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Nanocomposites deposited by reactive magnetron sputtering and their applications

Streszczenie. *Cienkie warstwy nanokompozytów ze względu na ciekawe właściwości znajdują coraz szersze zastosowanie w różnych gałęziach przemysłu, od elektroniki, przez mechanikę po fotowoltaikę. W pracy zostały przedstawione możliwości wykorzystania reaktywnego rozpylania magnetronowego do nanoszenia warstw kompozytów o rozmiarach charakterystycznych 10 – 300 nm. Omówione zostały właściwości mieszanin tlenków i azotków z metalami (Al, Ti) i wstępnie scharakteryzowane pod kątem możliwych zastosowań.*

Abstract. *Nanocomposite thin films are popular in various industries, from electronics, mechanics to photovoltaics, because of their unusual properties. In paper, the possibility of composite deposition with characteristic size 10 to 300 nm (grains or single layers) with the use of reactive magnetron sputtering technology was indicated. The properties of mixture of oxides or nitrides with metal (Al, Ti) were discussed. The electrical and optical properties of nanocomposites were compared with those of clean oxides and then pre-characterized in terms of possible applications.* ***(Nanokompozyty osadzane metodą rozpylania magnetronowego i ich zastosowania)***

Słowa kluczowe: reaktywne rozpylanie magnetronowe, nanokompozyty, cienkie warstwy.
Keywords: reactive magnetron sputtering, nanocomposites, thin films.

Introduction

Nanocomposites are multiphase solid materials with at least one of the phases of nanometer scale dimensions. This type of coating comprises of no less than two phases: a nanocrystalline phase and an amorphous phase, or two nanocrystalline phases. According to the shape of the crystallites or grains we can broadly classify nanomaterials into four categories [12]: zero (atomic clusters, filaments and cluster assemblies), one (multilayers), two (ultrafine-grained overlayers or buried layers), and three (nanophase materials consisting of nanometer sized grains) as shown in the figure 1. Sputtering of composites from the first category (zero) would be discussed later.

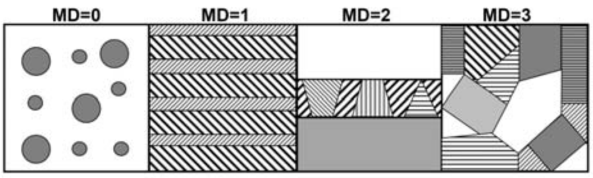

Fig.1 Schematic examples of microstructures for nanostructured coatings

Nanocomposite materials could be found in nature as well as obtained in the laboratory. Materials such as bone, tooth are natural nanocomposites of proteins and minerals which have superior strength [5]. Nanostructured materials received special attention due to their unique structural and physical properties. With very small size of grains or layers the role of boundary regions between phases becomes significant and causes behaviour in a different way compared to the conventional materials. By preparing nanocomposites made of compound films with nano-sized semiconductor or metal particles, we can create systems with unusual optical and electrical properties. Nanostructured materials are becoming increasingly important for electrochemical and electrical energy storage [1,6]. They could be used also as optical coatings with third order nonlinear optical effects, photoluminescence, and photocatalysis [7,11,15].

Magnetron sputtering

Nowadays, the nanocomposite coatings are prepared using many different methods, both physical and chemical [8,9,14]. However, it is magnetron sputtering which seems to be the most suitable for industrial production of the nanocomposite thin films.

Magnetron sputtering is a widely used PVD (Physical Vapour Deposition) technique to deposit thin films and it is based on the generation of a magnetically enhanced glow discharge, so-called magnetron discharge. It is a special diode system, in which over the cathode (target) surface properly directed magnetic field is produced. Secondary electrons are moving in this field producing ions from the working gas. A glow discharge starts when the cathode bias reaches proper value. When a reactive gas is added to the discharge atmosphere, it becomes possible to deposit compound materials. The addition of the reactive gas results in the formation of the compound not only on the substrate but also on the target. This could cause a sudden decrease of the deposition rate and the poisoning effect, which leads to hysteresis of process characteristics. The compound formation on the etched target surface defines mode of magnetron work [2]. The metallic mode refers to sputtering of material not covered with compound, transient refers to partially covered and reactive mode to fully covered.

One of main advantages of the magnetron sputtering is a nonequilibrium process at an atomic level. The Condensing atoms have a high energy compared with, for example the evaporation process (several eV to about 0.1 eV). It is quite simply to sputter alloys and their compounds, such as nitrides, oxides and carbides, as well as it is possible to form a nanocomposite [3]. The formation of high-temperature phases on unheated substrates is also the great advantage. Moreover, in most cases magnetron sputtering process could be scaled-up from the laboratory to industrial application.

Experimental details

The sputtering processes were performed in a vacuum system equipped with a rotary and diffusion pump with a pumping speed of 2000 l/s. The final pressure of the deposition chamber was about 2.6 mPa. In the presented research the unbalanced WMK-50 magnetron was used. The titanium and aluminium target with 50 mm in diameter was sputtered in a mixture of working gas – argon and reactive gas – oxygen or nitride with total gas pressure 0.53 Pa. Gas inflow was placed on the top of vacuum chamber (50 cm from magnetron source). The partial pressure was measured by ion gauge. The available maximum target power density was about 1000 W/cm2. Thin films were deposited on silicon and Corning 7059 glass substrates at a substrate–target distance $d_{S\text{–}T}$ = 80 mm. The medium frequency sputtering processes were carried out using the Dora Power Supply (DPS—5kW) operating at a frequency of 100 kHz with a 4 kHz pulse quantity modulation (PQM) for the output power control [4,10]. The effective power was 1.5 kW.

Results

With DPS power supply it is possible to control magnetron sputtering process in situ and indicate modes of magnetron work. The use of this power supply allows to control sputtering process based on power supply parameter – circulating power P_C is very useful. It is sensitive to any changes in discharge plasma impedance, especially to ion induced secondary electron emission. This helped to determine working point for nanocomposite deposition, because P_C was changing with reactive gas partial pressure (Fig.2.). For aluminium it was right before circulating power sudden increased.

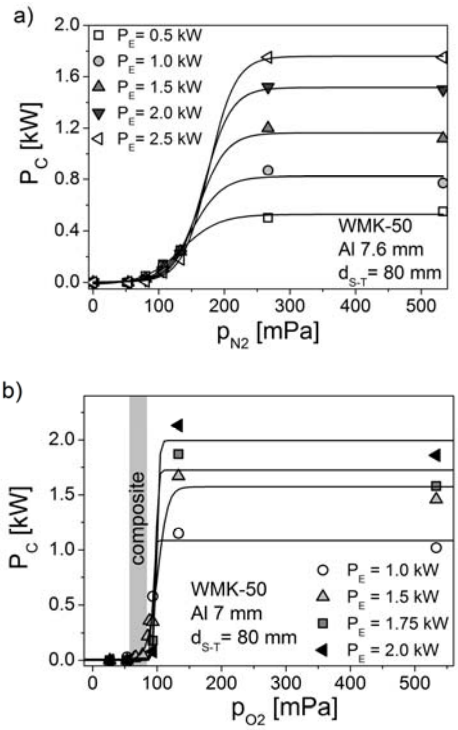

Fig.2. Circulating power P_C versus reactive gas partial pressure for magnetron sputtering of Al target: a) sputtering in N_2+Ar gas mixture b) sputtering in O_2+Ar gas mixture

Simultaneously deposition of compound matrix and metal grains could be realized only in metallic mode of magnetron work. The amount of metal species is then high enough to form metal grains on substrate surface. Moreover, in metallic mode the process could be carried out without extra control equipment. In transient mode the hysteresis effect could be observed, which makes the control of sputtering quite complicated and the amount of metal cluster is too low to change significant material properties.

One of the disadvantages of this method is quite chaotic distribution of metal clusters. They could form single grains (~100 nm) as well as combine in group of clusters (Fig.3). The density of metal inclusions also depends on the profile of the deposition. The result is more intensive metal grains formation in front of the magnetron 'race track'- the area of highest target erosion. The significant influence of magnetron sputtering process parameters on electrical properties of thin film could be seen for aluminium oxide deposition. The nanocomposite materials (p_r = 69 - 75 mPa) differed from dielectric film (88 mPa). In the impedance spectra of composites lower capacity and significant dispersion could be observed (Fig.4). This kind of materials could be used, for example, as charge trapping thin film.

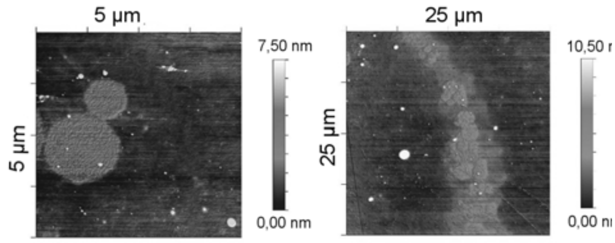

Fig.3. Topographic AFM images of Al_xO_y+Al composite surface

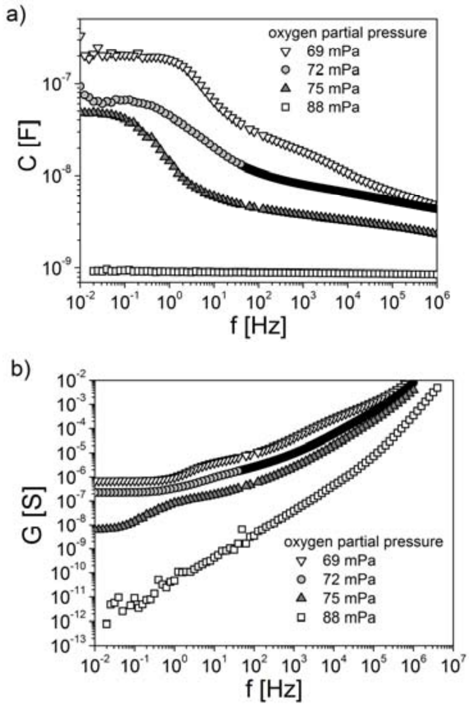

Fig.4. Impedance spectra of the Al–(Al_xO_y + Al)–Al structure for different oxygen partial pressures: a) capacitance, b) conductance.

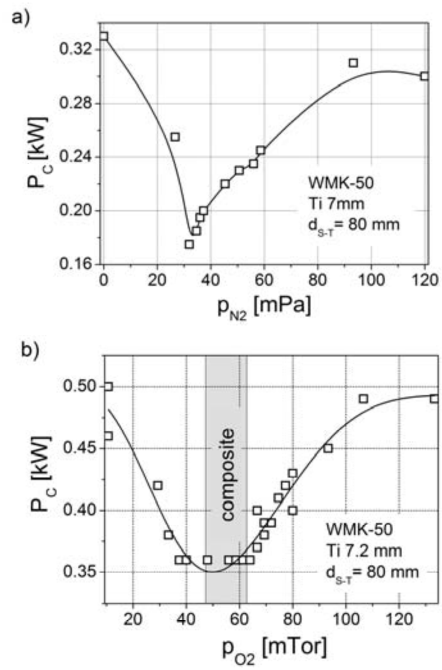

Fig.5. Circulating power P_C versus reactive gas partial pressure for magnetron sputtering of Ti target: a) sputtering in N_2+Ar gas mixture b) sputtering in O_2+Ar gas mixture

The process control with the circulating power did not work ideally in every case. For example, sputtering of titanium in $Ar+N_2$ or $Ar+O_2$ gas mixture exhibited some extraordinary electrical characteristics of the target. It was already reported for cathode voltage behaviour [13]. Reactive sputtering of titanium had minima and maxima of the circulating power as the target got more and more poisoned (Fig. 5). However, with proper calibration, repeatable deposition of $Ti-TiO_2$ nanocomposite could be achieved.

Optical properties of deposited titanium oxide films were investigated. $Ti-TiO_2$ is promising material for optical applications, especially for transparent slightly conductive coatings. The $Ti-TiO_2$ nanocomposite was transparent with metallic blue shine. It had interesting characteristic of refractive index compared to stoichiometric TiO_2 film (Fig.6) and at the same time it could be a conductive material (Fig.7).

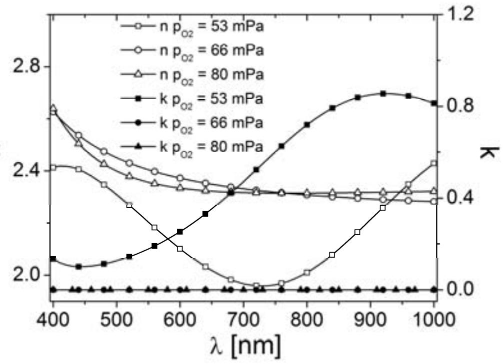

Fig.6. $Ti-TiO_2$ thin films - n and k versus wavelength for three different oxygen partial pressures

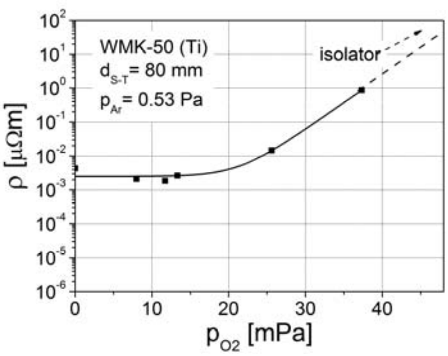

Fig.7. Resistivity versus reactive gas partial pressure of $Ti-TiO_2$ thin films

It is possible to use oxygen deficient titanium dioxide as static charge elimination coating for example on spacecraft surfaces such as solar panels. $Ti-TiO_2$ films are easier to deposit than combination of ITO (Indium tin oxide) and insulator materials. In all presented cases sputtering in metallic mode of magnetron process provided high efficiency close to characteristic for metallic film deposition. Thanks to this, magnetron technology could be used in industrial applications.

Conclusions

It is possible to deposit nanocomposites using magnetron sputtering technology, thanks to deposition in metallic mode of magnetron work. This method implicates the amorphous structure of material matrix and composition rich in metallic phase. Due to magnetron sputtering technology limits, the distribution of grains is chaotic and their density in single layer depends on the sputtering profile. On the other hand, the amount of metal grains could be controlled by reactive gas partial pressure and power supply parameters. The small modify of process environment could diametrically change amount of nano-grains and hence properties of thin film. This enables the use of sputtered nanocomposites in a range of new applications also in industrial scale, owing to high efficiency and simple scaling-up of magnetron sputtering technology.

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REFERENCES

[1] Aricò A. S., Bruce P. et al., Nanostructured materials for advanced energy conversion and storage devices, *Nature materials*, 4 (2005), 366-377.
[2] Berg S., Nyberg T., Fundamental understanding and modeling of reactive sputtering processes, *Thin Solid Films*, 476 (2005), 2, 215- 230.
[3] Cavaleiro A., De Hosson J., *Nanostructured Coatings*, Springer–Verlag, 2006.
[4] Dora J., Polish Patent No. 313150, 1996.
[5] Ji B., Gao H., Mechanical properties of nanostructure of biological materials, *Journal of the Mechanics and Physics of Solids*, 52 (2004), 9, 1963-1990.
[6] Liu Y., Chen T.P. et al., Charging effect of Al2O3 thin films containing Al nanocrystals, *Applied Physics Letters*, 93 (2008), 142106.
[7] Long H., Chen A. et al., Third-order optical nonlinearities in anatase and rutile TiO2 thin films, *Thin Solid Films*, 517 (2009), 19, 5601-5604.
[8] Musil J., Hard and superhard nanocomposite coatings, *Surface and Coatings Technology,* 125 (2000), 1- 3, 322- 330
[9] Musil J., Bell A. J. et al, Formation of high temperature phases in sputter deposited Ti-based films below 100◦C, *Journal of Vacuum Science Technology A*, 14 (1996), 4, 2247- 2250
[10] Posadowski W.M., Wiatrowski A., Dora J., Radzimski Z., Magnetron sputtering process control by medium-frequency power supply parameter, *Thin Solid Films,* 516 (2008), 14, 4478-4482.
[11] Revaux A., Dantelle G. et al., Synthesis of YAG: Ce/TiO2 nanocomposite films, *Optical Materials*, 33 (2011), 7, 1124-1127.
[12] Siegel R.W., Nanophase Materials, *Encyclopedia of Applied Physics*, VCH Publishing, Weinheim, Germany, 11 (1994), 173-200.
[13] Sproul W.D, Christie D.J., Carter D.C., Control of reactive sputtering processes, *Thin Solid Films*, 491 (2005), 1- 2, 1-17.
[14] Veprek S., Nesladek P. et al., Recent progress in the superhard nanocrystalline composites: Towards their industrialization and understanding of the origin of the superhardness, *Surface and Coatings Technology*, 108–109 (1998), 138-147.
[15] Yu J., Xiong J., Cheng B., Liu S., Fabrication and characterization of Ag–TiO2 multiphase nanocomposite thin films with enhanced photocatalytic activity, *Applied Catalysis B: Environmental*, 60 (2005), 3- 4, 211-221.

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