Combined Control Techniques for Reactive Sputtering of Wear/Abrasion Resistant TiN, Cr_2N, CrN and AlN Films on Compliant and/or Temperature Sensitive Substrates

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ABSTRACT

A combination of real-time *in situ* target voltage monitoring and ellipsometric techniques are used to streamline process development of reactively sputtered thin films, as well as provide a simple means of insuring transferability from research to production scale processes. Using low-energy ion assisted growth conditions, TiN, CrN, Cr_2N, and AlN films have been reactively sputtered from metallic-targets. An optimal operating environment for the deposition of stoichiometric compound coatings was very rapidly determined from analysis of the state of the target, and thin film stoichiometry and properties optimized using real-time *in situ* ellipsometry during growth. This combination of techniques resulted in a more than ten-fold reduction in process development time, and a monitoring/control system is being developed so these same techniques can be used to first scale-up and then monitor/control processes in both research and production systems. To demonstrate the quality of the coating that can be produced using this process design approach, an array of single and multi-layer Cr-N coatings with microhardness > 2000 Hk and critical loads > 6 kg have been deposited at low temperatures (< 200°C) on three model substrates; A2 tool steel, 52100 stainless steel, and 2024-aluminum. The pin-on-disk wear performance of these Cr-N based films was exceptional, with no measurable wear in severe dry sliding wear over sliding distances of more than 9000 m against a WC ball, even for Cr-N films on 2024Al under a 4 N load. Using this approach wear-resistant metal-nitride architectures have been *efficiently* developed for use on several temperature-sensitive and more compliant substrate materials.

INTRODUCTION

Control and scale up of reactive sputtering processes has long been recognized as one of the most significant barriers to the development of second generation ceramic hard coatings [1],[2]. In recent years, scientists and engineers have become increasingly interested in understanding the processes occurring both at the target and at the substrate during reactive sputtering as a means of improving process control. This paper examines two techniques for increasing the efficiency of process development using a smaller research sized sputtering system, while still insuring that these same processes can be readily scaled-up into industrial processes with a minimum of re-development [3]. Both target voltage and ellipsometric target substrate monitoring methods have their relative advantages, but in tandem the time to develop and optimize four different coating materials has been reduced by more than an order of magnitude. Even changes in film chemistry and structure induced by ion bombardment of the growing film can in some instances be evaluated *in situ*.

EXPERIMENTAL METHODS

To examine the effectiveness of these two monitoring/control techniques, several well characterized transition metal nitride thin films, namely: TiN, Cr_2N, CrN, and AlN, were deposited on Si(100) wafers to simplify x-ray analysis. To better illustrate the physical and mechanical properties that can be achieved using these combined process development and monitoring techniques, a number of Cr-N based films of differing architectures were also deposited onto M2 tool steel, 52100 bearing steel, and 2024 aluminum alloy coupons. While the present study involves only metal nitride thin films, the processes of target poisoning and gettering of the reactive species, by both film and chamber, are common to all reactive processes and hence, the results of this work are applicable to a very wide range of reactive sputtering processes.

All of the metal-nitride thin films were deposited using a 16” diameter cylindrical system pumped with a 1000 l/s turbomolecular pump, equipped with two 180 mm (6 in) diam. unbalanced magnetron sputtering cathodes, a sample insertion load-lock, a mass flow controlled gas handling system, and a 44-wavelength *in situ* ellipsometer. In this work, only one of the system’s two face-to-face targets was used in conjunction with a UHV compatible Helmholtz coil to provide a variable level of ion-bombardment during film growth. The load-lock inserted samples were mounted on an electrically isolated, DC biased holder at a distance of about 140 mm in front of the target. To permit the substrate ion current to be easily varied, a electromagnetic coil was positioned just behind the substrate holder, co-axially with the magnetron. A rotatable shutter was placed about 5 mm in front of the substrate to prevent contamination during the target warm-up. A schematic diagram of the deposition system is shown in Figure1. The magnetic field interactions between the two-cathode magnet arrays and the Helmholtz coil have been investi-

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gated using finite element modeling techniques, and are reported in detail elsewhere [4].

The discharge was operated in a current control mode using a 5 kW DC power supply, and an independent DC supply to bias the substrates during film growth. The state of the target during growth was monitored using an X-Y recorder to record the change in the target voltage (V_T) as a function of the nitrogen flow (Φ_{N2}). In a separate experiment reported elsewhere, a flat plasma probe was used to determine the ion flux density onto the substrate surface [5]. During film growth partial pressures of the reactive and background gases could be separately monitored using a dedicated *in situ* quadrapole mass spectrometer.

Prior to initiating film growth, the chamber was pumped down to a base pressure of less than $5x10^{-7}$ Torr. The Si(100) substrates were prepared by sequential cleaning in trichloroethylene, acetone, and methanol, after which they were dried in a N_2 flow. Metal substrate coupons were solvent cleaned and plasma etched prior to film growth. Ar etching was found to be more effective than N_2 etching in removing surface impurities, while maintaining low substrate temperatures (<200 °C). Etching conditions were as follows: Ar pressure of 30 mTorr, bias voltage of -1200 V, and duration of 10 min. The deposition cycle began by increasing the Ar flow until a pressure of 3.0 mTorr was achieved. The discharge was ignited in pure Ar, with the substrate protected by the shutter, and the N_2 flow was gradually increased to the desired level. All film growth experiments were carried out in constant current mode, using either a 6 A or 4 A discharge current depending on the source material used. For each set of experiments the change in the target voltage, V_T, was recorded as a function Φ_{N2} using an X-Y recorder. Once the desired level of target nitridization has been determined, the flow only to the desired level and monitored for fluctuations or significant deviations using the X-Y recorder.

A range of bias voltages was investigated, but in general a substrate bias of -20 V was found to be near optimum, for all of the materials investigated. Likewise, while a range of different Helmholtz coil currents have been evaluated; however, for the purpose of this study the current through the magnetic coil was set at 5 A. After the nitrogen flow was set, the shutter was opened and deposition allowed to proceed for 10 min if using Si-wafers, or until a 2 µm film thickness was achieved for Cr-N based films on engineering substrates. During deposition, the substrate temperature increased from room temperature to a maximum of approximately 150°C, as measured by a chromel-alumel thermocouple mounted adjacent to the substrate.

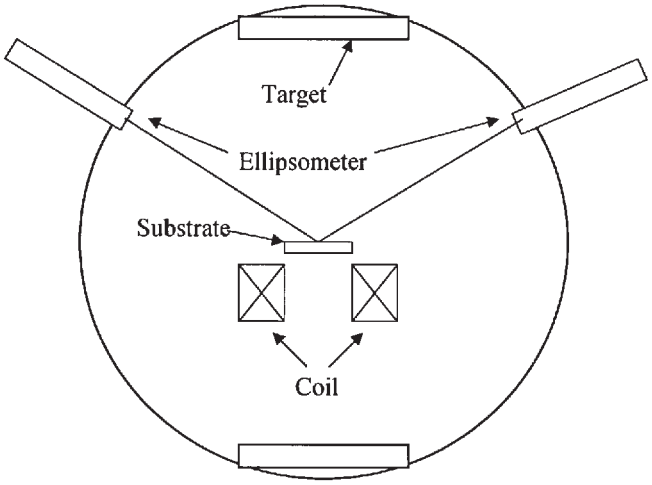

Figure 1. Schematic diagram of the geometric arrangements inside the deposition chamber.

The resulting coating thicknesses were evaluated using a Dektak profilometer. The X-ray diffraction analysis of coating phase and orientation was performed using Cu K_α radiation and a Rigaku diffractometer in a Bragg-Bretano geometry. The stoichiometry of selected Ti-N and Cr-N samples was determined by Rutheford Backscattering Spectroscopy (RBS) with a 2 MeV incident He+ ion beam. The surfaces of a number of the films have been studied using scanning electron microscopy (SEM) and the structure of a select group was analyzed using transmission electron microscopy (TEM), for brevity these results are not presented here. For samples on metallic substrates, the microhardness and critical adhesion load were measured. More detailed studies of the Cr-N based films in various monolithic and multi-layered forms have been presented previously [6].

EXPERIMENTAL RESULTS AND DISCUSSION

With the advent of more stable switching power supplies, monitoring the target voltage versus the reactive gas flow in current controlled reactive sputtering provides a great deal more information regarding the state of target surface. Illustrated in Figure 2, is the variation in the target voltage versus nitrogen flow for a pure Ti-target. This variation in target current is well correlated with changes in the resulting film composition, with near stoichiometric TiN being deposited at the peak voltage.

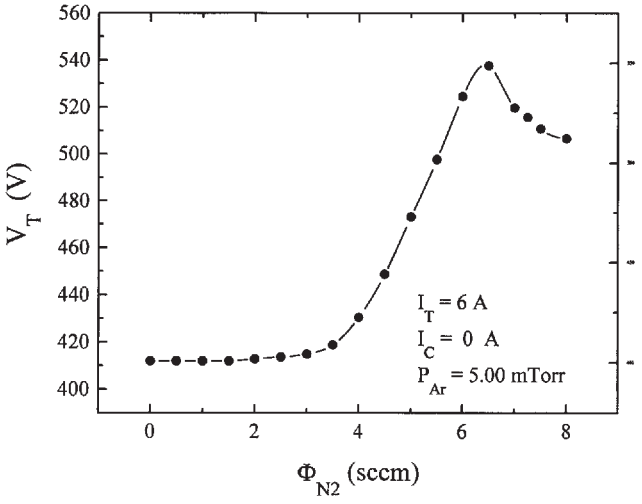

Figure 2. Target voltages vs. nitrogen flow rate for a reactively sputtered Ti-target and a 6A discharge current.

From this we can postulate that the peak in target voltage corresponds more directly to the formation of stoichiometric TiN on the target surface, which is only approximately reproduced in the film composition, especially in the case where ion-assisted growth generated variations in sticking coefficients and preferential re-sputtering rates are well documented [7]. Thus, while useful in identifying an approximate reactive gas flow rate at which near-stoichiometric films are produced and providing a reproducible tool for monitoring the "poisoning" state of the target during growth, this method alone is insufficient for real-time prediction of film stoichiometry. To this end a more direct indicator of the substrate chemistry is required.

Spectroscopic ellipsometry has proven to be very successful in semiconductor and optical film applications, where is commonly used to provide accurate real-time film thickness data necessary for phase-locked epitaxy. Ellipsometry is also very sensitive to changes in surface chemistry, and it is this aspect of ellipsometric analysis that is exploited in the real-time analysis Ti-N optical constants during film growth. As illustrated in Figure 3, large variations in the optical parameter (Ψ) are observed as a function of film chemistry, which was varied as a function of time in this experiment. The nitrogen flow was increased in a stepwise fashion over time, such that at each nitrogen level the film thickness increased producing an optically opaque layer. During the initial stages of film growth at each Φ_{N2} level, the optical signal detected is that of the new layer superimposed on the previous one. Once optically opaque the Ψ value for a given wavelength and composition are constant. As the nitrogen content of the film increases the spread of Ψ values measured as a function of wavelength increases dramatically. This is indicative of the point at which stoichiometric films are produced on the substrate surface. In the case of TiN, stoichiometric films coincide with the point of maximum Ψ variation with wavelength, illustrated as point D in Figure 3, which coincides with the N_2 flow rate just beyond the maximum of the curve in Figure 2.

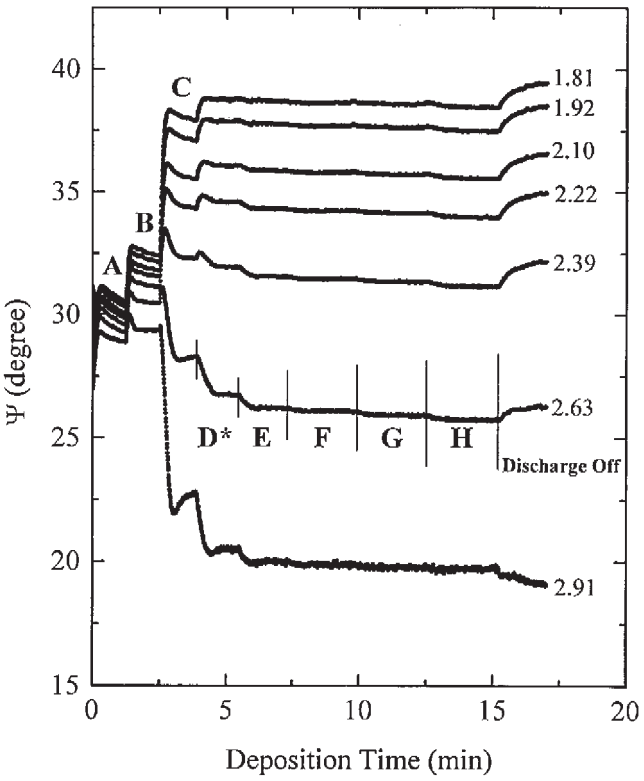

Figure 3. Ellipsometrically determined Psi values as a function of time, where the N2 flow is increased stepwise as over time.

The sensitivity of the measured optical parameters to substrate temperature from 20 to 300°C and increasing surface roughness for films up to 10 μm thick has been found to be very small in comparison to the variations induced by changes in the N_2 flow rates (i.e. film chemistry) and energetic particle bombardment during film growth. It was possible in case of TiN to optimize not only film chemistry, but also the substrate ion current density and energy *in situ* by analysis of an optically determined resistivity. It has been demonstrated previously that dense, stoichiometric films have the lowest electrical resistivity, and thus using *in situ* spectroscopic ellipsometry to first optimize film chemistry and then minimize the optically determined resistivity of the films during film growth it was possible to fully optimize the growth process within a single coating run.

In summary, by first using target voltage versus N_2 flow monitoring to determine the peak voltage, the stoichiometry of the films can be directly adjusted in real-time using spectroscopic ellipsometry to fine tune the N_2 flow to achieve the

maximum spread in Ψ of a given range of wavelengths. This combination of methods has proven to be very reproducible both in terms of indicating the near optimal target voltage peak position for Ti-targets of differing size, and achieving reproducible film stoichiometry among films with identical optical parameters and growth conditions. If one or more of the growth parameters, such as total pressure or target current are changed, achieving the correct N_2 flow and other parameters required to achieve dense stoichiometric films takes only a few minutes, as the analysis can be done entirely *in situ* in two straightforward steps.To demonstrate the applicability of this two-step approach, films were produced by reactively sputtering a pure Cr-target in a mixed Ar-N_2 discharge. A typical V_T vs. Φ_{N2} curve is shown in Figure 4. The Cr-N curve, unlike the Ti-N curve of Figure 2, has two distinct peaks. X-ray analysis of the films deposited under N_2 flow rates corresponding to the two peaks in Figure 4, showed that the peaks correlated to Cr_2N formation for the lower N_2 peak and CrN for the higher N_2. However, as in the case of TiN, RBS results proved both Cr_2N and CrN films deposited at these target voltage maximums to be slightly substoichiometric. This indicated that the voltage peak relates more directly to the target state than to the actual film composition. In hindsight, it is likely that the Ti_2N phase, while more exacting in stoichiometry than Cr_2N, could also be isolated using these techniques. Using *in situ* ellipsometry it was again possible to achieve reproducible films compositions, and this was utilized in the low temperature growth of multi-layer Cr_2N/CrN films for use a wear-resistant thin films. Both monolithic CrN and multi-layered Cr_2N/CrN thin films on M2 tool steel and 2024-Al showed no measurable wear after more than 9000m of dry sliding contact against a WC wear surface, during pin-on-disk testing [4].

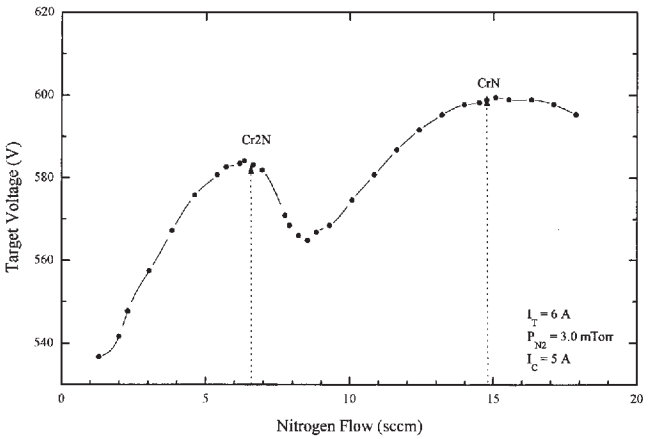

Figure 4. Target voltage vs. N_2 flow for reactive sputtering of a Cr-target.

This combination of techniques was very successful in providing rapid optimization of TiN, Cr_2N, and CrN films; thus indicating that this two-step approach is applicable for both cubic and hexagonal phases. However, not all compound metal-nitride thin films of technological interest in wear applications are conductive, and as such optically opaque at minimal thicknesses. Thus, analysis of AlN film growth using these two techniques was undertaken. AlN is both highly insulating and optically transparent, when stoichiometric, and it was expected that this would strongly influence both the measured target voltage characteristics and the resulting optical properties of the films. A typical V_T vs. Φ_{N2} for a pure Al-target sputtered in a mixed Ar-N_2 discharge is shown in Figure 5. The very small plateau region of the curve most closely corresponds to the point at which AlN was formed; however, the history of the target is important and this plateau region is less distinct on a newly cleaned target. Determination of the optimal gas flow based on target voltage monitoring alone could not be assured without *ex situ* X-ray phase analysis. The ellipsometric analysis is also greatly complicated by the fact that in optically transparent materials the variation in Ψ and Δ are strongly dependent on the film thickness and wavelength selected. A film growth experiment similar that of TiN in Figure 3, but instead going from stoichiometric AlN to substoichiometric AlN+Al films, results in a very complicated periodically varying pattern, an example of which is shown in Figure 6. Clearly, both the amplitude and period of the Ψ and Δ oscillations vary as a function of nitrogen content, but a quantitative assessment of this is not yet been established. It is not practical for AlN film growth to slowly increase the N_2 flow as was done for TiN; this difficulty stems from the fact that mixed AlN + Al phase films are very strongly absorbing. Thus, thin transparent AlN layers deposited on top of these very absorbing AlN+N layers are difficult to detect and nearly impossible to analyze. By reversing the process and first depositing a transparent pure AlN film produced from a fully poisoned film, and slowly decreasing the N_2 flow, yielded a much more useful result. Shown in Figure 7, the Ψ value at specific wavelength will begin to increase in the total amplitude of the oscillation and then drop precipitously as soon as a mixed AlN +Al film is deposited. Thus, while a bit more complicated to achieve initially, it is possible to determine the growth conditions necessary to produce stoichiometric AlN with minimal target poisoning entirely *in situ.* With further analysis of optical constants vs. film chemistry it should be possible to deconvolute the real-time data in order to develop a real-time process control system.

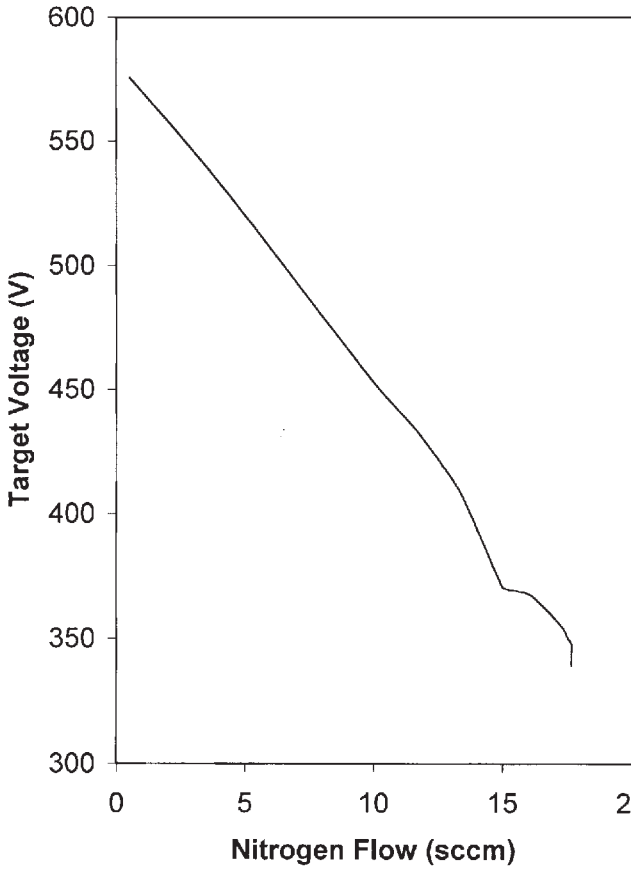

Figure 5. Target voltage vs. nitrogen flow rate for reactive sputtering of an Al-target. Pure AlN is observed beyond the plateau region at approximately 15 sccm.

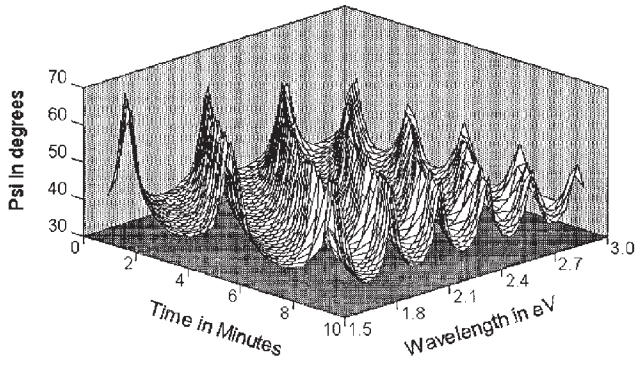

Figure 6. A ten minute ellipsometric study of Ψ vs. photon energy, for film growth under slowly decreasing N_2 flow. The film becomes substoichiometric at approx. 12 min.

CONCLUSIONS

In situ optimized growth of both highly conductive, optically opaque films such as TiN, Cr_2N, and CrN, as well as highly insulating, transparent AlN has been achieved using a combination of target voltage monitoring and *in situ* spectroscopic ellipsometry. Monitoring of the these processes, again using this combined technique, has proven to be very successful in providing reproducible film growth. Because the properties measured by these techniques are fundamental to the film structure/chemistry and the target/reactive gas combination, and thus not strongly system dependant the scale-up of processes from a research into production should be relatively straightforward. Rotation of the substrates during growth does not preclude the use of ellipsometric techniques, but some care is needed in insuring that a suitably flat surface can be reproducibly aligned with the source and detector at regular intervals. Since data acquisition takes only a few milliseconds to complete, it is not necessary for the rotation of workpiece to stop fully during the analysis. This combined technique shows great promise for improving both the efficiency with which reactive sputtering processes can be developed and scaled-up, and the accuracy with the which these complex processes can be reproduced.

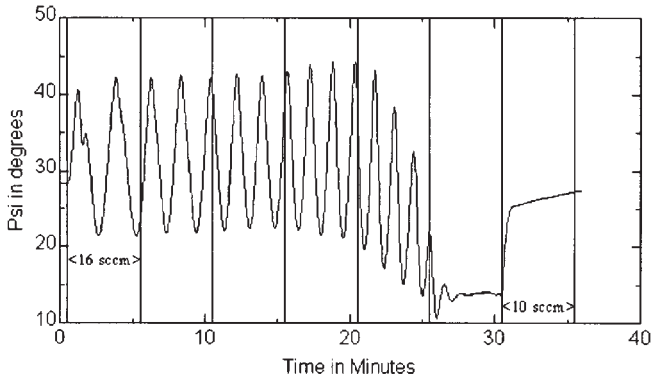

Figure 7. Variation in Ψ for single photon energy (i.e. wavelength) with a stepwise decrease in N_2 flow from 16 sccm to 10 sccm in 1 sccm increments.

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