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Mechanical properties optimization of tungsten nitride thin films grown by reactive sputtering and laser ablation

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ABSTRACT

Transition metal nitrides coatings are used as protective coatings against wear and corrosion. Their mechanical properties can be tailored by tuning the nitrogen content during film synthesis. The relationship between thin film preparation conditions and mechanical properties for tungsten nitride films is not as well understood as other transition metal nitrides, like titanium nitride. We report the synthesis of tungsten nitride films grown by reactive sputtering and laser ablation in the ambient of N_2 or N_2/Ar mixture at various pressures on stainless steel substrates at 400 C. The composition of the films was determined by XPS. The optimal mechanical properties were found by nanoindentation based on the determination of the proper deposition conditions. As nitrogen pressure was increased during processing, the stoichiometry and hardness changed from W_9N to W_4N and 30.8–38.7 GPa, respectively, for films deposited by reactive sputtering, and from W_6N to W_2N and 19.5–27.7 GPa, respectively, for those deposited by laser ablation.

1. Introduction

The term of hard coatings is applied to structures which improve wear resistance and extend the lifetime of the structure. Hard coatings are industrially used onto cutting tools, automotive engine parts, turbine blades, structural components, etc [1,2]. Traditionally, materials utilized as hard coatings had a single composition, crystalline phase, and microstructure. Some of the most common hard coatings used as thin films are diamond-like carbon (DLC), BN, B_4C, SiC, Al_2O_3, Si_3N_4 and WC [1]. A growing interest in the synthesis of transition metal nitrides has risen due to their chemical inertness and high hardness to be used as wear-resistant and hard protective coatings. In particular, TiN thin films and nanocomposites using TiN satisfy these requirements and have been extensively investigated by a variety of deposition techniques in the recent literature [1–5]. For instance, there is a close relationship between film composition and its mechanical properties for TiN films [3]. However, there are not as many reports as expected on other transition metal nitrides.

Tungsten nitride films have generated considerable interest in the manufacturing of semiconductor devices because they are an excellent barrier for Cu diffusion into Si at high temperatures [6]. The deposition of diffusion barriers motivated the synthesis of WN_x thin films by several techniques like CVD [7–9], dc reactive sputtering [10–13], ALD [14], rf reactive sputtering [15,16], ion beam sputtering [17], reactive laser ablation [18,19] and cathodic arc [20]. There are reports concerning to the mechanical properties of alloys containing tungsten nitride sputtered coatings, like Cr–W–N [21], Ti–W–N [22] and Si–W–N [23]. WN_x thin films are also a good candidate to be used as a hard coating [9,13,16,19,20]. The composition, mass density, electrical and optical properties of WN_x thin films on silicon wafers at room temperature grown by reactive laser ablation have been already published by our group but the study of the mechanical properties was missing [18]. This study investigates the best possible mechanical properties as a function of film composition and microstructure for WN_x coatings on stainless steel substrates synthesized by two different deposition techniques: reactive sputtering and laser ablation.

2. Experiment

As previously mentioned, the WN_x thin films were grown by two different deposition methods: RPLD and dc-sputtering. The experiment was carried out in a laser ablation system described elsewhere [24]. The system consists of three UHV stainless steel chambers: sample introduction, growth and analysis, as shown in Fig. 1. The base pressure of the chambers is approximately 10^{-7} Pa. A KrF excimer laser is focused onto a high purity (99.9% at.) tungsten disc of 5 cm in diameter at an angle of 50° off the surface normal in the growth or deposition chamber. The values of laser

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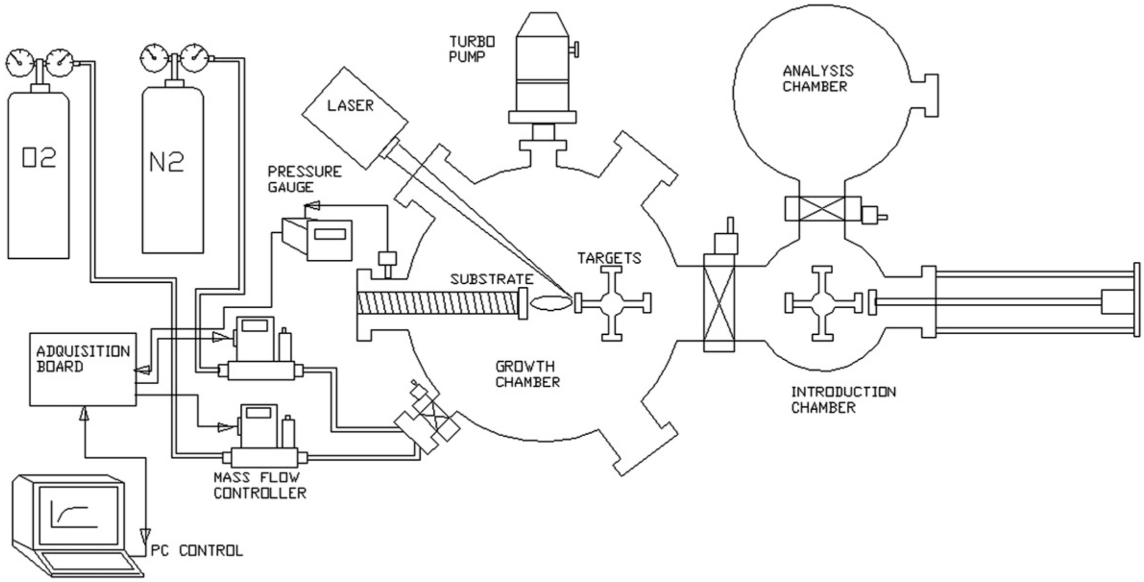

Fig. 1. Cross sectional view of the reactive pulsed laser deposition system. The gas control system is also displayed.

energy, number of pulses, and repetition rate were optimized in a previous experiment and were kept fixed at 260 mJ, 18,000 and 5 Hz, respectively [18]. The film composition was studied by introducing N_2 gas in the 0–10.0 Pa range. The ablated species were deposited on stainless steel ANSI304 substrates kept at 400 °C. Every film was *in situ* characterized by XPS at the end of the film processing.

The films were also grown in a reactive dc magnetron sputtering system, as shown in Fig. 2. A current-regulated dc power supply was used to provide a discharge with an input power of 100 W and a target-substrate separation of 3 cm. The target diameter and thickness are 5 cm and 0.6 cm, respectively. The power density is approximately 5 W/cm^2 with an input current of 170 mA. The WN_x films were grown on stainless steel ANSI304 substrates at 400 C by using the same tungsten target described above. Prior to deposition, the system was pumped down to a base pressure of 10^{-3} Pa. Afterwards, a flow of an Ar/N_2 gas mixture, independently regulated by mass-flow controllers, fed the deposition chamber. The partial Ar pressure was kept constant at 0.53 Pa for the whole experiment, while the N_2 partial pressure was varied from 0 to 1.6 Pa. Before film processing, the target was sputter cleaned for 5 min, with a shutter shielding the substrate. A deposition time of 10 min was used for every experimental run, the same for all depositions. The total pressure, P_t, as read from a Pirani-gauge was led to an analog input in a computer. This signal is compared to the preset pressure; the error signal is supplied to a proportional, integral, derivative (PID) algorithm. The PID output is used to compensate the gas flow controlled by the mass-flow controllers. The partial pressure of the reactive gas in the deposition chamber was estimated by knowing the total pressure, chamber volume, pumping speed, elapsed time, and gas flow of both gases [25]. This scheme is a closed-loop partial pressure regulator and it can be implemented to produce gas mixtures in a controlled way. For RPLD the same scheme was applied, even if nitrogen was the only gas. A Dektak profilemeter is utilized to measure the thickness of all samples. The thickness was between 0.5 and 0.7 μm for films grown by RPLD, and between 1.5 and 1.8 μm by reactive sputtering.

A Philips difractometer, model X'pert, was employed to determine the crystallinity of the samples by X-ray diffraction (XRD) using the Cu K_α line with a 0.154 nm wavelength. The film morphology and roughness were determined by atomic force microscopy (AFM) using a NanoScope III, Veeco Instruments, in contact mode. Several images of the samples surface were taken at scales of 10, 5, 2, 1 μm and 500 nm. The mechanical properties of the samples were measured using a TriboScope nanoindenter, Hysitron. The nanoindenter is used in conjunction with the AFM so that the area of indentation can be visualized with the same probe. The probe is a commercial Berkovich diamond tip attached to a transducer. This unit replaces the conventional optical head with a cantilever of the NanoScope III AFM. The tip penetrates into the sample from zero up to a maximum predetermined force (loading region); then, the tip returns to its original position (unloading region). The "golden rule" in nanoindentation to be used in the study of the mechanical properties of thin films is that the maximum depth of penetration in a test must be no more than 10% of film thickness [26,27]. The graph showing the relationship between force or load and penetration or displacement is called the indentation curve. The hardness, H, and reduced elastic modulus, E_r, were found from the unloading region of the indentation curve by means of the theory developed by Oliver and Pharr [28,29], and corrections to this theory for very shallow indentations [30]. After choosing a region on the sample, 4 indentations (for 4 different loads) were performed. These loads were 200, 400, 800 and 1500 μN; and 800, 1500, 2000 and 3000 μN for films processed by RPLD and reactive sputtering, respectively. A number of 4 different regions, corresponding to a total of 16 indentations, were analyzed.

3. Results

The WN_x thin films were deposited on stainless steel disks kept at 400 °C on both deposition methods. The nitrogen partial pressure was varied from 0 to 10.0 Pa in the RPLD system and from 0 to 1.6 Pa in the sputtering system. The analysis was *in situ* performed immediately after each deposition for the films grown by RPLD, while it was done *ex situ* for those grown by reactive sputtering.

The only elements present in a typical XPS spectrum of a WN_x film grown by RPLD were W, N, and O. Meanwhile, W and N were just observed in the XPS spectrum for the film synthesized by reactive sputtering. Fig. 3 shows the relative atomic concentrations of tungsten, nitrogen and oxygen obtained by XPS as a function of nitrogen pressure for WN_x films grown by RPLD. The relative atomic concentration of nitrogen steadily grows in steps from 0 to