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CrN thin films deposited by HiPIMS in DOMS mode

F. Ferreira *, J.C. Oliveira, A. Cavaleiro

SEG-CEMUC, Mechanical Engineering Department, University of Coimbra, Polo II, Rua Luís Reis Santos, 3030-788 Coimbra, Portugal

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ABSTRACT

It is well known that increasing the energy of the bombardment species, whether by using a bias or an additional ion source in direct current magnetron sputtering (DCMS) or by optimizing the deposition conditions in mid-frequency bipolar magnetron sputtering, enables us to tailor the properties of the CrN thin films. In the last fifteen years, several magnetron sputtering deposition methods have been developed which have aimed to produce highly ionized fluxes of sputtered material, thus enabling increased control over the energy and impinging angle distributions of the bombarding species. In this study, CrN thin films were deposited by deep oscillation magnetron sputtering (DOMS), a variant of High-power Impulse Magnetron Sputtering (HiPIMS), in order to study the effect of the additional control of the energetic ion bombardment on the film properties. The structural properties of the CrN films (lattice parameter and preferred orientation) showed that an intense energetic bombardment is always present in the DOMS deposition irrespective of the deposition conditions. This energetic bombardment was attributed to energetic N neutrals which are reflected at the target surface upon impingement of N_2^+ ions. A change from a columnar growth mode to a featureless one was observed with an increasing peak power at both 0.3 and 0.7 Pa. At the same time, the hardness of the films increased from 21–22 GPa to 28–29 GPa. This transformation was attributed to the increasing fraction of ionized sputtered species with increasing peak power. The columnar growth is interrupted by preventing the shadowing effect, i.e., due to the higher ionization fraction at higher pressure and/or peak power, rather than by overcoming the shadowing effect by using more energetic bombardment.

1. Introduction

In the past few decades, CrN films have been widely used in many engineering applications due to their considerable hardness, resistance to wear, low friction coefficients and high temperature stability [1–9]. Nowadays, both DC magnetron sputtering (DCMS) [3–6] and mid-frequency bipolar magnetron sputtering [8] are well-established methods for the reactive magnetron sputtering of CrN thin films. From the process point of view, relatively low levels of ion bombardment result in CrN films with [111] preferred orientation, lower stresses, lower hardness and lower density. Increasing the bombardment level gradually changes the preferential orientation to [002] or [220], while denser, harder and smoother coatings are deposited. The [002] or [220] preferred orientations can be obtained, for example, by increasing the deposition bias [5–7] or by enhancing the energetic bombardment in mid-frequency bipolar magnetron sputtering [9]. However, improvement in the mechanical properties of the coatings brings about a simultaneous increase in the film compressive stresses, which are detrimental in service. Zou et al. [10] also showed that the hardness of CrN films deposited by mid-frequency bipolar magnetron sputtering could be increased from 13 to 25 GPa by using an additional ion source. Once again, the increase in hardness occurred simultaneously with a preferential orientation change from [111] to [002]. The above results show that careful control of the ion bombardment is crucial for optimizing the properties of the CrN films.

In the last fifteen years, several magnetron sputtering deposition methods have been developed with the aim of producing highly ionized fluxes of sputtered material, thus enabling increased control over the energetic ion bombardment (energy and direction of the deposited species). Two of these recent developments are: High-power Impulse Magnetron Sputtering (HiPIMS) [11–14] and Modulated Pulsed Power Magnetron Sputtering (MPPMS) [15–17]. Both HiPIMS and MPPMS rely on the application of very high target power densities to increase the plasma density and therefore ionize the sputtered material. Such deposition conditions have been shown to be very useful for the tailoring of the microstructure and properties of CrN coatings [18–25]. Ehiasarian et al. [18] deposited dense and columnar CrN films by HiPIMS, clearly harder than conventional PVD CrN and with superior corrosion and wear resistant properties. Paulitsch et al. [19] showed that HIPIMS is much more versatile than DCMS for process up-scaling. The hardness of the CrN films (≈23 GPa) was maintained even when a 3-fold substrate rotation was used, while the hardness of the films deposited by DCMS decreased to less than 15 GPa. Lin et al. [22] also demonstrate that MPPMS enables the deposition of CrN films with higher hardness (25–26 GPa) than their DCMS counterpart (16 GPa). In a series of

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* Corresponding author.
E-mail address: fabio.ferreira@dem.uc.pt (F. Ferreira).

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studies [23–25] these authors also showed that MPPMS allows for the deposition of thick films (up to 55 μm) with high deposition rates.

Recently, a new deposition process, called deep oscillation magnetron sputtering (DOMS), was developed, based on MPPMS [26–30]. This process uses large voltage oscillation packets in long modulated pulses in order to attain high peak target currents and voltages. Such a configuration has been reported to decrease arcing in reactive deposition of insulating films and even allow virtually arc-free depositions. In a previous publication, the authors have shown that the microstructure of TiSiN films can be effectively tailored by changing the peak power in the DOMS process [30]. Two deposition regimes were identified. At low peak power, stress-free TiSiN films with [002] preferred orientation and a high degree of hardness (nearly 25 GPa) could be deposited. Increasing the peak power, i.e. increasing the bombardment intensity, resulted in an increase in hardness of up to 30 GPa, albeit with a concomitant increase in the films' defects and compressive stress, in a very similar fashion to that in the DCMS process. The main objective of the present work was to study the effect of the energetic ion bombardment of the growing films on the properties of CrN thin films deposited by DOMS. The energetic ion bombardment was controlled by changing the peak power and the deposition pressure (0.3 and 0.7 Pa). The structure, morphology and mechanical properties of CrN coatings were characterized. A CrN thin film was also deposited by DC magnetron sputtering (DCMS), using previously optimized deposition conditions, for reference purposes.

2. Experimental procedure

CrN films were deposited in reactive mode by DOMS (HiPIMS Cyprium™ III plasma generator, Zpulser Inc.) and DCMS (Hüttinger PFG 7500 DC). In both cases a square (150 × 150 mm) high purity Cr (99.9%) target was sputtered in reactive mode. Typical examples of the discharge voltage and current oscillating waveforms of the DOMS process are shown in Fig. 1. A DOMS pulse is made of a packet of 25 sequential single oscillations. In each oscillation both the voltage and the current gradually increase during the on-time (t_{on}) until they reach their maximum value (V_p and I_p). Then, both the voltage and current gradually decay, reaching zero before the end of the oscillation period (T). The DOMS depositions were performed using constant on-time (t_{on}), oscillation period (T) and pulse duration (D) of 6, 40 and 1000 μs respectively. The average power was controlled by the DOMS power supply software by automatic adjustment of the pulse frequency (F). A constant average power (Pa) of 1200 W was used in all depositions. In this study the peak voltage (V_p) and peak current (I_p) were calculated as the average value of the maximums of the voltage and current, respectively, in each oscillation, taking all the oscillations into account. The peak power (P_p) is defined as the product $V_p \times I_p$. A CrN film was deposited by DCMS using the same time average power (1200 W) as was used in the DOMS depositions. The DCMS film was deposited at 0.3 Pa with a bias of −80 V, resulting in a deposition voltage of −412 V and a 3 A.

All coatings were deposited onto (100) silicon samples. Prior to depositions, the substrates were ultrasonically cleaned in acetone for 15 min and [in] alcohol for 10 min. They were then fixed to a rotating substrate holder which revolved at 23.5 rev/min around the central axis of the chamber. Prior to all depositions a base pressure lower than 5×10^{-3} Pa was attained in the deposition chamber. The target to substrate distance was 80 mm. All the depositions were performed in reactive mode in an $Ar + N_2$ discharge gas. The $Ar:N_2$ gas flow ratio was maintained at 1:3. In order to enhance the adhesion of coatings a Cr adhesion layer of approximately 0.2 μm was deposited on the substrates before the final CrN layers.

The peak power was varied by progressively increasing the charging voltage (DC_{int}) of the DOMS power supply from 250 to 400 V. To further diversify the bombarding conditions on the growing films, two different deposition pressures were used (0.3 and 0.7 Pa). The main DOMS deposition parameters are compiled in Table 1. As shown in Fig. 2 using the values from Table 1 for the films deposited at 0.3 Pa, both I_p and V_p increased almost linearly with increasing peak power. A similar behaviour was found for the films deposited at 0.7 Pa (not shown).

The structure of CrN coatings was characterized by X-ray diffraction (XRD) (PANalytical X'Pert PRO MPD) with Cu Kα radiation (45 kV and 40 mA) using a parallel beam in symmetrical θ–2θ geometry. The XRD spectra were fitted using a pseudo-Voigt function to calculate both the area and the position (2θ) of the peaks. The lattice parameter was calculated by applying the Bragg's equation and using the geometrical relationship between the lattice parameter and the interplanar distance and Miller indices. The fracture cross section and surface morphologies of the coatings were examined by scanning electron microscopy (SEM). The composition of the CrN films was evaluated by Energy Dispersive Spectroscopy (EDS) using a CrN thin film previously studied by Electron Probe Micro-Analysis (EPMA) as standard. The hardness and Young's modulus of the films were evaluated by the depth-sensing indentation technique (Micro Materials NanoTest) using a Berkovich diamond pyramid indenter. A load of 8 mN was used in all the tests, in order to ensure an indentation depth of less than 10% of the coating's thickness. 16 hardness measurements were performed on each specimen.

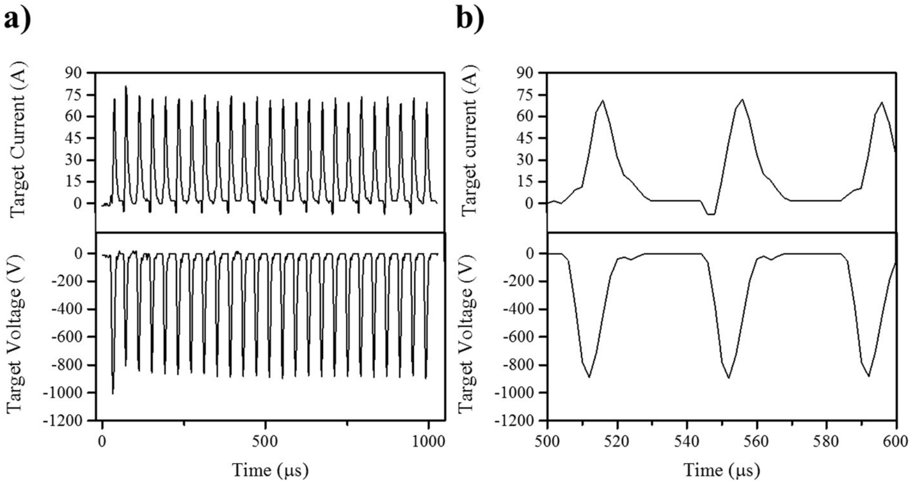

Fig. 1. a) The target voltage and current oscillation waveforms measured during the CrN coating depositions. b) Small oscillation pulses within one long pulse (P = 0.7 Pa; DC_{int} = 300 V; F = 233 Hz; D = 1000 μs; t_{on} = 6 μs; T = 40 μs).