Mass/Energy Analysis of a Modulated Pulse Power Plasma Compared to a DC Plasma

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Abstract
An electrostatic quadrupole plasma mass spectrometer was used to characterize the plasma during modulated pulse power (MPP) and conventional DC sputter deposition of Cr films with a pair of opposed-cathode in a closed field unbalanced magnetron sputtering system. Experiments were run with the different types of power applied to just one of the cathodes, but with the closed field configuration. The mass analysis detected Cr$^{+1}$, Ar$^{+1}$, Cr$^{+2}$, and Ar$^{+2}$ ions. The intensity of the Cr$^{+1}$ ions when the MPP power is used is significantly higher compared to when DC power is used. As the peak power and the average power of the MPP pulse were increased, the intensity of the ions also increased in the closed field condition as it did when DC power was used. The energy analysis revealed that the average energy for both the Cr$^{+1}$ and Ar$^{+1}$ ions in the MPP plasma is about 2 eV. However in the DC plasma, the average energy for the Cr$^{+1}$ ions is about 4 eV, and it is about 3 eV for the Ar$^{+1}$ ions. The ion energy distribution is relatively narrow, and there is a small high energy ion energy distribution tail that extends out to about 10 eV for Cr$^{+1}$ and Ar$^{+1}$ ions in both the MPP and DC plasmas.

Introduction
High power pulse magnetron sputtering (HPPMS), which is also known as high power impulse magnetron sputtering (HIPIMS), was first introduced to the world in a paper published by Kouznetsov et al. [1] in 1999. By applying a large amount of power to the sputtering target for a short period of time and then repeating the pulse periodically, they showed that it is possible to obtain a high degree of ionization of the sputtered material. Power densities on the target were on the order of 1,000-3,000W cm$^{-2}$ during the pulse, but the pulse width (full width half maximum) was only about 100-150µs. Pulse duty cycles were usually less than one percent.

The ability to produce a highly ionized flux of coating material from a sputtering process was particularly enticing because the potential could be seen to produce fully dense films with more uniform coverage, particularly on 3-dimensional substrates. Petrov et al. [2] demonstrated that for coating fluxes with high ion to neutral ratios, it is possible to achieve fully dense films with low ion energies on the order of 20eV. The low ion energy leads to less damage in the films from the arriving ions and hence the stress in the film can be low.

The advantages of HPPMS were quickly recognized, and research efforts to understand the HIPIMS process were started first in Linköping University in Sweden in Professor Ulf Helmersson’s group and shortly thereafter at Sheffield Hallam University in the UK in Professor Wolf-Dieter Münz’s group. From the efforts at these two universities, the word quickly spread about the advantages of HPPMS, and several other organizations in Europe became involved with HPPMS. In the United States, early work on HPPMS was carried out at Advanced Energy Industries, Inc. in Colorado under the direction of Dr. David Christie.

Although the advantages of HPPMS are important, there is one disadvantage with the technique, which is that there is a significant loss in deposition rate compared to conventional DC sputtering. The HIPMS deposition rate is typically only about 25-30% of the DC rate for an equivalent amount power input [3]. Christie [4] developed a model to explain the loss in the HIPMS deposition rate that shows that sputtered atoms that are ionized can be attracted back to the target surface instead of going to the substrate for film formation.

There is an alternative form of HPPMS called modulated pulse power (MPP) [5,6,7] sputtering that overcomes the rate problem with the Kouznetsov style of HPPMS. An MPP pulse is actually a multi-step pulse that is made up of packets of micro pulses [8]. Typically an MPP pulses has three parts to it. The first part is the ignition of the plasma, the second part is the stabilization of a weakly ionized plasma, and finally the third part is the transition to the strongly ionized plasma regime. This latter transition is accomplished by increasing the voltage applied to the sputtering cathode.

The peak power in an MPP pulse is typically less than what it is in a Kouznetsov type HIPMS pulse, and the peak MPP power is typically in the 100-300W cm$^{-2}$ range compared to 1,000-3,000W cm$^{-2}$ range for the Kouznetsov pulse. The MPP pulse length can be up to 2-3ms long.

Another distinct difference between these two different forms of HIPMS is that it is possible with MPP to not only equal the DC deposition rate, but to actually exceed it [6]. The reasons for the high deposition rate with MPP are not fully understood yet, but it is believe that the high rate is due to both sputtering and evaporation/sublimation processes taking place on the target surface [9].

Optical emission spectroscopy of the MPP plasma has shown that there is a high degree of ionization of the sputtered material [5], but with the equipment used to measure the optical emission only plus one peaks of the sputtered material were detected, which seemed unusual. There should be multiply ionized peaks in the MPP plasma, and thus in this work an electrostatic quadrupole plasma (EQP) mass spectrometer was used to characterize and compare the plasmas during sputtering of chromium using both conventional DC and MPP power. The positive ion mass distributions and the positive ion energy distributions (IED) were determined.

Experimental Procedures
Experiments were carried out in an opposed-cathode closed field unbalanced magnetron sputtering system with a pair of sputtering cathodes. During this work, only one cathode was powered at any given time. The average power was varied between 0.8 and 2.8kW. The distance between cathodes was 240 mm, and the sputtering pressure was 0.67Pa (5mTorr). The cathodes are from Teer Coatings Ltd., and the target size is 106mm x 298mm. A Hiden Analytical EQP was used to determine the time averaged positive ion mass distributions and the positive ion energy distributions during sputtering with MPP or DC power. The EQP probe was located where a substrate would normally be placed during deposition, but it was also tried in different orientations with respect to the target surface. It was found that the probe position influences the intensities of the ions but not the species detected. For the data reported in this paper, the barrel of the probe was parallel to the target surface, and
the inlet to the orifice at the end of the barrel was perpendicular to the target surface. Also the inlet to the probe at the end of the barrel was 120mm from the target surface and 2.5cm off of the centerline between targets. To show the effect of the closed-field unbalanced magnetrons on the plasma intensity, experiments were run with and without the closed field condition.

**Results**

The EQP ion mass scans detected ions of Cr$^{+1}$, Ar$^{+1}$, Cr$^{+2}$, and Ar$^{+2}$ at a point in the plasma where a substrate would normally be placed. In addition trace amounts of what is believed to be Cr$^{+3}$ and Cr$^{+4}$ have been detected. In Figure 1, the ion intensities in counts per second (cps) as a function of the average target power are shown for the principal ions detected during the sputtering of Cr with either MPP or DC power. The number of ions in the MPP plasma increase as the average power (and peak power) increases in the power range investigate in this work, but the Ar$^{+1}$ ions in the DC plasma level off after about 2kW. Why the number of Ar$^{+1}$ ions remains steady after 2kW is not known at this time. Additional work needs to be done to determine the effect of high average and peak power levels on the number of ions produced.

![Figure 1](image1.png)

**Figure 1. MPP and DC positive ion intensities as a function of the average target power.**

There are significantly more ions, both Cr$^{+1}$ and Ar$^{+1}$, produced in the MPP plasma compared to the number of ions produced in the DC plasma. For the DC plasma, the Ar$^{+1}$ ions dominate, and the number of Cr$^{+1}$ ions is small compared to the Ar$^{+1}$ ions.

It is somewhat surprising as to the number of Ar$^{+1}$ ions detected in the MPP plasma because earlier work reported by Vlcek [10] showed that there is significant rarefaction of the Ar gas in front of the target due to the high flux of energetic sputtered particles leaving the target surface and colliding with the Ar gas atoms. It may be that the closed magnetic field is very effective in confining the large number of secondary electrons that are emitted from the target surface. These secondary electrons can then undergo multiple electron impact ionization of the Ar atoms in the space where the substrate is placed. Why the number of Ar ions is so high is another one of the unanswered questions about the MPP process that needs further study.

The EQP measurements of the time averaged IEDs are shown in Figures 2 and 3 for the Cr$^{+1}$ and Ar$^{+1}$ ions, respectively, during sputtering of Cr with MPP and DC power at an average power level of 1.2kW. The number of MPP Cr$^{+1}$ ions is significantly greater than the number of DC Cr$^{+1}$ ions. The peak ion intensity for the MPP Cr$^{+1}$ ions is about 536,000cps compared to a peak intensity of about 8,600cps for the DC Cr$^{+1}$ ions. This data shows very distinctly how little of the sputtered material becomes ionized in a conventional DC sputtering process.

![Figure 2](image2.png)

**Figure 2. IED for Cr$^{+1}$ ions produced during MPP magnetron sputtering of Cr.**

![Figure 3](image3.png)

**Figure 3. IED for Ar$^{+1}$ ions produced during magnetron sputtering with conventional DC power.**

The time averaged IEDs for the Cr$^{+1}$ ions are relatively narrow for both types of power as is shown in Figure 2. The average energy for the Cr$^{+1}$ ions is 2eV, and only a small number of ions have an energy exceeding 5eV. The average energy for the DC Cr$^{+1}$ ions is slightly higher than that of the MPP Cr$^{+1}$ ions and is about 4eV. Both the MPP and DC Cr$^{+1}$ IEDs show a relatively small high energy tail. The upper energy value is about 10eV for the Cr$^{+1}$ ions produced by both types of power.

The time averaged IEDs for the MPP and DC Ar$^{+1}$ ions are shown in Figure 3. The difference in intensities for the Ar$^{+1}$ ions produced by both types of power is not as great as it was for the Cr$^{+1}$ ions. The MPP Ar$^{+1}$ ions have the highest intensity at about 600,000cps compared to an intensity of about 180,000cps for the DC Ar$^{+1}$ ions. The average ion energy for the MPP Ar$^{+1}$ ions is about 2eV, but it is higher for the DC Ar$^{+1}$ ions at about 3eV. Similar to the Cr$^{+1}$ IEDs, both the MPP and DC Ar$^{+1}$ IEDs have a relatively small high energy tail that extends out to about 10eV.
Mass/Energy Analysis

Both IEDs plots for the Cr$^{+1}$ and Ar$^{+1}$ ions show a small negative energy region. It is believed that that negative energy region is an artifact of ions being created inside the EQP probe during the measurements. For more details on this phenomenon, see the work by Lin et al. [8].

Summary

An electrostatic quadrupole plasma (EQP) mass spectrometer was used to characterize the plasmas during magnetron sputtering of chromium using both MPP and conventional DC power. The time averaged positive ion mass distributions and the positive ion energy distributions were determined. In the MPP plasma, ions of Cr$^{+1}$, Ar$^{+1}$, Cr$^{+2}$, and Ar$^{+2}$ ions were readily detected. The intensity was highest for the Cr$^{+1}$ ions, but the Ar$^{+1}$ ions were also abundantly present at the position in the plasma where a substrate would be placed. For the DC plasma, the Ar$^{+1}$ ions were the dominant species in the plasma. There were a small number of Cr$^{+1}$ ions, but they were significantly less than what was found in the MPP plasma. There were only trace amounts of the Cr$^{+2}$ and Ar$^{+2}$ ions in the DC plasma. The measurement of the IEDs for the Cr$^{+1}$ and Ar$^{+1}$ ions showed that the average Cr$^{+1}$ ion energy was about 2eV in the MPP plasma and about 4eV in the DC plasma at a position where a substrate would be placed. The Ar$^{+1}$ IED revealed that the average ion energy in the MPP plasma was about 2eV whereas it was about 3eV in the DC plasma. For both IEDs for the Cr$^{+1}$ and Ar$^{+1}$ ions, there is a small high energy tail extending out to about 10eV.

References


William D. Sproul is the founder and president of Reactive Sputtering, Inc. Throughout his technical career, he has been involved with reactive sputtering of oxide, nitride, and carbide coatings. He is the inventor of the high-rate reactive sputtering process, and he was instrumental in the development of multi-cathode unbalanced magnetron sputtering processes. More recently he has been involved with high power pulsed magnetron sputtering. He has authored or co-authored over 162 publications, he holds 11 U.S. patents, and he has given over 250 technical presentations. He teaches short courses on Tribological Coatings, Sputter Deposition, and The Practice of Reactive Sputtering, and he is currently a Research Professor at the Advanced Coatings and Surface Engineering Laboratory at the Colorado School of Mines. He was president of the AVS in 1996, and he also served as a member of the AVS board of directors. He recently completed a 3-year term on the SVC board of directors. In 2003, he was selected as the winner of the AVS Thornton Award and the SVC Mentor Award. He serves on the editorial boards for Surface and Coatings Technology and for Vacuum. He received his Sc.B., Sc.M., and Ph.D. degrees in Materials Science Engineering from Brown University in 1966, 1968, and 1975, respectively.

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