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Effect of pulsed magnetron sputtering process for the deposition of thin layers of nickel and nickel oxide

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Magnetron sputtered nickel and nickel oxide films have been studied for various applications. We may find, among others, these films in electrochromic display devices, in resistive type gas sensors, as metal electrodes in electronic devices, in solar thermal absorbers. Pure nickel films deposited using PVD technique possess good corrosion and wear resistant properties. Magnetron sputtering has several advantages in film deposition (in comparison to other methods) such as relatively low heating temperature of the deposited substrate during sputtering process, high energy of sputtered atoms (about 10 eV) at the substrate, which influences positively the films adhesion. From application point of view, the most valuable feature of these films is the possibility of scaling target dimensions, which makes feasible the deposition on a several square meter surfaces. The improvement of magnetron sputtering devices design may influence positively the optimization of the deposition technology and its efficiency. The thin nickel and nickel oxide films were prepared by pulsed magnetron sputtering using original type WMK magnetron device. Ni (99.9 %) has been used as a sputtering target of 100 mm in diameter and different thicknesses (3 mm, 5 mm, and 6 mm). The distance between the substrate and target was the same in all experiments and equal to 120 mm. Argon and oxygen gases were introduced during the reactive process through needle gas valves at a total pressure of 0.4 Pa. The sputtering power, sputtering pressure and oxygen partial pressure have been used as technological knobs for deposition processes. The helpful tool for controlling the pulsed magnetron sputtering process was the original parameter of supply (so called circulating power). Results from our experiments showed that the deposition of Ni films is possible even from targets of 6 mm thickness. Deposition rate increased proportionally with the sputtering power. The aim of this work is to use the acquired expertise to develop an efficient technology of thin nickel oxide layers for electrochromic systems.

Keywords: *pulsed magnetron sputtering; thin film; deposition; nickel; nickel oxide*

1. Introduction

Magnetron sputtering allows deposition of high purity thin conducting, semiconducting and dielectric films. This method is highly attractive due to wide scaling possibility of sputtering materials (targets) and ability to deposit films in stable, repeatable and efficient technological processes, onto large substrates surfaces. This quality becomes particularly useful in industrial processes. Currently, the most popular version of magnetron method is pulsed sputtering. Although so far applied techniques of deposition meet certain technological criteria, different sputtering devices testing are continued. The goal is further construction optimization in order to implement certain sputtering variations. One of disadvantages of magnetron sputtering is limited possibility of magnetic materials sputtering. Targets made of such materials are simply magnetic jumpers for magnetic system which significantly limits or even makes their sputtering impossible. Parallel component of magnetic field intensity becomes “suppressed”, Larmor radius of secondary electrons emitted from a target (during ion bombardment) increases, which leads, in consequence, to reduction of ionization efficiency of working gas particles. It highly affects the sputtering rate, leading to its decrease. The solutions are: using thin targets, which imposes more frequent targets exchange (uneconomical), specially prepared targets (e.g. channeling) or/and using of magnetic systems generating enough high intensity of magnetic field to cause magnetic saturation of such targets.

The goal of the study presented in this article was characterization of pulsed magnetron

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sputtering from nickel targets. The processes were realized using circular magnetron WMK-100, with magnetic system specially engineered for this purpose. This research was focused on seeking optimal conditions for nickel sputtering in terms of efficiency (deposition rate). Fundamental properties of obtained films depending on sputtering process parameters were investigated. The studies were conducted with a special attention to stating usability of nickel films for conducting films and nickel oxide films employed as elements of electrochromic devices. The layers made of these materials are used as: (i) conducting, anticorrosive coatings and (ii) in electrochemical gas sensors, thin film electrochromic devices, solar absorbers, etc.

2. Experimental

Technological processes were conducted using NP-500 vacuum setup equipped with a pump system (diffusion pump 2000 L/s + rotary pump 30 m^3/h). Base pressure in working chamber was $\sim 3 \times 10^{-3}$ Pa. Circular sputter gun WMK-100, adapted to sputtering of 100 mm diameter targets sputtering, was mounted in the vacuum chamber. Electrical characteristics of nickel targets (99.9 %) of thicknesses $d_{T\text{-}Ni} = 3$ mm, 5 mm and 6 mm were investigated. The goal was to state the maximal Ni target thickness which is still possible to be sputtered. Argon or argon and oxygen mixture were introduced to the working chamber using a needle valves system and working pressure during deposition process was fixed at $p_{Ar} = 0.4$ Pa. Distance between the target and substrate was constant in all deposition processes and equal to $d_{S\text{-}T} = 120$ mm. Ni and NiO_x layers were deposited on Corning 7059 glass and n-type, (1 0 0)-oriented silicon substrates.

2.1. Magnetron power supply

WMK-100 sputter gun was supplied with DPS (Dora Power System) MSS-10 kW. Characteristic feature of this system is a series resonant circuit with stabilized Q-factor used in the output stage of the supply. Load impedance mismatch causes a part of the energy gathered in resonant circuit to be directed back to the power block. Manufacturer named this energy as "circulating power" P_C [1]. P_C value varies inversely proportional to impedance value "seen" by the power supply. It is dependent on degree of targets coverage with reactive compounds, on the type and composition of working gas and on magnetic field intensity above sputtered surface (degree of target etching to base target thickness).

2.2. WMK-100 sputter gun magnetic assembly

The most important element of every magnetron is magnetic system built on NdFeB permanent magnets. The value and distribution of parallel component of magnetic flux density over the target surface defines directly glow discharge characteristics and thin film deposition process efficiency. The role of magnetron magnetic system parameters becomes more important during sputtering of targets made of magnetic materials. Such example is sputtering of nickel targets. In this case, sputtering of nickel is possible only if magnetic material (nickel) becomes saturated and magnetic field over the target is sufficient to initiate discharge in crossed magnetic and electric fields.

3. Results

Vital part of this study was determination of magnetic field distribution characteristics at different distances (target thickness) from its surface. Magnetic (Ni) and nonmagnetic target characteristics were investigated. Fig. 1 shows the characteristics obtained for nonmagnetic elements (for example Al discs) simulating targets (nonmagnetic) with different thicknesses.

It is worth noting that even with $d_T = 12.5$ mm thick nonmagnetic target, it is possible to carry out efficient sputtering process (efficient sputtering process requirement is $B_{||}\text{min} = \sim 200$ Gs).

Magnetic flux density distribution on the different thickness Ni targets ($d_{T\text{-}Ni} = 3$ mm, 5 mm and 6 mm) surfaces is shown in Fig. 2. Increasing those targets thickness causes significant decrease in magnetic intensity, because these targets "shorten" magnetic poles more and more. It can be seen that

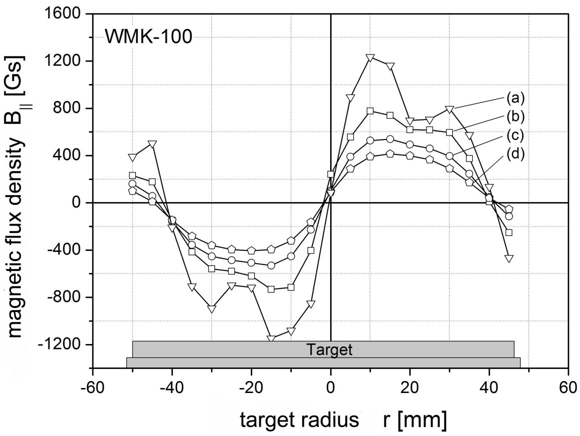

Fig. 1. Distribution of parallel component of magnetic flux density above WMK-100 magnetic system for different hallotron distances (positions) from the surface: (a) 3.5 mm, (b) 6.5 mm, (c) 9.5 mm, (d) 12.5 mm.

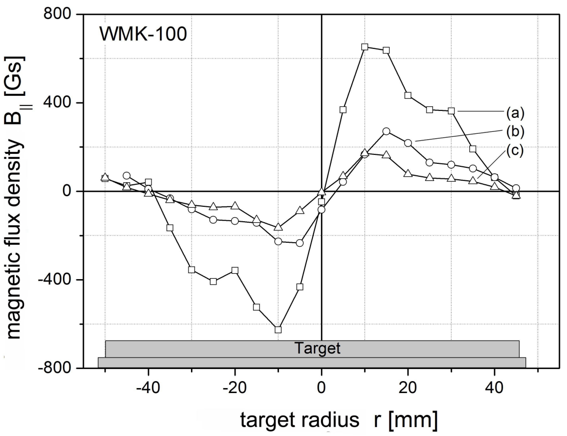

Fig. 2. Distribution of parallel component of magnetic flux density above WMK-100 magnetic system surface with different thicknesses of nickel targets: (a) 3 mm, (b) 5 mm, (c) 6 mm.

for $d_{T\text{-}Ni} = 6$ mm thick Ni target the sputtering process becomes problematic ($B_{||}$min $\leqslant$ 200 Gs) and it may cause target thickness limitation for effective sputtering process.

4. Ni thin films fabrication

With maximally driven MSS-10 pulsed power supply (period completely filled with pulses), the effective power emitted in a target is proportional to the number of ions bombarding the target. The number of ions (ionization efficiency) is a function of argon pressure (working gas) and magnetic field intensity [1].

Magnetron efficiency with maximal supply power was determined during sputtering of targets with different thicknesses under different argon pressures. In a standard sputtering process MSS-10 supply power can reach up to ~10 kW.

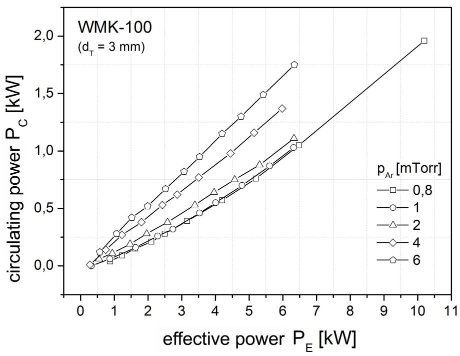

Fig. 3. Circulating power P_C versus effective power P_E during nickel target sputtering under different working gas pressures.

During sputtering of targets with $d_{T\text{-}Ni} = 5$ mm and 6 mm it was not possible to reach full supply power. It was due to magnetic field "shortening", with Ni target being magnetic jumper. During an attempt of sputtering the target with $d_{T\text{-}Ni} = 6$ mm, ignition took place at the argon pressure $p_{Ar} = \sim 0.4$ Pa. In spite of increasing the pressure up to $p_{Ar} = 1.2$ Pa (vacuum stand pump system limit), effective power emitted in the target did not exceed 300 W. It was corresponding to power density around 4 W/cm^2 and allowed deposition of thin layers of Ni on substrates but the process was not efficient. Measurable circulating power was not observed during the sputtering, which unambiguously pointed out insufficient magnetic field intensity above the Ni target. Analogous measurements were conducted for 5 mm thick target. Discharge ignition took place at $p_{Ar} = 0.26$ Pa and even though circulating power was still not measurable, it was possible, at the pressure to $p_{Ar} = 1.2$ Pa, to achieve ~2 kW effective power which corresponded to power density of 13 W/cm^2. Such power could provide efficient Ni thin layers deposition. While using $d_{T\text{-}Ni} = 3$ mm targets, it was possible to use the WMK-100 magnetron and MSS-10 power supply the most efficiently, and perform Ni films deposition, at maximal target power around 10 kW (120 W/cm^2).

The relationship between effective P_E and circulating P_C power during sputtering process was investigated. $P_C(P_E)$ characteristics were measured during $d_{T\text{-}Ni} = 3$ mm Ni targets sputtering (Fig. 3). These characteristics are very useful for the initial sputtering process “recognition” – they may inform about e.g. degree of target wear, phenomena taking place on sputtered material surface in reactive gas environment (e.g. mixture of argon, oxygen and/or nitrogen).

The deposition rate of thin nickel layers was investigated for Ni layers deposited from 3 mm thick target. Working pressure for each deposition process was set to be $p_{Ar} = \sim 0.4$ Pa. Deposited layers thickness were measured by means of interference method. Deposition rate was measured relating the layer thickness to its deposition time. The relation of layer thickness to effective power is shown in Fig. 4.

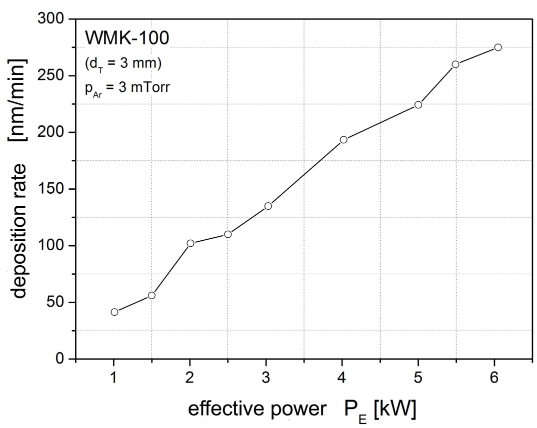

Fig. 4. Deposition rate versus effective power P_E dissipated in Ni target.

Selected electrical parameters of nickel thin layers

Ni layers were optically smooth and characterized by good adhesion to the substrate. Electrical resistance and temperature coefficient of resistance (TCR) were measured for samples sputtered at different sputtering powers. For each investigated case, the calculated resistivity was higher than bulk material resistivity $\rho_{bNi} = 6.9$ μΩ·cm and varied in the range of $\sim$16 μΩ·cm to 20 μΩ·cm, depending on target power. Such result could be expected due to fact that resistivity of thin film is determined by impurities brought into the film during deposition process, defects and size effect. Measurements of temperature coefficient of resistance were carried out for temperature difference $\Delta T \approx 75$ °C. Obtained values of TCR = $\sim$+1500 ppm/°C did not diverge significantly from the values found in the literature.

4.1. Nickel oxide (NiO_x) thin films fabrication

Oxygen doped nickel and nickel oxides layers were obtained as a result of Ni target sputtering in argon and oxygen presence (reactive process). Similarly as before, electrical characteristics were measured in different technological conditions (Fig. 5). Total gas pressure was set at 0.4 Pa. The measurements were made for the following oxygen content: 0 %, 10 %, 16 %, 23 %, 33 % and 66 %, defined as $(p_{O_2}/p_{Ar+O_2}) \times 100$ %. Observed variations in circulating power, as function of oxygen content indicate changes on target surface and around it. At 66 % oxygen content, sputtering was performed in dielectric mode (i.e. target surface fully covered with forming compound: oxide). In characteristics measured for 33 % oxygen content, the magnetron modes depended on effective power: (i) for $P_E < \sim 1.5$ kW – dielectric mode, (ii) ~ 1.5 kW $< P_E < 4$ kW – transient mode, (iii) $P_E > \sim 4$ kW – metallic mode.

The process of oxygen doped NiO_x layers fabrication was conducted under constant effective power of $P_E = 2$ kW. The layers were deposited under different oxygen content in working gas, varying from 3 to 30 %. The aim was to recognize the moment of covering target with nickel oxides.

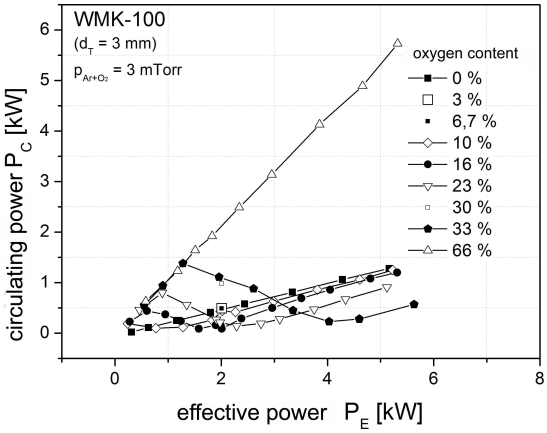

Fig. 5. Effect of oxygen content in working gas mixture on circulating and effective power relation during sputtering of 3 mm thick Ni target.

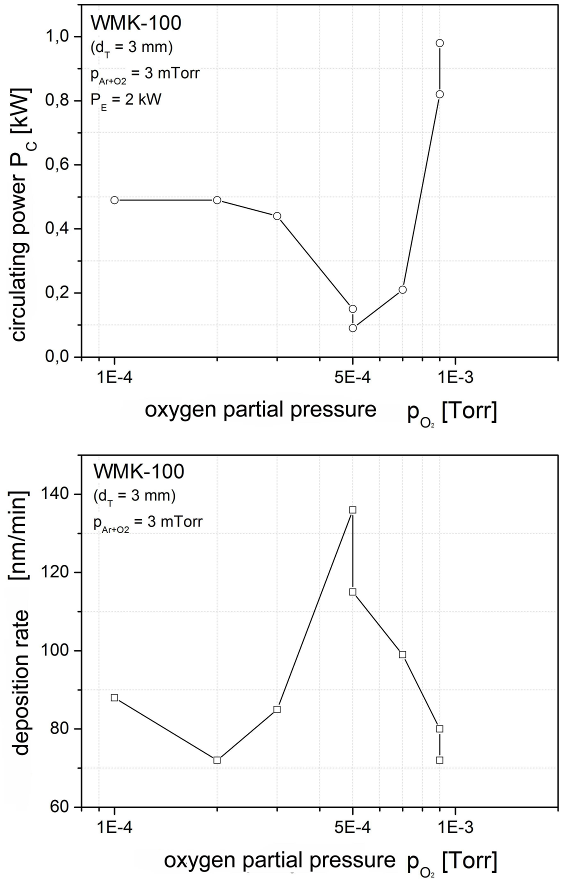

Fig. 6. Effects of oxygen partial pressure on circulating power and deposition rate during sputtering at a constant effective power.

The obtained layers were from 360 nm to 680 nm thick. From the characteristics shown in Fig. 6, it is seen that, the highest deposition rate was achieved for 16.7 % oxygen content in the working gas mixture. The changes in the deposition rate were strictly correlated with the changes in circulating power during the sputtering process, what once again proves usability of these parameters in reactive processes. It may be concluded that, different nickel and oxide compounds, in form of mixtures or different stoichiometry compounds, have been formed on the target surface.

The layers obtained in gas atmosphere with oxygen up to 10 %, were nothing different in appearance (color, roughness) than nickel films obtained in the previous processes; they were silver-white coloured and optically smooth. The films obtained at oxygen content exceeding 10 % were different in color, transparent but the surfaces were matt. The layers deposited on silicon substrates at higher oxygen content were locally exfoliating significantly less than those deposited on glass substrates. Thermal expansion coefficients for nickel oxide, Corning 7059 substrates and silicon are respectively: 32×10^{-6}/K, 4.6×10^{-6}/K and 2.6×10^{-6}/K, which could explain the delamination of NiO_x layers deposited on glass (most likely caused by stress). Due to poor condition of obtained films (deformed-exfoliated), only thickness measurements were done and then deposition rate was calculated (test resistors resistance was not possible to measure).

Electrical resistance and temperature coefficient were measured for the films obtained at 3.3 % and 10 % O_2 content. Properties of the layers obtained at 3.3 % O_2 content were similar to nickel films, their resistivity and TCR were also alike. The layers obtained at 10 % O_2 content had higher resistivity (around 60 μΩ·cm) and lower TCR. It would suggest that the obtained films were most probably nickel films with oxygen built-in but not forming chemical compound with nickel (nickel oxide). In such films. oxygen would act as defect rather but precise conclusion will be possible only after structural characterization, planned in the further investigations. Relating structural variations to circulating power, observed during sputtering processes, is one of further investigations goals. It is anticipated to keep track of deposited films structural changes *in-situ*.

5. Summary

Pulsed magnetron sputtering process of nickel based thin films using circular magnetron WMK-100 was investigated. Sputtering characteristics in pure argon and in argon-oxygen mixture were investigated and the process efficiency (deposition rate) was determined. The layers were deposited on silicon and glass substrates.

Sputtering of 100 mm diameter and 5 mm thick Ni target has not been reported yet in available literature. The results concerning magnetron sputtering of nickel based films achieved in this work prove advantageous parameters of the applied WMK-100 magnetic assembly. Significantly higher power densities (∼120 W/cm^2) in sputtered material (Ni) than reported by other authors have been achieved during sputtering of 3 mm thick target, (2 W/cm^2 to 12 W/cm^2) [2–5]. This resulted in notably higher efficiency of Ni films deposition which is advantagous from economical point of view. During rective sputtering (with higher oxygen content), NiO_x layers with poor adhesion were obtained. Substrate heating and/or electrical polarization could probably reduce or even eliminate this effect. This aspect will be studied in further investigation planned in the future, in particular for thin film for electrochromic device applications.

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