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Topographical evolution of sputtered chromium nitride thin films

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Abstract

The modification of the morphology, with special emphasis on the topographical evolution, of chromium nitride thin films has been studied by varying the sputter power, bias voltage, temperature, total pressure and Ar/N_2 ratio in an unbalanced magnetron sputtering process. Six different topography types (here designated pyramid, grain, crater, cone, ribbon and hillock) were identified. The growth conditions for each topography type are specified and summarized in a topography zone model showing the occurrence of each as function of temperature, Ar/N_2 ratio, deposition rate and bias voltage. Furthermore, the relationship between the size of the topographical features and the deposition parameters was investigated and is reported in detail. The control of topographical type and feature size appears sufficient to hold promise of generating topographies designed for specific functions.

Keywords: Chromium nitride; Film morphology; Surface topography; Growth mechanism

1. Introduction

In recent years, the importance of understanding and controlling the surface topography of films for their functionality has been recognized and is intensively investigated. One of the most popular phenomena in this context is the self-cleaning behaviour of surfaces (lotus effect); it has been demonstrated that super-hydrophobic coatings require not only low-surface energy, but also a certain surface topography (see for example, [1–3]). Recently, there has been a medical research focus on how cell growth or bacterial adhesion is influenced by the topography of coatings deposited onto implants and surgical instruments [4–7]. Other examples where the coating topography can have a major effect on functionality can be found in tribological coatings [8–10], optical coatings [11] or thermal barrier coatings [12,13]. Thus, knowledge about the correlation between deposition parameters and the topographical appearance of thin films and, further, the ability to modify the geometric dimensions of the topographical features in a controlled manner would provide a path for better exploitation (optimization) of topography-related properties of thin films and might result in a new approach for nanostructuring of thin films.

Over the last decades different models have been presented to describe coating morphology as a function of extrinsic or intrinsic process parameters [14–19]. However, these models were mainly focused on the evolution of the film microstructure and less on the surface topography of the films. Systematic investigations of the correlations between topography and deposition parameters with special focus on the modification of the topographical features as function of the process parameters have not been carried out for thin films, for chromium nitride (CrN films) in particular.

The goal of this work is to investigate the relationship between deposition parameters and the topography of the deposited thin film. For this purpose, the different topography types obtainable predictably by varying the deposition parameters need to be determined. Then the key deposition parameters influencing the topographical evolution were identified, and the growth conditions for each type of topography were specified. Furthermore, it was investigated how changes in process parameters modify the dimensions of the topographical features.

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This study was carried out for CrN, since CrN is well-established as a coating material in a wide range of applications, in which the topography may also influence the performance of the coating. For example, chromium nitride films offer potential for uses as tribological coatings [20,21], optical coatings, especially for selective solar absorbers [22–24], and in the field of microtechnology as diffusion barrier coatings in microelectronics [25,26], in phase-shift masks for photolithography [27] and in etch-resistant hardmasks for X-ray absorber patterning [28]. Quite recently, the application of chromium nitride films in nanostructuring of polymer surfaces has been shown [29].

2. Experimental work

2.1. Deposition experiments

The CrN films were deposited on polished Si wafers with (100) orientation by unbalanced magnetron (UBM) sputtering of chromium targets (99.9% Cr, Polema Ltd.) in argon/nitrogen atmospheres in the commercial deposition system Hauzer HTC 1000/4 which is described elsewhere [30].

After inserting the substrates, the chamber was evacuated to a base pressure of 0.005 Pa and then heated up to achieve the particular substrate temperature. Next, the silicon substrates were cleaned by Cr ion etching (15 min, 100 A, −1000 V and 200 sccm argon flow) from a cathodic arc evaporation source. Immediately after the ion etching, the deposition of the CrN film was started. The deposition time was always set to 4 h. In order to study the modification of the CrN morphology as function of the deposition process, the process parameters substrate temperature, bias voltage, the ratio of argon to nitrogen flow, the total pressure and the sputter power were varied in a systematic manner. The values applied for the parameters in the different deposition experiments are summarized in Table 1.

The ratio of ion flux J_i to atom flux J_a was calculated for all deposition experiments according to the following equation [31]:

$$\frac{J_i}{J_a} = \frac{M_r \cdot m_u \cdot i_i}{\rho \cdot e \cdot a_d} \quad (1)$$

where M_r is the average relative mass of a film-forming atom, m_u is the mass unit, i_i is the ion current density, ρ is the film density, e is the elementary charge and a_d is the deposition rate. All depositions were carried at relatively low ion to atom flux ratios of $J_i/J_a < 2$.

Since the deposition rate a_d is affected by a wide range of parameters (e.g. sputter rate, bias voltage, Ar/N_2 ratio), it varies in the different deposition experiments of this study. Thus, the deposition rate a_d was determined from the film thickness, t_f, measured on cleaved CrN coated wafers by scanning electron microscopy, and the deposition time t_d simply as

$$a_d = \frac{t_f}{t_d} \quad (2)$$

The substrate temperature was monitored by thermocouples attached to the substrate holders and therefore exposed to the same conditions as the substrates throughout the deposition process. The power to the two resistive-element heaters in the chamber was adjusted according to the readings of the thermocouples. Following common usage [14–19], the homologous temperature T/T_m (for melting temperature T_m) is considered instead of the substrate temperature T in the rest of this report. Because the process parameters vary over a wide range, the films obtained can consist of Cr_2N, CrN or mixed phases. Based on data found in literature [32,33], the melting temperature appears to be similar for Cr_2N and CrN and is taken to be $T_m = 1500$ °C. Hence, deposition experiments were carried out at homologous temperatures of $T/T_m = 0.10$, 0.17, 0.23 or 0.30, respectively.

Table 1
Values of the process parameters applied to deposit CrN thin films

Process parameter	Applied values
Substrate temperature (T)	150, 250, 350, 450 °C
Bias voltage (U_b)	−50[a], −75, −125[a], −150, −200[a], −250, −350, −300[a], −450, −600[a] V
Argon flow/nitrogen flow ratio (Ar/N_2)	0.7, 1.1, 1.3, 1.5
Total pressure	0.4, 1.0 Pa
Sputter power	2, 4, 6, 8, 10 kW

[a] Applied only in selected experiments.

The magnetrons were driven by 5 kW Advanced Energy MDX Direct Current power supplies. An additional MDX power supply was used as the substrate bias supply. The magnetron drivers were operated in power regulation mode, whereas the bias supply was operated in voltage regulation mode. A defined argon/nitrogen ratio was obtained by adjusting the gas flows of argon (purity: 99.5%) and nitrogen (purity: 99.5%) resulting in the total pressure in the deposition chamber.

2.2. Film morphology

To evaluate the morphology (microstructure and topography), all deposited films were examined by scanning electron microscopy (SEM, PHILIPS FEG 30 XL) and selected samples by transmission electron microscopy (TEM, PHILIPS XM-200 LaB6 source). Cross-sectional specimens for the TEM investigations were prepared as follows: two 10×5 mm^2 specimens were glued face to face using an epoxy resin of low viscosity, and then cut perpendicular to the coating–substrate interface into slices with an approximate thickness of 2 mm. After grinding and polishing down to 20 μm, each thin specimen was attached to a Ti holder for ion milling. The final thinning was performed by argon ion milling (BAL TEC RES 100): the rough milling was carried out in oscillation mode using a voltage of 4 kV at a current of 2.5 mA and incidence angle of 20° angle. For the fine polishing, the voltage was reduced to 3 kV and the incident angle was adjusted to between 3° and 5°.

The height H and the lateral dimension L of the topographical features of the types pyramid (P), grain (G), cone (C), ribbon (R) and hillock (H) were determined from the SEM images. The definition of the lateral dimensions is shown in Fig. 12 for those topography types. The dimensions of at least 50 features were measured for each topography type to provide a statistical guarantee for the measurement results. Since the features of