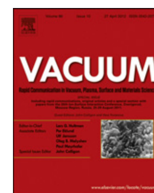
Vacuum 87 (2013) 96–102

Contents lists available at SciVerse ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum



High-rate pulsed reactive magnetron sputtering of oxide nanocomposite coatings

Jindrich Musil*, Pavel Baroch

Department of Physics, Faculty of Applied Sciences, University of West Bohemia, Univerzitni 22, 306 14 Plzen, Czech Republic

ARTICLE INFO

Article history:
Received 17 June 2011
Received in revised form
24 November 2011
Accepted 20 February 2012

Keywords:
Reactive magnetron sputtering
Dual magnetron
Nanocomposite coatings
Thermal stability
Oxidation resistance
Toughness

ABSTRACT

The article reports on the oxide nanocomposite coatings reactively sputtered by a pulsed dual magnetron and is divided into two parts. The first part briefly describes main problems in the reactive sputtering of oxides, i.e. low deposition rate a_D and arcing at the target surface and then focuses on the discharge of the dual magnetron. The ways how a_D can be increased and arcing eliminated are shown. The second part is devoted to transparent oxide coatings. Two types of oxide coatings are described in detail: (1) Si–Zr–O coatings containing ≤5 at.% of Zr and (2) Zr–Al–O coatings with Zr/Al > 1. It is shown that (a) Si–Zr–O coatings exhibit high thermal stability up to 1500 °C, almost 100% optical transparency and can be deposited with very high $a_D \approx 800$ nm/min from a molten magnetron target and (b) Zr–Al–O coatings with relatively high hardness $H \approx 18$–19 GPa, low effective Young's modulus E^* satisfying the ratio $H/E^* > 0.1$ are highly elastic (the elastic recovery $W_e > 70\%$) and exhibit an enhanced resistance to cracking. The last finding is of key importance for development of new hard coatings with enhanced toughness.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Reactive magnetron sputtering is a process where the metallic target is sputtered by positive ions incident at its surface from the discharge generated by a magnetron in a mixture of argon and reactive gas (RG). The target sputtering is controlled by a sputtering yield γ which is determined by the chemical composition (ChC) of the target surface and the energy of incident ions E_i, i.e. $\gamma = f(\text{ChC}, E_i)$. It means that the target sputtering depends on the flow rate φ_{RG} of the RG, the magnetron discharge voltage U_d (E_i is approximately proportional to U_d) and the discharge current I_d, i.e. on the power delivered to the sputtered target.

In the formation of oxides the oxygen is used as RG. The sputtering process gradually changes from the sputtering in the metallic mode (MM) through the sputtering in the transition mode (TM) to the sputtering in the oxide mode (OM) as φ_{O2} increases [1–4], see a schematic illustration of the reactive magnetron sputtering process displayed in Fig. 1. The metallic mode is characterized by the highest deposition rate a_D of sputtered films and by very low values of the partial pressure of oxygen p_{O2} because almost all oxygen atoms and molecules in the deposition device are gettered by sputtered atoms [5]. The transition mode is characterized by a very rapid (avalanche) conversion of the target surface from the metal (Me) to the MeO_x oxide, called "the target poisoning", which is accompanied by (i) increase of p_{O2}, (ii) decrease of a_D and (iii) strong instability of the sputtering process (stabilization of the operation point OP on $a_D = f(\varphi_{O2})$ is very difficult). The oxide mode is characterized by (i) the lowest value of a_D, (ii) linear increase of p_{O2} with increasing φ_{O2} because the whole target surface is already fully oxidized and (iii) the decrease of U_d compared to that measured in pure argon, for instance, when Al, Si, Zr, Mg, etc. targets are used or the increase of U_d in the case when Ag, Au, Cr, Cu, Nb, Pt, Re, Ti etc. targets are used [6–8]. The conversion of the target surface from metallic to oxide results in a hysteresis effect. It is an undesirable effect which can be, however, eliminated if a pumping speed S of the deposition device is greater than a critical value S_{cr} [9].

1.1. Deposition rate of transparent oxides

The highest transparency of oxide films is obtained for stoichiometric films. These films can be easily formed in the oxide mode. However, the main problem is a *very low deposition rate* a_D of oxide films formed in OM of sputtering. The deposition rate a_D of transparent oxide films formed in OM of sputtering is approximately 10–12 times lower than the deposition rate $a_{D\ in\ MM}$ of films sputtered in MM, i.e. $a_{D\ in\ OM} < 0.1\ a_{D\ in\ MM}$.

The increase of a_D of some transparent oxide films, e.g. Al_2O_3, SiO_2, MgO, etc. produced in OM is very difficult task because the plasma impedance of the magnetron discharge and the discharge

* Corresponding author. Tel.: +42 377632200; fax: +42 377632202.
E-mail address: musil@kfy.zcu.cz (J. Musil).

0042-207X/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.vacuum.2012.02.023

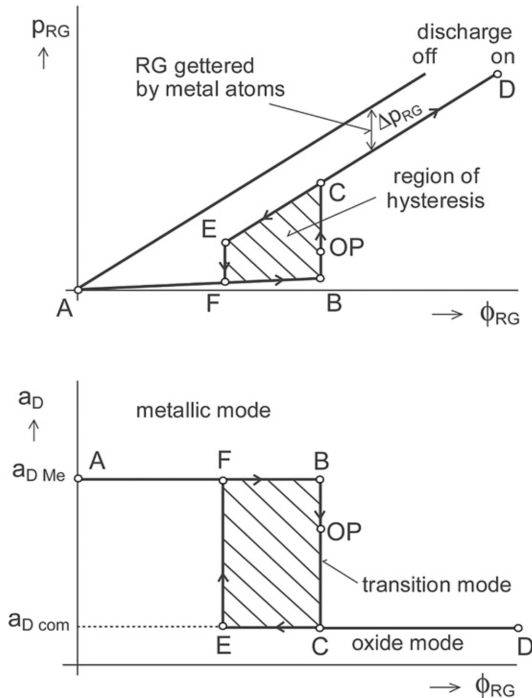


Fig. 1. Schematic illustration of reactive magnetron sputtering of oxide films from metallic target. Adapted after Ref. [3].

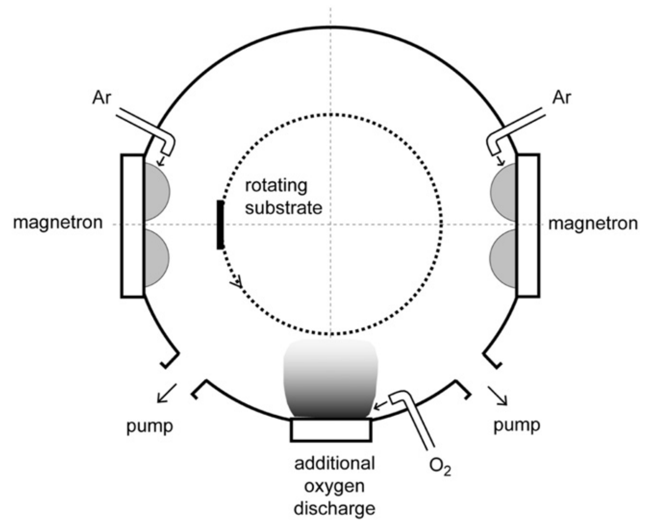


Fig. 2. Schematic illustration of deposition device used for *interrupted reactive sputtering process* of transparent oxide films with additional oxygen discharge. Substrate is rotating and oxygen discharge is separated from one or more magnetron discharges by efficient pumping units. This process is patented as the MetaMode™ process [10].

voltage U_d are low due to an efficient production of secondary electrons at oxidized target. Low U_d results in a low sputtering yield γ, which depends on the energy of incident ions, i.e. $\gamma = f(E_i \propto U_d)$, and thus results also in a low deposition rate $a_{D\ in\ OM}$ of oxide films sputtered in OM. The increase of power P_d delivered to the magnetron discharge is not an efficient way to significantly increase the deposition rate $a_{D\ in\ OM}$ of transparent oxide films in OM because the increase of the power to the magnetron results in further decrease of the plasma impedance and thus in a minimal rise of U_d.

At present, there are three ways enabling to deposit transparent oxide films with $a_D > a_{D\ in\ OM}$: (1) the intensification of magnetron discharge, production of higher amount of atomic oxygen O at a given partial pressure of oxygen p_{O2} and shift of the operation point OP from OM (the line CD) to TM of sputtering, (2) the interrupted reactive sputtering as schematically illustrated in Fig. 2 and (3) the pulsed magnetron sputtering with the target power density $W_t = P_d/S_t \geq 100\ W/cm^2$; S_t is the whole area of sputtered target. Last two methods operate with deficiency of O and continuous oxidation of Me atoms in intervals between the exposure of film surface to the flux of Me atoms sputtered from magnetron target or between pulses applied to magnetron target. These methods make it possible to deposit transparent oxide films with deposition rate a_D close to $a_{D\ in\ MM}$.

Deposition rates a_D of oxide films approaching $a_{D\ in\ MM}$ are, however, still insufficient in applications where very thick films (hundreds of micrometers) are required. For these applications extremely high rates a_D are needed. These extremely high rates a_D can be achieved if oxides are reactively deposited from a molten magnetron target [11]. As the target power density W_t is increased the sputtering is gradually transformed first to the sublimation and later to a combined sputtering + evaporation process. This fact is illustrated in Fig. 3. Here the evolution of a_D of Si–Zr–O oxide films, reactively deposited on glass substrate at the $d_{s\text{-}t} = 80$ mm, the substrate temperature $T_s = 500\ °C$ and the total pressure $p_T = p_{Ar} + p_{O2} = 1$ Pa, is displayed as a function of W_{ta}. At $W_{ta} > (W_{ta})_{cr}$ the evaporation dominates over sputtering and extremely high $a_D \gg a_{D\ in\ MM}$ is achieved. As can be seen from Fig. 3, Si–Zr–O oxide films containing ~3 at.% of Zr were deposited with $a_D = 530$ nm/min.

1.2. Elimination of arcing in reactive sputtering

The reactive magnetron sputtering of electrically insulating compounds (e.g. MgO, TiO_2, Al_2O_3, SiO_2, etc.) from a metallic target (Mg, Ti, Al, Si, etc.) is accompanied by undesirable arcing on uneroded areas of target surface covered by a dielectric layer. The arcing occurs when a positive electric charge accumulated on uneroded areas achieves a critical value necessary for its discharging to the well electrically conductive metallic surfaces (the surface of target under the erosion zone, the surface of magnetron hidden anode, etc.). The arcing results in an uncontrollable damage of the deposited films by the evaporated material and in instability of the reactive sputtering process. Both phenomena are undesirable and therefore the arcing must be eliminated. To avoid the arcing the

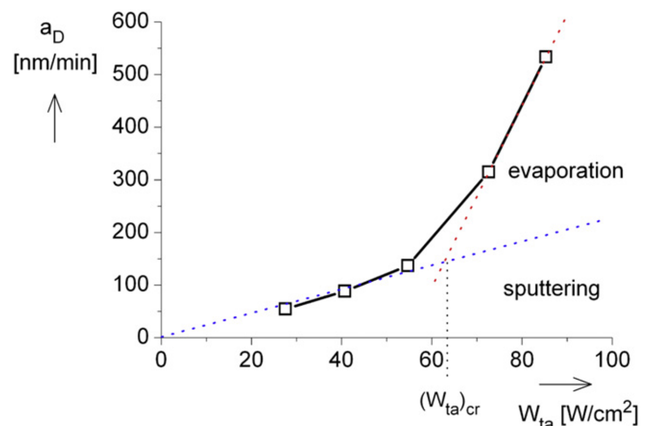


Fig. 3. Deposition rate a_D of transparent Si–Zr–O oxide films, reactively deposited by AC pulsed dual magnetron at $d_{s\text{-}t} = 80$ mm, as a function of target power density W_{ta} averaged over the pulse period [11].

Download English Version:

https://daneshyari.com/en/article/8045368

Download Persian Version:

https://daneshyari.com/article/8045368

Daneshyari.com