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Reactive magnetron sputtering of thin films: present status and trends

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Abstract

This paper gives a critical review of the present state of the knowledge in the field of dc reactive magnetron sputtering of compound films. It analyses (i) the hysteresis effect and the methods of its elimination, (ii) problem of stability of reactive sputtering and (iii) deposition of transparent oxides in the transition mode of sputtering. It shows the conditions under which oxides are reactively sputtered with high deposition rates $a_{D\ oxide}$ achieving up to approximately 77% of that of a pure metal $a_{D\ Me}$, i.e. $a_{D\ oxide}/a_{D\ Me} \approx 0.77$. A special attention is devoted to the elimination of arcing in sputtering of insulating films using pulsed dual magnetron or sputtering of oxides from a substoichiometric target. Also, the ion bombardment of films growing on insulating or unbiased substrates in dc pulsed magnetron sputtering is discussed in detail. As an example, a new possibility to form superhard single-phase films based on solid solutions using dc reactive magnetron sputtering is shown. At the end, future trends in dc reactive magnetron sputtering are outlined.

Keywords: DC continuous and pulsed reactive magnetron sputtering; Compounds; Deposition rate; Nanocomposites; Film properties

1. Introduction

Since approximately 1980, a reactive sputtering of thin films is intensively investigated because the sputtering of metallic targets in the presence of reactive gas (RG) makes it possible to easily form compound films, such as nitrides, oxides, carbides or their combinations. The reactive sputtering process can be, according to the amount of RG used in the film deposition, divided into three modes: (a) metallic, (b) transition and (c) reactive. A typical characteristic of the reactive magnetron sputtering is a low deposition rate of compounds $a_{D\ com}$ produced in the reactive mode compared to that of the pure metallic or alloyed films $a_{D\ Me}$ produced in the metallic mode (see Fig. 1a). The ratio $a_{D\ Me}/a_{D\ com}$ is relatively small (3–4) for nitrides but achieves high (10–15) values for oxides.

The decrease in a_D of films sputtered in the reactive mode is due to a reaction of the RG with the surface of the sputtered target and its conversion to a compound, for instance, Ti changes to TiN or TiO_2 when nitrogen or oxygen is used as RG. This results in (1) decrease of (i) sputtering yield ($\gamma_{Me}>\gamma_{com}$, e.g. $\gamma_{Ti}>\gamma_{TiN}$) and (ii) magnetron discharge voltage U_d and (2) rise of the hysteresis effect (see Fig. 1b). The decrease in a_D strongly depends particularly on the material of the sputtered target and the kind of RG. The electrical conductivity of the sputtered target after its reaction with RG is also important. When the reaction product is electrically insulated, two further problems occur: (1) non-sputtered surfaces of the target (very significant in planar magnetrons) are covered by thick dielectric layers, which are charged up, and cause an arcing when the charge achieves a threshold value; and (2) the anode of the magnetron disappears also due to its dielectric layer cover.

From this short survey, it is seen that there are three main limitations of the reactive sputtering: (1) hysteresis effect, (2) jump transition from the metallic to the reactive mode of sputtering, which exclude to produce compound films in a certain interval of their stoichiometry x defined, for instance, as x=N/Ti for the TiN_x film, and (3) arcing and "disappearing anode", when dielectric films are sputtered. In

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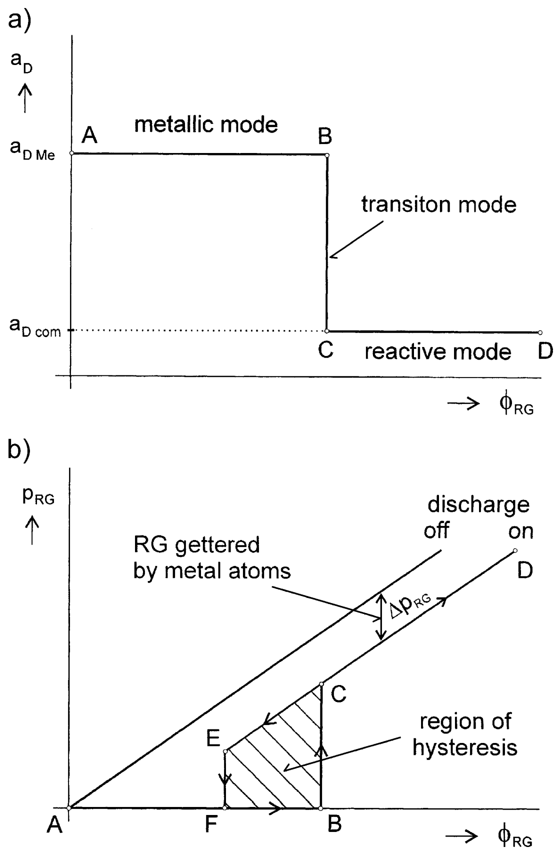

Fig. 1. Schematic illustration of (a) deposition rate, a_D, of sputtered films, and (b) partial pressure of RG, p_{RG} as a function of flow rate of RG, ϕ_{RG}.

recent years, some of these limitations were already successfully overcome as reported by excellent review articles [1–20]. This paper reviews the present state-of-the-art in the high-rate reactive magnetron sputtering of compound films with prescribed stoichiometry and elimination of arcing when deposited films are dielectric. A special attention is devoted to reactive magnetron sputtering of nanocomposite coatings composed of a mixture of very fine grains of different crystallographic orientations. The formation of ionized atoms of sputtered material during dc pulse sputtering at high (>500 W/cm^2) target power densities is also briefly given.

2. Hysteresis effect

Many problems encountered in the preparation of non-stoichiometric compound films by reactive sputtering are due to a hysteresis effect (see Fig. 1). This effect arises in consequence of two competitive processes: (1) the sputtering of the target surface and (2) the covering of its surface by reaction products. Fig. 1b illustrates the dependence of RG partial pressure, p_{RG}, as a function of the flow rate, ϕ_{RG}, of the RG supplied into the deposition chamber with and without discharge. The hysteresis occurs in the presence of discharge only.

At low values of the RG flow rate ϕ_{RG} (interval AB), all RG is gettered by the sputtered metal. At point B, the flow rate ϕ_{RG}(B) into the chamber is equal to the gettering rate of sputtered metal. Every small increase in ϕ_{RG} results in a sudden (1) increase of p_{RG} in the deposition chamber and (2) decrease of the film deposition rate a_D. A further increase of ϕ_{RG} (interval CD) results in a linear increase of p_{RG} and almost constant a_D, which is typical for reactive mode of sputtering. The decrease of ϕ_{RG} from D to E is accompanied by decrease of p_{RG}, but a return to the metallic mode (interval EC) is delayed. This is because p_{RG} remains high until a compound layer on the surface of the sputtered target is fully removed and metal is again exposed to be sputtered. As a result, the consumption of RG increases and p_{RG} decreases to the background level. A closed hysteresis loop is formed in this way.

The hysteresis is an undesirable phenomenon because it (1) prevents to form MeRG$_x$ compound films with stoichiometry x corresponding to p_{RG} in the interval BC; here Me=Ti, Cr, Zr, etc., and RG=N, O, C, B, etc., and (2) is responsible for unstable sputtering at ϕ_{RG} in a close vicinity of the transition from BC. Therefore, a considerable effort has been devoted to find means for its elimination. First, it was suggested by Maniv et al. [21] to introduce a baffle between the substrate and the target with Ar inlet into the baffle and RG inlet into the system on the substrate side. However, this modified magnetron system called "baffled" magnetron suffers from three principal drawbacks: (1) frequent cleaning of the baffle grid, (2) reduction of the metal flux to the substrate through grid and (3) reduction of plasma bombardment of the growing film if the baffle is grounded. Despite those, the last problem may be solved by either placing a positively biased electrode in the substrate region to pull out the plasma from the baffle, or by biasing the substrate. This solution is not, however, suitable for an industrial production. For this purpose, simple systems with no obstacles, such as the baffles or grids, between the sputtered target and the substrate, are needed. It requires either fully eliminating the hysteresis effect or ensuring a stable sputtering in the transition mode. These requirements meet sputtering systems with a pumping speed S larger than a critical pumping speed, S_c [22–24], sputtering systems controlled by plasma emission monitoring (PEM) [25,26] or gas pulsing [27,28], dual magnetrons [12,29], magnetrons with a full target erosion [30–33], magnetrons equipped with substoichiometric ceramic targets [34], and recently developed advanced closed field dual target sputtering systems without magnetron racetrack.

3. Elimination of hysteresis with a high pumping speed of the pumping system

A condition necessary for the elimination of the hysteresis effect can be derived from an equilibrium state between the gettering of RG by sputtered material and the