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Characterization of the hardness and the substrate fluxes during reactive magnetron sputtering of TiN

S. Mahieu *, D. Depla, R. De Gryse

Ghent University, Department for Solid State Sciences, Krijgslaan 281/S1, 9000 Ghent, Belgium

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Abstract

Aiming for enhanced mechanical properties, materials are coated with thin films. However, despite all efforts, basic relations between mechanical properties of the thin film and its intrinsic properties, i.e. stochiometry, microstructure, and crystallographic orientation are still relatively unclear. TiN thin films were grown by means of reactive magnetron sputter deposition. By varying the target–substrate distance and the N_2-flow, a relation between the resulting thin film hardness and the ion, momentum, and energy flux towards the substrate during deposition is investigated.

Keywords: Reactive magnetron sputtering; TiN; Hardness; Energy flux; Ion flux; Momentun flux

1. Introduction

The thin film community is seeking for new deposition methods and/or thin film structures to obtain coatings with improved mechanical properties. Actually, most research is focusing on the development of High Power Impulse Magnetron Sputtering (HPPMS) [1,2], and on the development of nanostructured [3] or nanocomposite [4] thin films. However, although the growth and properties of TiN films deposited by magnetron sputtering have been extensively studied and reported in literature [5–8], the fundamental relations between the deposition parameters and the mechanical properties of the TiN films are not yet fully understood.

Many deposition parameters, even often related to each other, can influence the final film properties such as the hardness. The same deposition parameters will also influence all fluxes towards the substrate during deposition. For instance, the metallic, ion, momentum, and energy flux will be a function of many deposition parameters. Finally, also the intrinsic film properties, such as the microstructure, crystallographic orientation, stoichiometry, and density will be influenced. In principle, the direct relation between the deposition parameters and the final film could be determined. However, finding out this relation is a tremendous task, due to the huge amount of deposition parameters, which are sometimes difficult to control, e.g. the target usage, chamber wall conditions, impurity flux… Therefore, a more convenient approach can be to look for a relation between the fluxes towards the substrate on the one hand, and the intrinsic and final properties of the thin film on the other hand.

In this work, the hardness and crystallographic out-of-plane orientation of TiN films deposited as a function of the target–substrate distance d_{T-S} and N_2-flow will be compared to the calculated ion/Ti, momentum/Ti and energy/Ti flux ratios.

2. Experimental setup and results

TiN thin films with a thickness between 1 and 1.5 μm were deposited on amorphous glass or stainless steel substrate by unbalanced reactive magnetron sputtering of a Ti target in an Ar/N_2 mixture. The substrates were not heated intentionally. The discharge current was kept constant at 0.9 A, the discharge pressure at 0.55 Pa, and the total flow ($Ar+N_2$) at 60 sccm. d_{T-S} was changed from 7 to 15 cm and the N_2-flow from 3 to 18 sccm, always resulting in stoichiometric TiN films, as measured with XPS and EDX. The out-of-plane orientation was measured by XRD θ/2θ (Brüker D8) and the hardness with nano-indentation,

* Corresponding author. Tel.: +32 9 264 43 73.
E-mail address: stijn.mahieu@ugent.be (S. Mahieu).

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using a Micro Materials apparatus (Nanotest 600, with Berkovitch tip). Indentations were made to penetration depths of 200 nm. The hardness was calculated by using the method of Oliver and Pharr [9].

The results of these measurements are shown in Figs. 1 and 2. As observed in Fig. 2, the hardness increases with increasing N_2-flow and with decreasing d_{T-S}. The hardness of the TiN films deposited at low d_{T-S} and high N_2-flow could not be measured accurately due to a rather bad adhesion.

3. Calculated fluxes towards the substrate

3.1. Metallic Ti flux

In order to determine the ion, momentum and energy flux per incoming Ti particle, the Ti-flux towards the substrate as a function of d_{T-S} and N_2-flow need to be determined first.

The deposition rate can be deduced by dividing the film thickness with the deposition time. The thickness of the deposited TiN layers has been measured by profilometry and by Scanning Electron Microscopy of a cross-section. However, the Ti-flux towards the substrate could not be deduced from this experimentally determined deposition rate, since the influence of d_{T-S} and N_2-flow on the film density is unknown.

Therefore, a thickness monitor (Maxtek, Thickness monitor, TM200-R) was mounted into the vacuum chamber, at the position of the substrate. The flux of metallic Ti-particles has been measured as a function of the target–substrate distance (7–15 cm) for a Ti target sputtered in 0.55 Pa, 60 sccm Ar. The same influence of d_{T-S} on the metallic flux towards the substrate has been modeled by a binary collision Monte Carlo code [10]. Both methods (simulation and thickness monitor) show that the metallic flux decreases more or less with a $1/(d_{T-S})^2$ rule.

The relative influence of the N_2-flow on the metallic Ti-flux was measured by mass spectrometry. Therefore, an energy resolved mass spectrometer (Pfeiffer Vacuum, PPM421) was installed at the position of the substrate. Due to a too low sensitivity of the mass spectrometer for fast neutrals, the signal of positive ions with a mass of 48 amu (Ti^+) and 62 amu (TiN^+) were measured. Since the ionization degree is hardly influenced by the N_2-flow, as was checked by Langmuir probe and cylindrical probe measurements, the influence of the N_2-flow on the normalized incoming ($Ti^+ + TiN^+$) flux is equal to its influence on the normalized (Ti + TiN) flux towards the substrate.

The influence of d_{T-S} and the N_2-flow on the Ti-flux towards the substrate is shown in Fig. 3. This Ti-flux decreases strongly with increasing N_2-flow due to target poisoning.

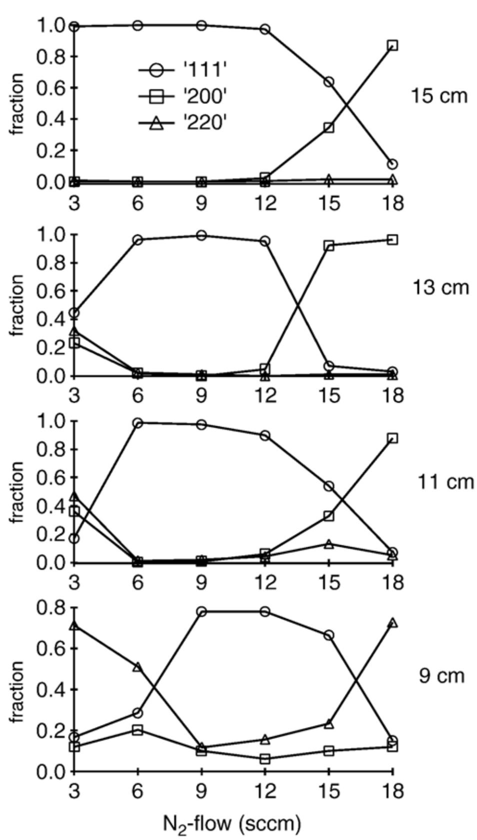

Fig. 1. Evolution of the volume fraction of (111), (002) and (220)-oriented grains, as a function of the target–substrate distance and N_2-flow.

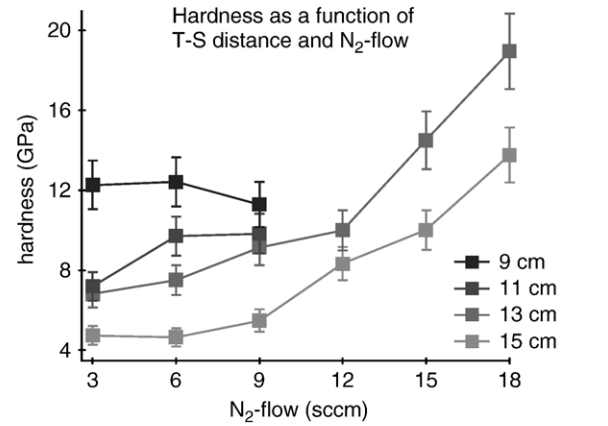

Fig. 2. Evolution of the hardness of the TiN films, as a function of the target–substrate distance and N_2-flow as measured by nano-indentation. The indentation depth was limited to 200 nm, avoiding a possible influence of the substrate. The TiN films deposited at small target–substrate distance and high N_2-flow could not be measured due to a too bad adhesion.

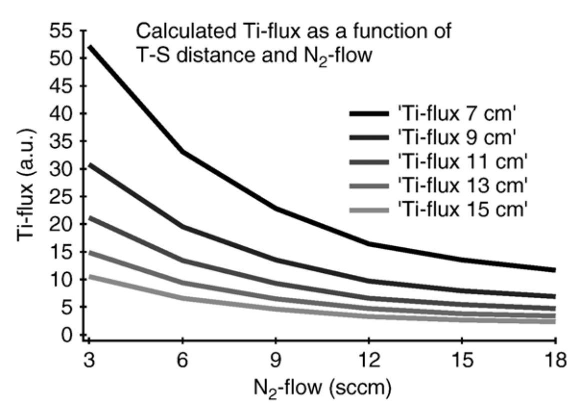

Fig. 3. Influence of the target–substrate distance and the N_2-flow on the calculated Ti-flux towards the substrate.