

MPP Deposition of Thick Tantalum Coatings

W.D. Sproul, The George S. Ansell Department of Metallurgical & Materials Engineering, Colorado School of Mines, Golden, CO and Reactive Sputtering, Inc., San Marcos, CA; J. Lin and J.J. Moore, The George S. Ansell Department of Metallurgical & Materials Engineering, Colorado School of Mines, Golden, CO; S.L. Lee, U.S. Army ARDEC Benét Labs, Watervliet, NY; and J. Wang, Department of Vacuum Technology and Process Equipment, HeFei University of Technology, HeFei, China

ABSTRACT

Tantalum coatings with thicknesses up to 100 μm were sputter deposited onto steel substrates at floating potential using Modulated Pulse Power (MPP) in a dual magnetron opposed cathode unbalanced magnetron sputtering system at sputtering pressures between 2.3 and 12 mTorr. Deposition rates up to 13-14 $\mu\text{m/hr}$ at an average power of 4.5 kW have been achieved. An electrostatic quadrupole plasma mass spectrometer was used to characterize the plasma during the MPP depositions as a function of the process pressure. Ta^+ , Ar^+ , and Ta^{2+} ions were detected with the Ta^+ ions being the dominant species. The intensities of the ions increased up to a pressure of 7.0 mTorr and then decreased after this pressure. All of the ions had an average energy of about 2.5-3 eV, and all ions had a small high energy tail. Both alpha and beta phases of tantalum were deposited depending on the deposition pressure and coating thickness. For argon pressures below 4.0 mTorr, the coatings have the bcc α -Ta crystalline structure, whereas for pressures greater than or equal to 5.0 mTorr, the crystalline structure is the tetragonal β -Ta. The hardnesses of the coatings peak at a deposition pressure of 5.0 Pa as do the moduli of the coatings. The α -Ta coating is much softer than the hardness of the β -Ta coatings. For the α -Ta coatings deposited in the pressure range of 2.3 to 4.0 mTorr, the hardness varied from about 9 to 11 GPa. For the β -Ta coatings, the peak hardness of about 20 GPa occurred at a deposition pressure of 5.0 mTorr, and the hardness decreased to about 18 GPa as the pressure was increased to 10.0 mTorr. The modulus for both the α - and β -Ta crystalline structures was in the range of 210 to 230 GPa. The thickness of the coating also affected the crystalline structure of the coatings. At floating potential for coatings deposited with thicknesses less than 7 μm , the coatings had the β -Ta structure, but for thicknesses $\geq 7 \mu\text{m}$ the coatings had the α -Ta structure.

INTRODUCTION

Tantalum is an interesting material that has many industrial applications. It is used in many electrical/electronic applications [1, 2], but it is also used in many wear and corrosion resistant applications [3, 4, 5]. Tantalum has two crystalline forms, which are the bcc alpha-tantalum and the tetragonal beta-tantalum. The application determines which crystalline form is needed, and thus it is important to know the effect of process parameters on the crystalline structure.

In this study, the Modulated Pulse Power (MPP) form of high power pulse magnetron sputtering (HPPMS) [6, 7] was used to deposit tantalum coatings at different deposition pressures to determine the effect of the process pressure on the structure and properties of the deposited Ta coatings. Traditionally, sputter deposited coatings have been restricted in thickness of the deposit because the residual stress in the film increases as the coating thickness increases. When the stress gets too high, the coating will delaminate. However with the introduction of HPPMS and MPP, both of which produce a highly ionized flux of the sputtered material, it has been demonstrated that it is now possible to deposit coatings with low residual stress compared to coatings deposited by the more convention forms of magnetron sputtering [8].

The goal of the work reported here was to determine the effect of the process pressure on the structure and properties of Ta coatings deposited by MPP and to determine if it is possible to deposit Ta coatings with thicknesses in excess of 50 μm . It was found that Ta coatings with thicknesses up to 100 μm could be deposited with good scratch adhesion test strengths to the substrate, and thicknesses in excess of 100 μm were not attempted in order to conserve target material. It is very probable that thicker coatings can be deposited if need be.

EXPERIMENTAL CONDITIONS

All of the MPP depositions were carried out in a closed field dual opposed cathode unbalanced magnetron sputtering system. During the depositions only one of the Teer Coatings Ltd cathodes was powered with a Zpulsor Solo/Axis-180™ power supply. The target to substrate distance was 120 mm, and the substrates, either were pieces of AISI 304 stainless steel or A257 hardened steel, were stationary during the deposition. Prior to being placed in the coating chamber, the substrates were cleaned ultrasonically first in acetone and then in ethylene for 15 minutes each. After the substrates were loaded into the chamber and the base pressure reached a pressure of 1×10^{-6} Torr or lower, the substrates were sputter etched using conventional pulsed DC power from an Advanced Energy Pinnacle Plus power supply with the voltage set at -450 V with a pulse frequency of 100 kHz and duty cycle of 90% for 30 minutes. During deposition, no negative bias was applied to the substrates. Substrates were at floating potential.

The MPP power supply was run in a constant pulse repetition rate mode set at 100 Hz, and the cathode voltage, current, and power varied as a function of the Ar working pressure. The MPP pulse shape recorded at a pressure of 5.0 mTorr is shown in Figure 1. The overall pulse length was 1000 μ s, and half of the pulse time was spent in the low power weakly ionized plasma regime with the remaining time spent in the highly ionized high power regime. This pulse shape was used for all of the pressure experiments.

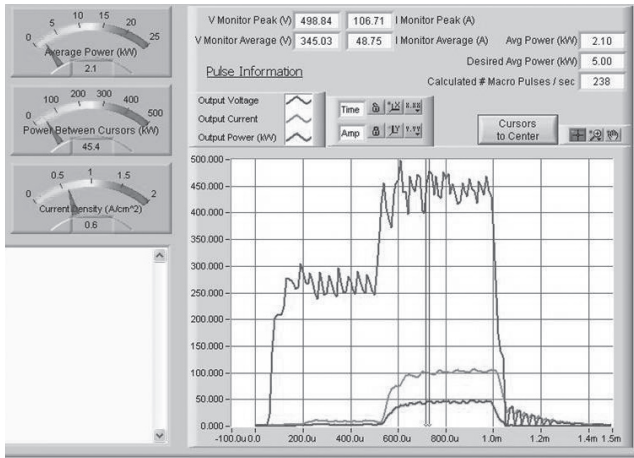


Figure 1: MPP pulse shape generated at a pressure of 5.0 mTorr and a repetition rate of 100 Hz.

The ion mass and energy distributions (IMD and IED) were measured during the Ta depositions using a Hidden Analytical Electrostatic QuadruPole (EQP) mass spectrometer. The EQP probe was located at a point where a substrate would be placed in the middle between the two cathodes. During the IMD measurements, a voltage of -20V was placed on the filament within the probe in order to attract positive ions from the plasma into the probe. For the IED measurements, scans were conducted by varying the filament voltage from -5 to 100V with a step size of 0.5V. Dwell time was 100 ms.

A Siemens X-Ray diffractometer, model KRISTALLOFLEX-810 operating with $\text{CuK}\beta_{\alpha}$ radiation at a voltage of 30 kV and a current of 20 mA in the θ - 2θ mode, was used to measure the crystal structure of the Ta coatings. Coating cross sections were examined with a JSM-7000F field-emission scanning electron microscope (SEM) operated with an accelerating voltage of 5 kV. The thickness of the coatings was measured both with the SEM and with an optical microscope. The hardness and Young's modulus of the coatings was measured with a MTS Systems Corporation nanoindenter (NanoIndenter XPTM) outfitted with a Berkovich diamond indenter. In order to obtain reliable mean value and standard deviation, a minimum of 20 indents was done for each sample.

RESULTS AND DISCUSSION

The variation in the argon pressure had a significant effect on the cathode voltage, current, and power for the pulse shape that was used at the repetition rate of 100 Hz. Changes in the cathode voltage, current, and power as a function of the argon pressure are shown in Figure 2. As the pressure was increased, the average target voltage decreased from 370 to 325V, a drop of 12%. The peak target voltage only dropped slightly. For the target current, both the average and the peak current increased significantly as the pressure was increased from 2.3 to 12 mTorr. The average target current went from 35 to 64A, an increase of 83%, and the peak current went from 77 to 150A, an increase of 93.5%.

Since the current rose faster than the drop in voltage, both the average and peak target power increased as the pressure increased over the same range. The average target power increased by 62.5%, and the peak target power increased by 71%.

The increase in the argon working pressure improved the probability of secondary electrons from the target colliding with the gas atoms, which resulted in the drop of the cathode voltage. However more ions were produced as the pressure was increased, which increased the target current. Since the current went up faster than the voltage dropped, the target power increased.

The deposition rate for the Ta coatings varied from 35 nm/min at the 2.3 mTorr pressure up to 67 nm/min at the 12 mTorr pressure. For the deposition of 100 μ m thick Ta coatings, these deposition rates would have resulted in extremely long deposition times. In order to overcome this issue for the very thick depositions, the average target power was increased to 4.5 kW at an Ar pressure of 5 mTorr. Under these conditions with the substrate at the floating potential, the deposition rate was 13-14 μ m/hr, which resulted in deposition times of 7-8 hours for the 100 μ m thick Ta coatings.

The EQP IMD measurement results are shown in Figure 3. The Ta^+ ions are the dominant species in the plasma followed by the Ar^+ ions and then the Ta^{2+} ions. The intensities of the Ar^+ and Ta^+ ions increased as the pressure was increased from 2.3 to 7.0 mTorr, and then the intensities dropped as the pressure was increased further. For the Ta^{2+} ions, the intensity of ions peaked at 5.0 mTorr, and then decreased as the pressure increased beyond this pressure. It is believed that scattering effects led to this decrease in intensities at the higher pressures.

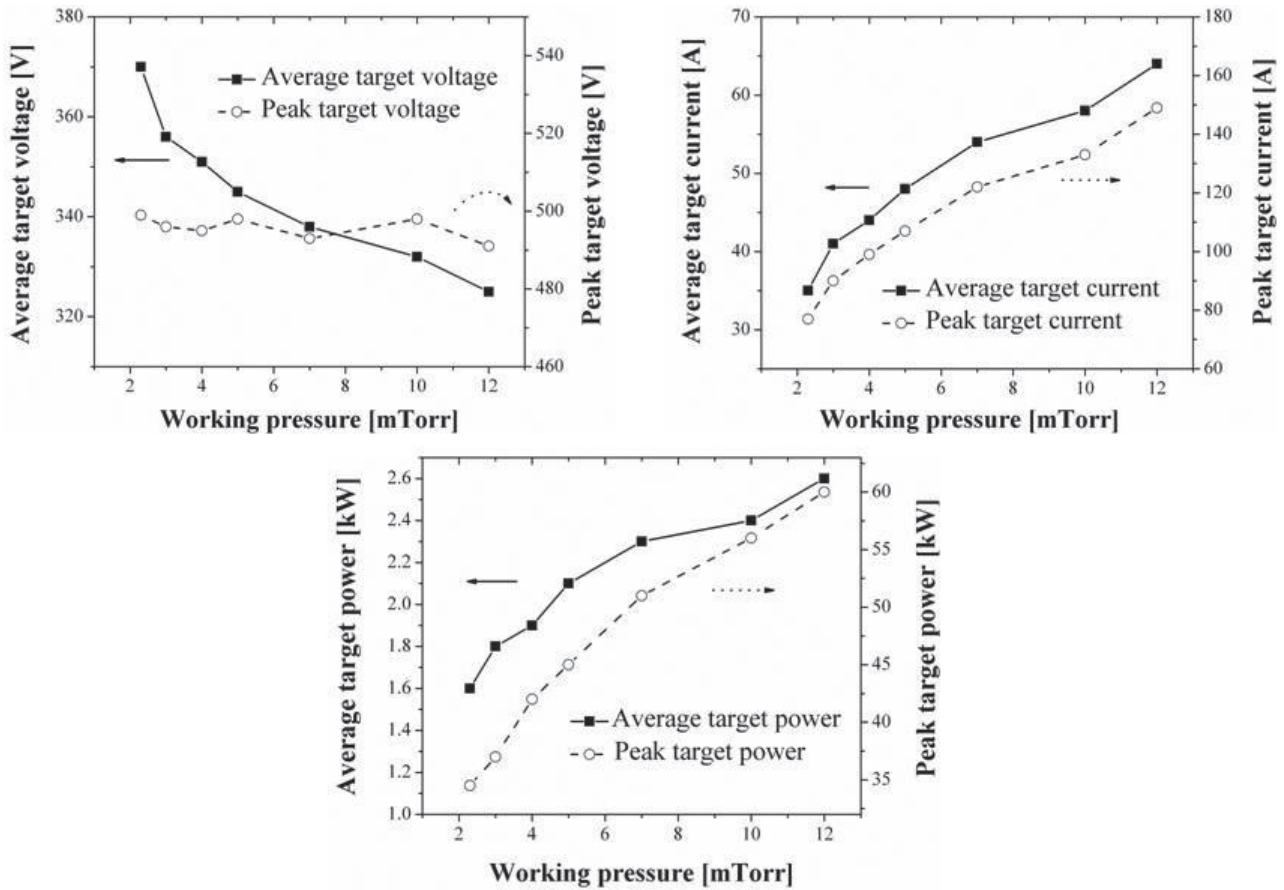


Figure 2: The cathode voltage, current, and power as a function of the Ar pressure at a constant pulse repetition rate of 100 Hz.

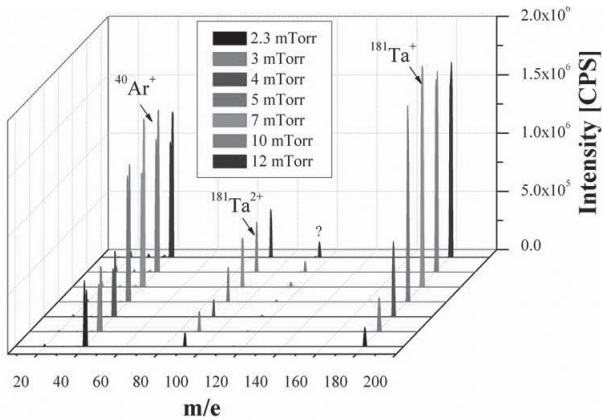


Figure 3: EQP ion mass distribution measurements as a function of the Ar pressure.

The EQP IED measurements showed that the three ion species peaked in intensity between 5.0 and 7 mTorr, and that the average ion energy was in the range of 2.5-3 eV. All three ions had a relatively low high energy tail. For the Ar⁺, Ta⁺,

and Ta²⁺ ions, the high energy tail extended out to 15, 13, and 10 eV, respectively. The slight difference in the maximum tail ion energies of these ions is due to their mass difference which will affect the time taking the ions to cross from the plasma to the EQP.

The dominance of the Ta⁺ ions can be seen in Figure 4. Here the integrated ion flux intensities are shown over the pressure range of 2.3 to 12 mTorr. Once the pressure exceeds 4 mTorr, the Ta⁺ ions are the dominant species in the plasma.

For the Ta coatings deposited at the floating substrate bias potential, the crystallographic structure and morphology are a function of the deposition pressure as can be seen in Figure 5. For pressures at or below 4 mTorr, α-Ta coatings were deposited. The coatings have a columnar structure that appears to become denser and less columnar as the pressure is increased. SEM images of the surfaces of the coatings showed that the coating deposited at 5.0 mTorr had the least amount of porosity visible on the top surface of the coating.

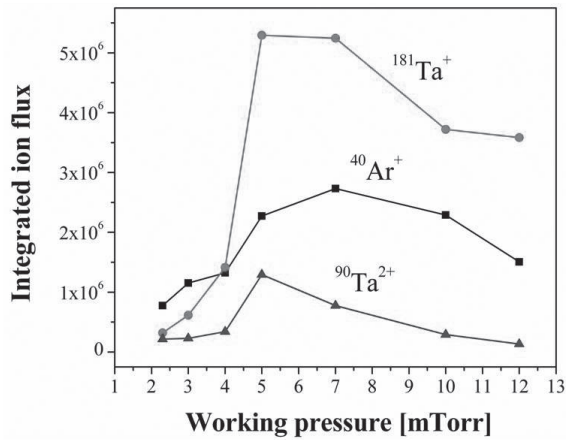


Figure 4: The integrated ion flux intensities for Ta^+ , Ar^+ , and Ta^{2+} over the pressure range of 2.3 to 12 mTorr.

Nanoindentation tests showed that the α -Ta coatings were the softer coatings compared to the β -Ta coatings as can be seen in Figure 6. The α -Ta coatings had hardnesses in the range of about 9.5 to 11 GPa whereas the β -Ta coatings had

hardnesses in the range of 18 to 20 GPa. These hardness values are higher than those of the dcMS α -Ta (500 HV/5 GPa) and β -Ta (1600 HV/15.6 GPa) coatings, as reported by Lee et al [9]. The peak hardness for all of the Ta coatings was 20 GPa for the coating deposited at the 5.0 mTorr working pressure. There was some variation of the Young's modulus for the Ta coatings, but there was not a significant difference for the two crystalline phases. The Young's modulus had a range of about 210 to 233 GPa over the range of the working pressures studied.

For Ta coatings deposited at the floating substrate potential and a pressure of 5.0 mTorr, the crystallographic structure of the coatings was also a function of the coating thickness as can be seen in Figure 7. For coating thicknesses less than 7 μm , β -Ta coatings were deposited, but at thicknesses greater than or equal to 7 μm , α -Ta coatings were deposited. Even though these coatings were deposited with the floating bias potential, the stress in the coatings did increase as the thickness increased. It is believed that at thicknesses equal to or greater than 7 μm , the stress in the coating is sufficient to cause the transition from β -Ta to α -Ta to occur.

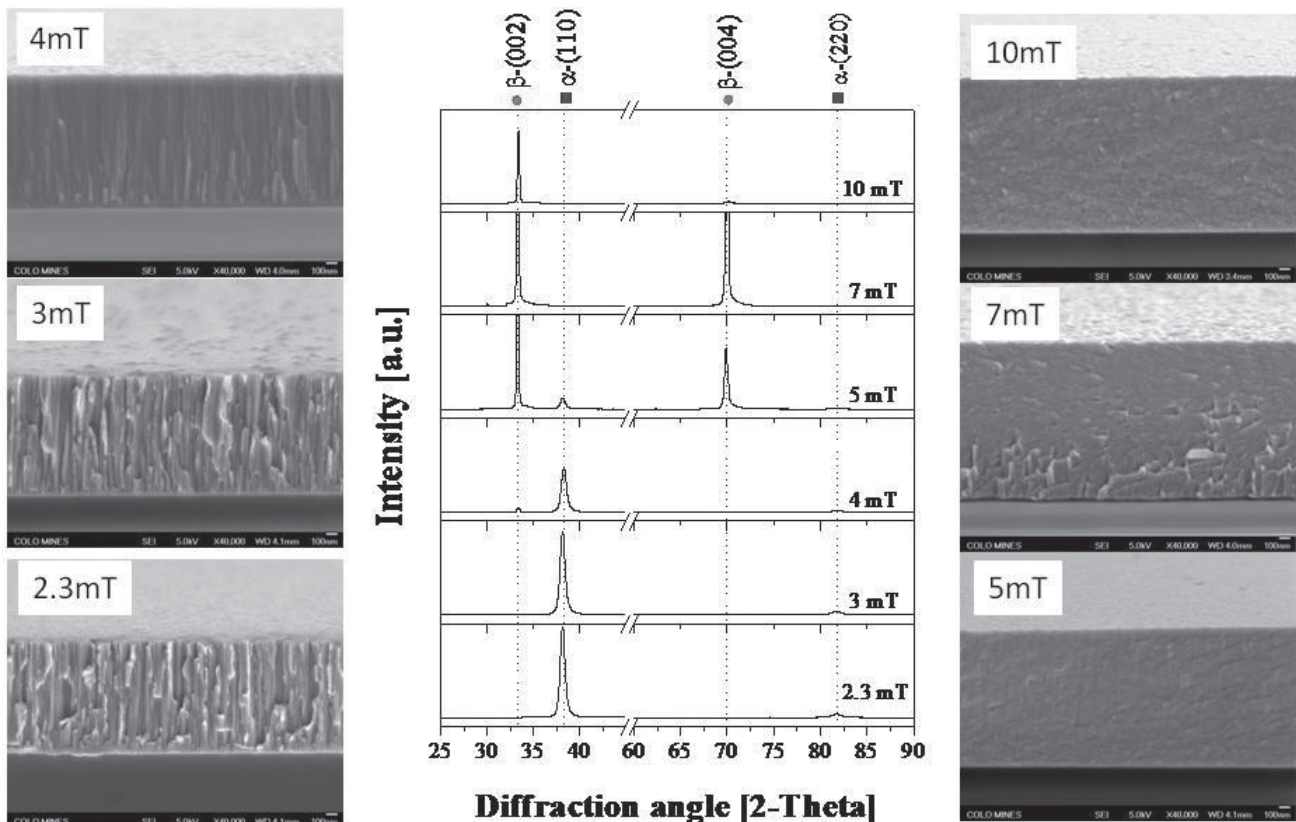


Figure 5: The X-Ray diffraction and SEM cross-section photomicrographs of the Ta coatings deposited over the 2.3-12 mTorr range.

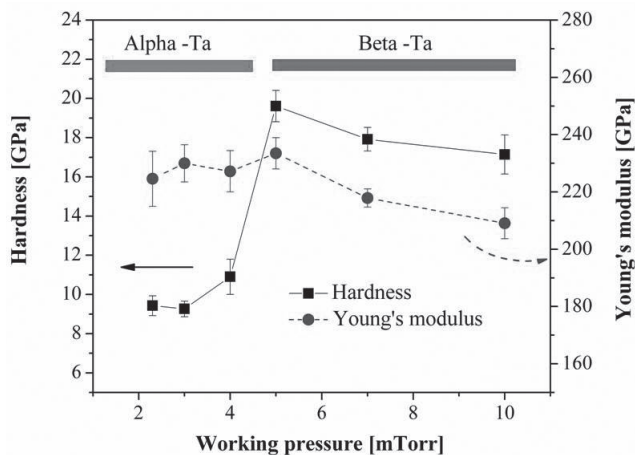


Figure 6: Nanoindentation hardness and Young's modulus values for the Ta coatings deposited over the pressure range of 2.3-12 mTorr.

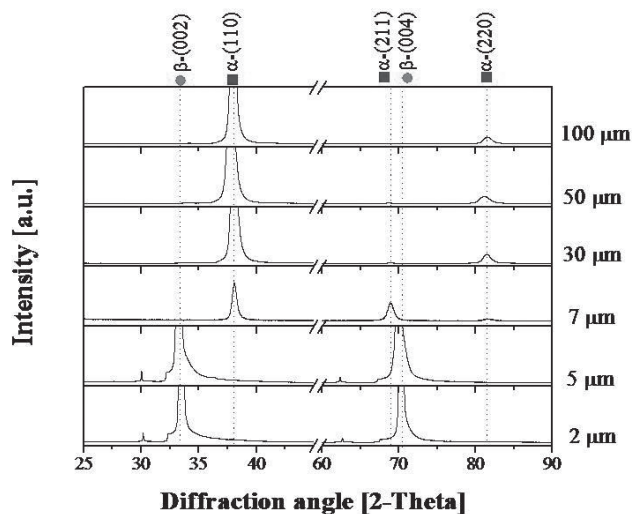


Figure 7: X-Ray diffraction patterns of Ta coatings with different thicknesses deposited with a floating substrate bias. The crystalline structure changes from β -Ta but changes to α -Ta once the coating thickness is $7 \mu\text{m}$ or greater.

Although there are stresses in the coatings, they were not so high as to cause delamination problems. Several coatings done at different Ar working pressures were deposited with thicknesses of $100 \mu\text{m}$, and none of these coatings delaminated during the scratch adhesion test.

SUMMARY

MPP power in a fixed pulse repetition rate mode was used to deposit Ta coatings at different Ar working pressures in the range of 2.3 to 12 mTorr with the samples at floating bias potential. The change in the Ar pressure had a significant effect on the target power, current, and power. While the target

voltage decreased somewhat as the working pressure changed from 2.3-12 mTorr, both the current and power increased significantly. EQP measurements showed that Ta^+ ions were the dominant species in the plasma, exceeding the Ar^+ ions by a factor of 2 in intensity in most cases. The average energy of these ions was in the range of 2.5-3 eV, and the high energy tails were less than 15 eV. The working pressure controlled the crystalline structure of the coatings. At pressures ≤ 4.0 mTorr, α -Ta coatings were deposited, but for pressures ≥ 5.0 mTorr β -Ta coatings were deposited. The hardness of the α -Ta coatings was about half of the hardness of the β -Ta coatings, but there was only a small difference in the Young's modulus for the α - and β -Ta coatings. The thickness of the coating can also affect its crystallographic structure. For coatings deposited at 5 mTorr with floating substrate potential, β -Ta coatings were deposited when the thickness was less than $7 \mu\text{m}$, but when the thickness exceeded $7 \mu\text{m}$ under the same deposition conditions, α -Ta coatings were deposited.

ACKNOWLEDGEMENT

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