particles flux could be observed. According to the OES study, the dispersion nature of plasma components contributes to the variable thermal energy dissipation mechanism existing also on the growing films, and simultaneously effecting disturbances in the columnar structure growth. Moreover, the resistivity of the film deposited with frequency of 100 Hz reached 43,2 μΩcm, which seems to be highly promising in the context of the possible application of molybdenum films for CIGS solar cells, as a back ohmic contact. Our investigation revealed, that the modulation frequency is a significant factor of the synthesis process based on implementation mPMS method, also for proceeding in the reactive plasma environment [22-23].

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