Surface & Coatings Technology 205 (2010) 118–130

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Microstructure control of CrN_x films during high power impulse magnetron sputtering

G. Greczynski [a,*], J. Jensen [a], J. Böhlmark [b,1], L. Hultman [a]

[a] Thin Film Physics Division, Department of Physics (IFM), Linköping University, SE-581 83, Sweden
[b] Sandvik Tooling RTC, Lerkrogsvägen 19, SE-126 80 Stockholm, Sweden

ARTICLE INFO

Article history:
Received 17 March 2010
Accepted in revised form 5 June 2010
Available online 11 June 2010

Keywords:
High power pulsed magnetron sputtering
HPPMS
High power impulse magnetron sputtering
HIPIMS
CrN
Magnetron sputtering

ABSTRACT

The microstructure and composition of CrN_x ($0 \le x \le 1$) films grown by reactive high power pulsed magnetron sputtering (HIPIMS or HPPMS) have been studied as a function of the process parameters: N_2-to-Ar discharge gas ratio, ($f_{N2/Ar}$), negative substrate bias (V_s), pulsing frequency, and energy per pulse. The film stoichiometry is found to be determined by the composition of the material flux incident upon the substrate during the active phase of the discharge with no nitrogen uptake between the high power pulses. Scanning electron microscopy investigations reveal that for $0 < f_{N2/Ar} < 0.15$ and 150 V bias, a columnar film growth is suppressed in favor of nano-sized grain structure. The phenomenon is ascribed to the high flux of doubly charged Cr ions and appears to be a unique feature of HIPIMS. The microstructure of column-less films for $100\ V \le V_s \le 150\ V$ is dominated by the CrN and hexagonal β-Cr_2N phases and shows a high sensitivity to V_s. As the amplitude of V_s decreases to 40 V and self-biased condition, the film morphology evolves to a dense columnar structure. This is accompanied by an increase in the average surface roughness from 0.25 nm to 2.4 nm. CrN_x samples grown at $f_{N2/Ar} \ge 0.3$ are columnar and show high compressive stress levels ranging from −7.1 GPa at $f_{N2/Ar} = 0.3$ to −9.6 GPa at $f_{N2/Ar} = 1$. The power-normalized deposition rate decreases with increasing pulse energy, independent of $f_{N2/Ar}$. This effect is found to be closely related to the increased ion content in the plasma as determined by optical emission spectroscopy. The HIPIMS deposition rate normalized to DC rate decreases linearly with increasing relative ion content in the plasma, independent of $f_{N2/Ar}$ and pulsing frequency, in agreement with the so-called target-pathways model. Increasing frequency leads to a finer grain structure and a partial suppression of the columnar growth, which is attributed to the corresponding increase of the time-averaged mean energy of film-forming ions arriving at the substrate.

1. Introduction

High power impulse magnetron sputtering (HIPIMS or HPPMS) is a sputtering technique that relies on the creation of high-density plasma in front of the sputtering source [1]. The increase in plasma density is achieved by increasing the peak power applied to the target in short (typically less than 100 μs) pulses, with a low (a few percent) duty factor. Since the thermal load of the target is limited by the average power rather than the peak power, the latter quantity can be very high during the active phase of a discharge. The applied voltage can reach a couple of kilovolts, resulting in a peak discharge current density of the order of a few amperes per square centimeter and a peak power density of several kilowatts per square centimeter. This results in electron densities exceeding $10^{19}\ m^{-3}$ in the vicinity of the magnetron [2–4]. The high density of electrons increases the probability for electron impact ionization of the sputtered atoms, and results in a highly ionized flux of target material [1,3,5]. The high degree of ionization opens new opportunities for film design, since the ions may be controlled by the use of electric and magnetic fields [6] through ion–surface interactions. Specially, the energy of film-forming ions arriving at a surface may be steered by the use of a substrate bias, which strongly affects the properties of the growing film [7]. A high degree of target ion content created in the vicinity of the target surface is a reason for the commonly observed drop in the deposition rate [8–10] which has been associated with the HIPIMS technique. This is in contrast to the conventional ionized PVD where the secondary plasma is created away from the target to ionize the flux of sputtered atoms on its way to the substrate [11]. The former effect is believed to be caused by the fact that a certain fraction of the ionized flux of target material is back-attracted by the cathode field, which results in a severe rate drop especially for materials characterized by low self-sputtering yields [12,13].

Up to date HIPIMS has been used in the reactive mode to deposit a number of industrially-attractive coatings [14–23]. Despite the still growing number of publications dealing with characterizations of thin

* Corresponding author. Tel.: +46 13 28 1213.
E-mail address: grzgr@ifm.liu.se (G. Greczynski).
[1] Previously at Chemfilt Ionsputtering AB.

0257-8972/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2010.06.016

films prepared using this technique a basic parameter study revealing the nature of the reactive HIPIMS processing is missing.

The focus of this work is the effect on the film growth from process parameters that are unique to HIPIMS, namely pulsing frequency (f), energy delivered to the target in each pulse (E_p) and pulsed negative substrate bias (V_S). CrN was chosen as a model system due to the limited reactivity of Cr towards nitrogen (resulting in a high partial pressure required for a turnover from metallic to nitrided target state), which allows for a better control of film composition while investigating the relationship between the flow of reactive gas and the pulsing frequency [24]. In contrast, N-rich CrN_x films have been deposited by a number of sputtering techniques and are relatively well characterized [25–31].

2. Experimental

All film depositions were performed in an industrial CC800/9 coating system manufactured by CemeCon AG in Germany [32]. The base pressure of the vacuum chamber is 2×10^{-3} Pa. A single rectangular Cr target of dimensions 88×500 mm² was sputtered in Ar/N_2 atmosphere. HIPIMS power supplies integrated into the coating unit were employed, except for the part of the studies on dependence on substrate bias in Sec. 3.3, where the cathode was operated by an external Sinex 3 power supply manufactured by Chemfilt Ionsputtering AB, Sweden. Control experiments indicated no significant dependence of the resulting film microstructure on the type of power supply used. Silicon (001) wafers with a native oxide layer were used as substrates. Prior to depositions, the substrates were ultrasonically cleaned in acetone and isopropanol. For each film, the deposition process consisted of the following steps: (1) radiation heating (2 kW heating power for 30 min), (2) radiation heating (0.5 kW heating power for 30 min) resulting in the substrate temperature, $T_s\approx200$ °C and the background pressure of the order of 1–2 mPa, (3) deposition of a ~30 nm thick Cr film in order to improve adhesion and reduce stress at the substrate interface (heating power kept at 0.5 kW), and (4) deposition of CrN_x films (typically: 40 min at 300 Hz and scaled correspondingly for other frequencies to keep the total number of pulses constant). All films were deposited at a constant total pressure of 0.4 Pa. Resulting film thickness was in the range from 0.8 to 2.1 μm, depending on the amount of nitrogen in the sputtering gas mixture. The peak power levels achieved in these experiments were of the order of 240 kW, resulting in the peak power density of 0.55 kW/cm² (calculated for the whole target area) while the average power density did not exceed 5.2 W/cm². A Tektronix DPO4054 500 MHz bandwidth digital oscilloscope was used to monitor and record the current and voltage transients during all depositions.

Elemental composition of the films was measured by Time-of-Flight Elastic Recoil Detection Analysis (ToF-ERDA) at the Tandem Laboratory in Uppsala, Sweden. The primary ion beam was 40 MeV $^{127}I^{9+}$ ions, the recoil scattering angle was 45°, and the incident angle was 67.5° relative to the surface normal. The obtained ToF-ERDA data were evaluated using the CONTES code [33]. Cross-sectional electron microscopy investigations were carried out on fractured films using LEO 1550 FEG scanning electron microscope. The crystalline structure was determined by XRD with a Philips diffractometer operated in $\theta-2\theta$ mode using Cu Kα radiation. For each sample, a set of $\theta-2\theta$ scans was recorded at the tilt angle, ψ , scanned between 0° and 85° (in steps of 5°) allowing for (i) accurate identification of crystal phases present, (ii) determination of film texture, and (iii) residual stress estimation by the $\sin^2\psi$ method using Young modulus values derived from nanoindentation tests (E varying between 281.5 GPa and 323.6 GPa) and the Poisson ratio, $\nu=0.2$, in order to be consistent with other authors [26]. Since tilting of the sample affects the paths of incident and diffracted X-ray beams, all $\theta-2\theta$ scans were corrected with the absorption factors according to the procedure described in [34]. AFM was performed using a Veeco Dimension 3100 instrument with a Nanoscope IIIa controller. The optical emission spectroscopy (OES) signal was measured in the line-of-sight geometry with the probe placed outside the port window of the chamber (cf. [32]) and directed towards the race track. Here, a spectrometer (Mechelle Sensicam 900) connected to a collimator via an optical fiber was used to record the emission from the plasma. The spectral range of the spectrometer was 300–1100 nm. The shutter speed of the spectrometer was set to 100 ms allowing for data averaging over multiple HIPIMS pulses. Measured line intensities were corrected for transition probabilities and level degeneracy using the database by Kurucz et al. [35] and following a procedure described elsewhere [5,36].

The pulse energy, E_p, is defined here as the integral of the product of target current, $I(t)$, and target voltage, $V(t)$, over the pulse period, $T=1/f$, $E_p=\int_0^T dtV(t)I(t)$. It is emphasized that any variation of E_p corresponds to change in the value of the peak target current, as the pulse width is kept constant at 200 μs.

3. Results and discussion

This part of the paper is organized as follows. In Sec. 3.1 film growth rates and film compositions for different pulsing frequencies are analyzed as a function of $f_{N2/Ar}$ (at the constant total pressure of 0.4 Pa) with the help of cross-sectional SEM and ToF-ERDA. Important aspects of kinetics during film formation are discussed including the issue of inter-relation between nitrogen partial pressure, pulsing frequency, and resulting film composition. For this analysis, E_p was chosen such that a significant ionization of the target material could be achieved (roughly one-to-one ratio in the bulk of the plasma, as determined by OES). The frequency was set in the middle of the power supply specification (300 Hz) in order to allow for potential adjustments later on. The negative sample bias, V_s, was set relatively high (150 V) in order to manifest ion bombardment effects, in case any differences should appear while varying $f_{N2/Ar}$. The rest of the paper is divided into sections discussing changes in the film microstructure as a function of: gas composition (Sec. 3.2), substrate bias (Sec. 3.3), pulse energy (Sec. 3.4), and pulsing frequency (Sec. 3.5). The samples of relevance are listed in Table 1 along with essential process parameters.

3.1. Film growth and composition

The changes in deposition rate with increasing nitrogen fraction in the sputtering gas mixture are shown in Fig. 1A, whereas trends in the resulting film composition are depicted in Fig. 1B. Similar to conventional reactive sputtering, an increased flow of reactive gas leads to a drop in the deposition rate of the HIPIMS process due to the target poisoning. However, in contrast to DC operation, where the condition of the target is determined by the flow of the reactive gas, an additional "knob" exists in the present case; namely that of the pulsing frequency. It is a unique feature of reactive HIPIMS that the typical pause between the pulses (usually 1–10 ms) matches quite well monolayer formation times for typically used partial pressures of the reactive gas (of the order of 0.1–1.0 Pa). This means that the degree of target poisoning may be steered by varying the pulsing frequency allowing for (some) control over the growth rate (per pulse) and the nitrogen content in the film. This is illustrated in Fig. 1A. A comparison between the growth rates obtained at different frequencies indicates that, indeed, the deposition rate per pulse scales with increasing pulsing frequency, independent of $f_{N2/Ar}$. The difference is particularly significant between 100 Hz and 300 Hz, while very subtle between 300 Hz and 500 Hz. Similar trends are also observed for self-biased films as discussed below.

The film composition determined from ToF-ERDA is shown in Fig. 1B. As expected, for a given pulsing frequency and sample bias, a decreasing