THE HARDNESS AND ELASTIC MODULUS OF TiN FILMS AS DETERMINED BY ULTRA-LOW LOAD INDENTATION⁺

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The mechanical properties of a series of titanium nitride films on stainless steel substrates have been evaluated using an indentation technique with a mechanical properties microprobe (MPM). The MPM makes possible measurement of film properties without contribution by the substrate material. The titanium nitride films were deposited with a PVD technique known as sputter ion plating (SIP). Deposition substrate bias was varied from 0 to -120 V, while keeping other deposition parameters constant. With increasing negative substrate bias, dramatic increases in hardness and elastic modulus have been observed.

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INTRODUCTION

Titanium nitride (TiN) has very desirable properties including high hardness, good wear resistance, low friction, and resistance to oxidation up to 500°C [1]. The development and refinement of these properties by gaining insight into the relationship between them and the process parameters employed during deposition is of utmost importance.

TiN can be deposited by either chemical vapor deposition (CVD) or physical vapor deposition (PVD). The films studied herein were deposited with a PVD technique known as sputter ion plating (SIP). The substrate bias applied during deposition has been shown to affect the morphology of the resultant films [2]. The hardness of the films as measured with a Vicker's indenter (and interpreted using the volume law-of-mixtures model) has also been shown to be a function of substrate bias [2].

In this study, the effect of substrate bias on hardness and elastic modulus was determined using a Mechanical Properties Microprobe (MPM). The MPM is an ultra-low load indentation hardness tester which records load, indenter displacement, and time continuously during loading and unloading of the indenter. These data can then be used to calculate the elastic modulus and the hardness of the material.

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The MPM is well suited for use on thin films because its extremely shallow indentation allows for sampling of the film without effecting any contribution from the substrate material. The instrument has been utilized with great success in similar applications reported previously [3-5].

EXPERIMENTAL DETAILS

The TiN films were deposited onto stainless steel substrates as described by Rickerby and Newbery [6] with substrate biases from 0 to -120 volts.

The samples had macroscopically smooth surfaces as-deposited, but in order to obtain surfaces smooth enough for random placement of the nanoindentations, a dimpling technique [3] was employed.

A commercially available MPM was used for the measurement of the elastic modulus and hardness. The displacement of the indenter is measured with a capacitive displacement gauge with a resolution of 0.16 nm. The load is applied by passing a current through a coil which is positioned in a magnetic field. The resolution of the system is 0.3 μN .

A minimum of 10 indentations were made on each sample to depths of 100nm. Each indentation yields data for calculation of the mechanical properties from 50, 75, and 100nm.

DATA EVALUATION

Data from the MPM is acquired three times per second during the indentation sequence, i.e., the entire time the indenter is in contact with the sample. Plotting the load data against the indenter displacement yields a curve representing the loading on the indenter, and a hysteresis which represents the load as a function of displacement during unloading. These data, representing the elastic-plastic response of the material, coupled with a functional relationship between the indenter's displacement and contact area, make possible the calculation of the hardness and elastic modulus. The mathematical relationships between the raw data and the results are described in greater detail by Pethica, Hutchings and Oliver [7] and Doerner and Nix [8].

RESULTS AND DISCUSSION

Hardness of the TiN films increases with increasing negative substrate bias throughout the substrate bias range studied. With no potential the hardness was 5.4 GPa while application of a -120V bias produced a film with a hardness of 34 GPa. This increase is seen in figure 1 where the hardness is plotted against negative substrate bias for the three indentation depths. It has been shown previously that contribution to the hardness by the substrate is indicated by a change in hardness as a function of indenter displacement (or indentation depth) [4]. The error bars

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Figure 1 - Hardness as a function of negative substrate bias for three indentation depths. Error bars are one standard deviation of the data for the 50nm depth indentations.

of one standard deviation on the 50nm depth data indicates that the hardness is statistically independent of indenter displacement. The hardnesses measured, then, are considered to be free of the substrate's influence.

The greatest increase in hardness is clearly at low bias, i.e., from 0 to -35V. This increase is attributed to changes in the morphology and density of the films as was found previously [2]. The structure of the film with no applied bias is of the zone 1 type (Thornton's model [9]) while the application of a negative potential causes the deposition of a film with the zone T type structure. Densification with increasing negative bias is also credited with a role in the increase in hardness with bias throughout the range studied.

Elastic modulus increases with negative substrate bias also, seeing the greatest increase at low voltages (figure 2). The modulus increases from 117 GPa at no bias to 450 GPa at -60V bias. Substrate potentials of greater than -60V appear to have no effect on the elastic modulus. The marginal increase in hardness with bias at potentials greater than -60V is contrasted with the essentially constant elastic modulus in the same range. The substrate biasing in this range causes increasing densification

Figure 2 - Elastic modulus as a function of negative substrate bias for three indentation depths.

and internal stress [6] which could account for the increase in hardness without any effect on the modulus.

CONCLUSIONS

Titanium nitride films deposited with substrate biases from 0 to -120V were studied to determine the effect of substrate bias on hardness and elastic modulus. Hardness increased with negative substrate bias throughout the range studied. At the greatest potential the hardness was found to be 500% higher than that of the unbiased sample. Elastic modulus increased between 0 to -60V, but remained constant throughout the remainder of the range. The increase in modulus was found to be 280%.

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