Reactive Cylindrical Magnetron Deposition of Titanium Nitride and Zirconium Nitride Films

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ABSTRACT

Hollow cathode sputtering (also known as inverted cylindrical magnetron sputtering) is commonly used to coat wires and fibers. However, many of the features of hollow cathodes are also desirable for applications involving larger, more complex substrates. To demonstrate this, ZrN and TiN, which are commonly used as wear-resistant and decorative coatings, were reactively sputtered from metallic targets using a 19 cm diameter by 21 cm long hollow cathode magnetron. Measurements were made of the deposition rates in both cases. The axial and radial deposition uniformities have also been measured for pure Ti. The film properties important for typical applications of these materials are presented.

INTRODUCTION

Inverted cylindrical magnetron sputtering (also known as hollow cathode magnetron sputtering) has been in use for over 20 years. [1, 2, 3] The geometry of a typical cylindrical magnetron is shown schematically in Figure 1. The sputtering target is the inner surface of a cylinder and the substrate is placed within the cylinder so that it receives a relatively uniform flux of coating material. This makes cylindrical magnetrons particularly well-suited for coating non-planar substrates. Because the coating flux is isotropic, the average deposition rate is much higher than is possible with a point or planar source using substrate rotation. Furthermore, the coating efficiency (defined as the percentage of sputtered material that is ultimately used in the coating) is quite high, because much of the material which is not deposited on the substrate(s) is redeposited on the target to be used again. And, as a consequence of the design of cylindrical magnetrons, the target erodes uniformly rather than in a "racetrack", so that a high percentage of the target material is consumed before it must be changed. This leads to target utilization values between 50% and 90%, depending on the design.

Many of the published references to the use of cylindrical magnetrons have been for coating fibers and wires, which is obviously an excellent application for the technology. However, the growing need for decorative and functional coatings on complex shapes has caused increased interest in cylindrical magnetron sputtering for these applications as well. One reason is that the combination of excellent material efficiency, good target utilization and lower target costs leads to significantly lower material costs. Table 1 compares the material cost for a typical drill bit coated with TiN using planar magnetron sputtering with the cost for the same part when using cylindrical magnetron sputtering. The assumption is that each finished drill bit has 60 mg of Ti on it in the form of TiN. We have estimated that half of the material sputtered from the planar magnetron arrives on the substrates, which is probably generous. In contrast, the coating efficiency of cylindrical magnetrons is determined to first order by the ratio of the total substrate area to the area of the cathode ends, where the only material losses occur. This efficiency can be made quite high, even for small substrates, by coating numerous parts simultaneously.

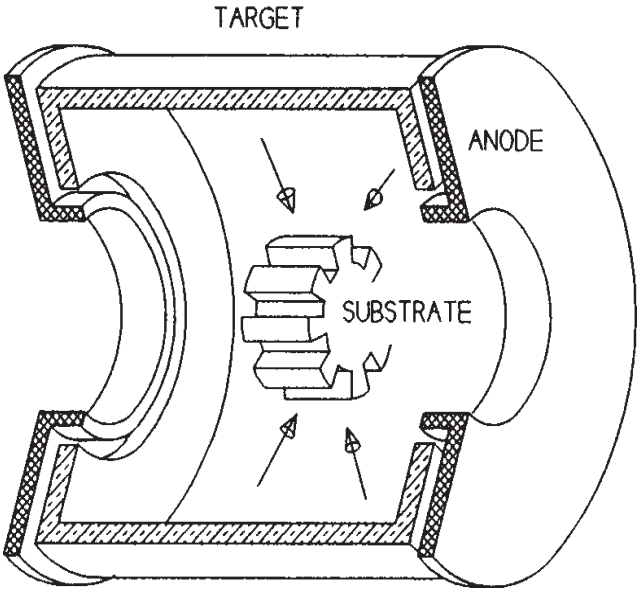

Figure 1. Schematic illustration of an inverted cylindrical magnetron (or hollow cathode magnetron) sputtering source.

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Table 1

	Planar Magnetron	Cylindrical Magnetron
Target Mass (kg)	4.5	4.5
Efficiency	50%	75%
Utilization	30%	70%
Parts per Target	11,700	41,100
Target Cost	$1,500	$1,000
Material Cost/Part	**$0.128**	**$0.024**

The lower target cost for the cylindrical magnetron arises from the ability to use rolled sheets that slip into place without bonding, thereby simplifying the fabrication. The table shows that even these conservative estimates lead to a reduction in material cost by a factor of five.

In addition to lower material costs, cylindrical magnetrons provide uniform coatings on relatively large single parts or multiple small parts without substrate rotation. This allows simplified machine designs, leading to greater reliability and lower costs. Finally, because the size of the cylindrical cathode can be matched to the size of the parts being coated, it is possible to modularize and automate the coating operation. Examples of such systems have been described previously.[4]

When considering cylindrical magnetrons to coat three-dimensional objects, it is important to know the deposition rates and thickness uniformities that are produced. Thornton and Hedgcoth have shown that, neglecting end effects and assuming a cosine distribution of sputtered material, the deposition rate close to the axis of a cylindrical magnetron will equal the target erosion rate.[2] In practical cathodes with low aspect (length to diameter) ratios, end effects cannot be ignored. The coating flux will also not arrive in a line-of-sight fashion and scattering by the working gas will influence the material distribution. The purpose of this paper is to characterize the coating uniformity of relatively large-diameter cylindrical magnetrons and compare them with model results. In addition, in order to investigate the application of cylindrical magnetron sputtering to materials of practical interest, TiN and ZrN have been deposited and characterized.

EXPERIMENTAL PROCEDURES AND RESULTS

A. Thickness Uniformity

The cathode used for these measurements is shown schematically in Figure 2. It has a target with an outside diameter of 19.1 cm and a length of 20.6 cm. Grounded anodes extend approximately 2 cm in from each end. Targets were made from commercially pure Ti and Zr by rolling sheets to the correct diameters and sliding them in place. Coating uniformity

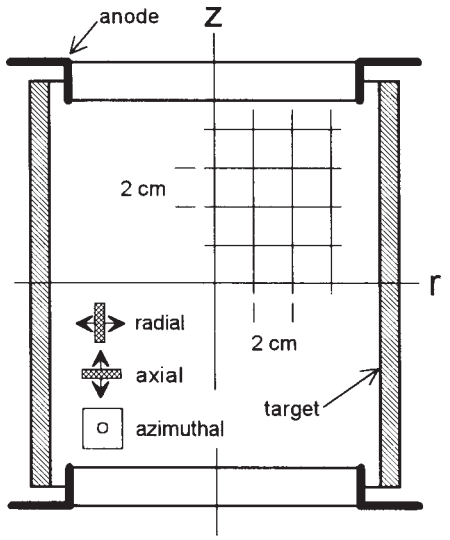

Figure 2. Schematic of the cylindrical magnetron used in these experiments, approximately to scale. At each of the points shown on a 2 cm by 2 cm grid, thickness measurements were made on substrates in each of three orientations.

measurements were made using a Ti target sputtering in 1.5 mTorr of Ar with a cathode power of 4 kW. The deposition time for each of the uniformity runs was 5 minutes. Substrates were placed (in separate runs) on a grid in the r-z plane of the cathode, as shown in Figure 2. At each location, three coating directions were measured, as indicated by the arrows. With the substrate normals oriented in the radial (r) direction, the thicknesses on both sides of each substrate were measured, giving what we define as the radial deposition rates at each position, both facing in and facing out. Similarly, substrates with their normals perpendicular to the r-z plane were used to determine the azimuthal deposition rates and substrates oriented with their normals in the axial (z) direction were used to determine the axial deposition rates. In the cases of the radial and azimuthal rates, measurements were made in two cathode quadrants and averaged, since they should be the same by symmetry. There were 47 such paired thickness measurements, and their pooled standard deviation was 16 nm. This gives us an estimate of the accuracy of the stated thicknesses

The expected radial deposition rates were modeled by assuming a uniform erosion profile along the cathode length, a cosine distribution for the sputtered material and line-of-sight transport. The target current of 8.0 amps was used along with a sputter yield for Ti of 0.5 to estimate that each 5 minute run resulted in a total of 1.5 gm of Ti being sputtered from th e inner surface of the target. If this were removed uniformly from the target surface, it would correspond to a thickness of 2.7 microns.

Figure 3 shows the measured radial thicknesses for substrates facing in (3a) and facing out (3b) as functions of the radial and axial positions within the cathode. Only one quadrant of

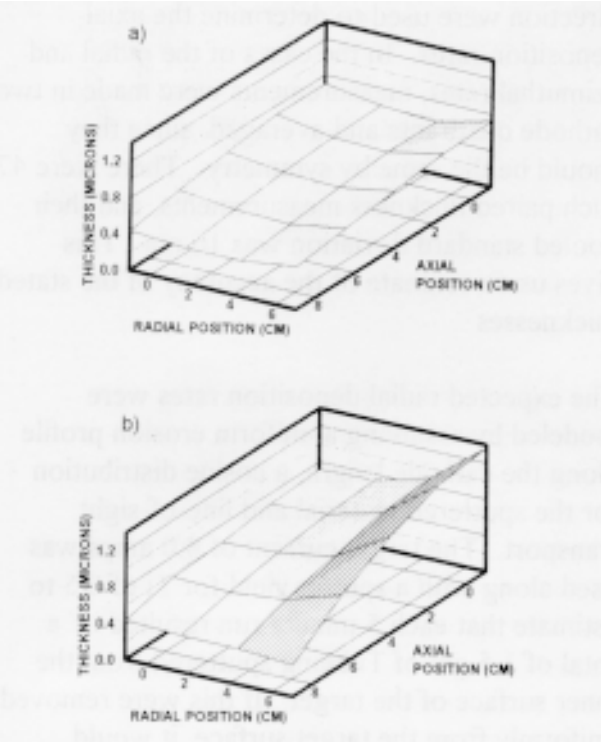

Figure 3. Measured thickness as a function of position for substrates with their normals in the radial (r) direction, facing in (a) and facing out (b)

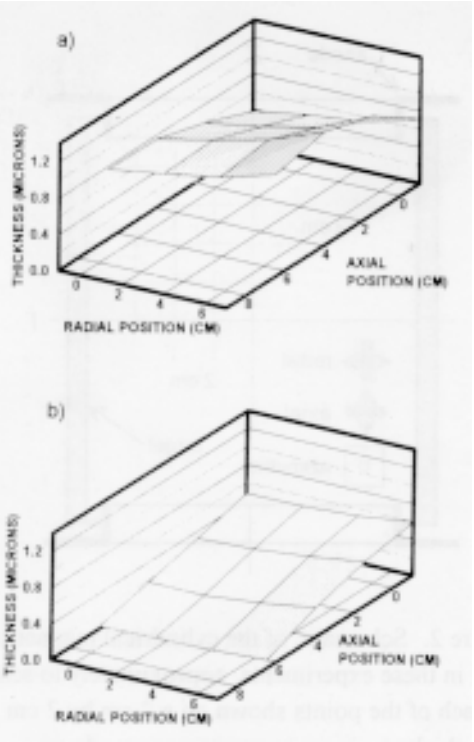

Figure 5. Measured thickness as a function of position for substrates with their normals in the axial (z) direction, facing in (a) and facing out (b).

the cathode is shown. We see a relatively uniform profile over the central portion, with an increase in the measured thicknesses as the substrates are placed closer to the cathode wall, whether they face in or out. We will discuss this in more detail later.

Figure 4 shows the measured azimuthal thickness as a function of position within the cathode. The overall shape is similar to that of the radial thickness profile shown in Figure 3b for the case of substrates facing radially outward.

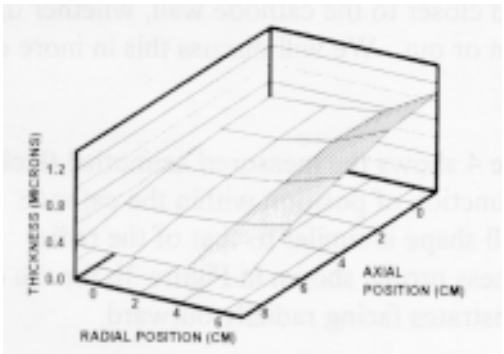

Figure 4. Measured thickness as a function of position for substrates with their normals in the azimuthal direction (perpendicular to the r - z plane).

Finally, Figure 5 shows the thicknesses on substrates with their normals in the axial direction, both facing in (5a) and out (5b). As would be expected, substrates facing in accumulate thicker films as they are placed closer to the end of the cathode, while those facing out accumulate thinner films as they are placed closer to the end of the cathode.

Figures 3, 4 and 5 allow us to predict the coating uniformity that is expected in various applications. For example, we see that within a central cylindrical volume approximately 8 cm in diameter and 8 cm long, the radial and azimuthal thicknesses taken together have a range of about 25% above and below the average thickness. Therefore, an array of small objects placed within this volume will receive coatings of this uniformity on surfaces whose normals are approximately perpendicular to the axial (z) direction, neglecting shadowing. The coating thicknesses on the end faces (which are dependent on the axial deposition rate) will be sensitive to the substrate location within this volume, as shown by Figure 5.

As another example of a possible application, we consider coating a gear as shown in Figure 1. We can predict the uniformity on the gear surfaces by comparing the radial thickness for substrates facing out (representing the faces and lands of the gear teeth) with the azimuthal thickness (representing the sidewalls of the gear teeth). We see from Figures

3 and 4 that these thicknesses are the same to within approximately +/- 10% at all radial positions. Therefore, neglecting shadowing, a gear centered in the cathode will receive a relatively uniform coating regardless of its overall radius. The uniformity will be determined almost entirely by the length of the gear.

Figure 6 shows the calculated thickness profiles for substrates with their normals in the radial direction, both facing in and facing out. There are a number of interesting contrasts when comparing these plots to Figure 3. For example, the predicted rate at the cathode center is almost a factor of three higher than the measured rate. And, while the model predicts a slight rise in thickness for substrates facing out as they are moved toward the cathode wall, it is small compared to the increase of almost a factor of two seen in the measured data in Figure 3b. Finally, the modeled radial thicknesses for substrates facing in does not predict the measured decrease in thickness as they are moved away from the cathode wall (Figure 3a).

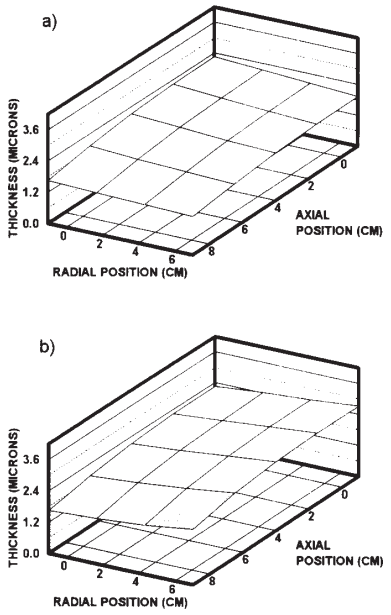

Figure 6. Calculated thickness as a function of position for substrates with their normals in the radial (r) direction, facing in (a) and facing out (b)

All of these results are consistent with large-angle scattering of the sputtered Ti, which could result in significant redeposition on the target surface. The mass of Ti is very close to the mass of the Ar working gas, making large-angle scattering likely. The slight rise in thickness for substrates close to the cathode wall and facing in is difficult to explain by any other mechanism, since the model confirms that it is not a geometrical effect.

To check this hypothesis, the measured data are compared to a model (solid line in Figure 7) that assumes the calculated removal rate at the target surface and an exponential decrease in Ti flux moving away from the target surface. As the decay constant, we use the mean free path for Ti in Ar at 1.5 mTorr, as estimated from Westwood, which is 3.2 cm.[5] Also shown in Figure 7 is the calculated thickness assuming line-of-sight transport (the model used in Figure 6). The slight dependence of thickness on position in this case is purely geometrical. The points are the measured data for substrates facing out at an axial position of 4 cm. (The data at z = 4 cm was chosen on the assumption that if there is an axial nonuniformity in the target erosion rate, the average rate and actual rate will be approximately the same midway between the cathode center and end.) We see that the measurements appear to be approaching the exponentially decaying expression near the target surface. This supports the view that the key differences between the measured and calculated thicknesses can be explained by scattering of the Ti by the working gas. This also suggests that heavier target materials and/or lower sputtering pressures will give thickness profiles more like those shown in the model of Figure 6.

Consistent with that prediction, our measured thickness at the cathode center for pure Zr sputtered at 4 kW for 5 minutes in Ar at 1.5 mTorr was 1.3 microns. The calculated thickness at the cathode center, based on a sputter yield of 0.7 and neglecting scattering, is 1.7 microns in a 5 minute run. Therefore, pure Zr deposits at 76% of the predicted rate. This is significantly better agreement than we found for Ti, which deposited at 33% of the predicted rate. Zr is over twice as massive as Ar, which would lead to less high-angle scattering than would be the case for Ti. Furthermore, for a smaller diameter but similarly designed cylindrical magnetron, we have observed that measured Pt deposition rates 2.5cm from the target surface are in excellent agreement with the calculated rate.

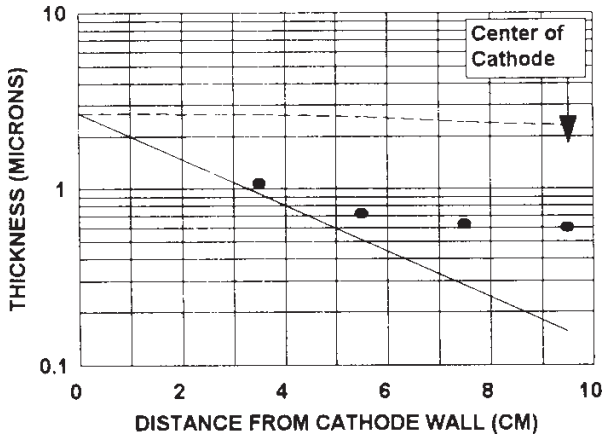

Figure 7. Comparison of the radial thickness data (points) with a model asuming an exponential decrease in flux (solid line) and a model assuming line-of-sight transport (dashed line).

B. Titanium Nitride Deposition

The cathode described previously was used to reactively sputter TiN onto AISI-M2 steel. The 1 cm by 1.5 cm substrates had a Vickers hardness of 1200 kg/mm² and were fine polished using 0.3 micron alumina grit. They were presputtered in Ar at a pressure of 23 mTorr and bias power of 70 W for 30 seconds before coating.

The general characteristics of TiN reactive sputtering are well-known and we operated our process on the knee of the flow-pressure hysteresis curve.[6] The target was first sputtered in pure Ar at a pressure of 1.8 mTorr and power of 4 kW for 25 minutes to produce a clean surface. The flow of N_2 gas was then increased until the target voltage rose to its maximum value, which indicated that the desired operating point had been reached. This condition was found to be stable and reproducible. The substrate was then inserted into the cathode at the location r = z = 0 and coated for 60 minutes. A substrate bias of-150 V was used. The accumulated film thickness was 6.3 microns, giving a deposition rate of 1.8 nm/sec or 74% of the rate for pure Ti at the same cathode power. During coating, an equilibrium temperature of 372 C was measured.

The films were the characteristic gold color of stoichiometric TiN. A microindentation technique was used to determine their Vickers hardness. Two independent measurements produced an average value of 2780 kg/mm², which compares well with values reported elsewhere for reactively sputtered TiN.[7, 8]

C. Zirconium Nitride Deposition

The same procedure described above for TiN was used to deposit ZrN films. The only differences were that a 20 minute target preclean was used and the deposition was 50 minutes long, resulting in a 4.5 micron thick ZrN film. As mentioned previously, the deposition rate for pure Zr at the center of the cathode was 4.3 nm/s and the rate for ZrN was 1.5 nm/s, or approximately 35% of the Zr rate. We were not using feedback to control the flow of N_2 and found that the ZrN process was more difficult to control than the TiN process under these circumstances. It is possible that the Zr target was fully poisoned during the ZrN deposition, leading to lower relative rates.

Vickers hardness tests on the ZrN films resulted in an average value of 2930 kg/mm², which is also good in comparison with published values.[7, 8]

CONCLUSIONS

We have found that for a 19 cm diameter by 21 cm long cylindrical magnetron sputtering cathode, within a central volume 8 cm in diameter by 8 cm long the radial and azimuthal deposition rates are isotropic within approximately +/- 25%. Furthermore, for essentially cylindrical objects with relatively small surface convolutions, such as gears, the uniformity is approximately +/- 10% over a larger interior volume.

A rapid decrease in the deposition rate moving away from the target surface has been seen for Ti. This is consistent with large-angle scattering of Ti by the Ar working gas, leading to significant redeposition on the target surface. (This effect, of course, is not peculiar to cylindrical magnetrons and will affect the deposition rate in planar magnetrons as well.) If this explanation is correct, lower working pressures or heavier target materials will produce flatter deposition profiles. The observations with Zr and Pt are consistent with this.

TiN and ZrN films with good visual appearances and hardnesses which compare favorably with those reported in the literature have been produced. Typical reactive sputtering conditions reported for planar magnetrons transferred readily to the cylindrical magnetron used in this study.

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