Effect of Negative Substrate Bias on the Structure and Properties of Ta Coatings Deposited Using Modulated Pulse Power Magnetron Sputtering

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***Abstract*—Crystalline phase control is critical for obtaining desired structure and properties of Ta coatings deposited by magnetron sputtering. We have shown the approach to control the alpha and beta Ta phase formations by tuning the negative substrate bias voltage during modulated pulse power (MPP) magnetron sputtering, which generates a large fraction of target metallic ions in the plasma providing enhanced ion bombardment on the growing film. It was found that the peak and mean substrate ion current densities increased rapidly from 42 to 165 mAcm^{-2} and 16 to 55 mAcm^{-2}, respectively, as the negative substrate bias voltage was increased from -20 to -50 V and became saturated with a further increase in the negative substrate bias voltage. As the negative substrate bias voltage was increased from 0 to -100 V, the MPP Ta phase changed from an all beta phase when the bias voltage was at 0 V and a floating bias, to a mixed alpha and beta phases when the bias voltage was in the range of -30 to -40 V, and finally to an all alpha phase when the negative bias voltage was -50 V or greater. In this paper, alpha Ta coating with thicknesses up to 100 μm were successfully deposited using the MPP technique with high deposition rate. The residual stress of the thick Ta coating was measured using an X-ray stress analyzer. The adhesion strength of the thick Ta coating was evaluated using Rockwell-C indentation and scratch tests. The possibility to coat complex-shaped substrates with good coating coverage on the substrate's surface placed orthogonal to the target has also been demonstrated.**

***Index Terms*—High power pulsed magnetron sputtering (HPPMS/HiPIMS), modulated pulse power (MPP), negative substrate bias, tantalum (Ta) coating, thick coating.**

I. INTRODUCTION

As ONE OF the refractory metal materials, tantalum (Ta) exhibits many interesting physical and chemical properties which make it an important candidate coating material for various applications. Ta thin films and coatings have been widely used in high temperature and wear protection applications, e.g., gun bore protection, due to its high melting temperature ($T_m = 2996\ ^\circ C$), good thermal impact resistance, low thermal conductivity, and excellent corrosion resistance [1]–[3]. It is also an important barrier material for copper metalization in integrated circuits [4], [5]. Since nonequilibrium thermodynamic growth is inherent to thin film vapor deposition, magnetron sputtered Ta thin films can exhibit a body center cubic (bcc) structure (known as α-Ta), or a tetragonal structure (known as β-Ta), or a mixture of two phases, as what has been widely reported [6], [7].

Comparing the electrical properties of these two phases, β-Ta has a higher electric resistivity ($150-200\ \mu\Omega$.cm) than that of α-Ta ($15-80\ \mu\Omega$.cm) [8], [9]. Therefore, β-Ta can be used as thin-film resistors providing a stable resistance property in a wide temperature range due to its smaller temperature dependence on the electrical resistance, whereas α-Ta is more suitable for low resistant barriers for diffusion.

Comparing the mechanical and tribological properties of these two phases, β-Ta has higher hardness than α-Ta [2]. Nevertheless, β-Ta is more brittle and has a much smaller temperature coefficient of resistance than α-Ta [1]. Therefore, it has been suggested that α-Ta is more suitable than β-Ta for high temperature wear and erosion applications, for example as a protective gun-barrel coating which has been widely investigated [1], [2], [10]. Basically, there are three important aspects that are needed to be considered for such an application: one is that the crystal phase of the coating needs to be an α-Ta, the second is that the thickness of the coating needs to be large enough ($> 70\ \mu$m) to assure excellent wear resistance and increased service life of the coating, and the coating also needs to be able to cover the steps of the gun barrel with excellent adhesion strength to the substrate.

Early work on the deposition of Ta coatings as a high temperature wear resistance coating largely used dc magnetron sputtering (dcMS) [1], [2], [10]. The effects of various deposition parameters and substrate conditions, including sputtering gas, stress, ion bombardment, substrate surface roughness, substrate material, substrate surface oxide layer, etc., on the Ta coating phase formation have been intensively investigated [2], [9],

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[11]–[14]. Among these factors, it was found that the ion bombardment on the growing film played an important role in affecting the obtained phase of Ta coatings. In the conventional dcMS, the ionization degree of the target material is low (e.g., 1%–3%), and the ion bombardment usually was enhanced by using a negative substrate bias.

In recent years, with the development of high power pulsed magnetron sputtering (HPPMS/HiPIMS) [15]–[18] and modulated pulse power (MPP) magnetron sputtering [19]–[22], a considerably large fraction of ionized target metal species has been created by applying a large amount of peak power (up to hundreds of kilowatts) and peak current (up to hundreds of amperes) to the sputtering target for a short period of time using the pulsed waveform. The pulse is repeated periodically to produce an average power that is comparable to that normally used in dcMS. Since the HPPMS/HiPIMS and MPP plasmas contain large amount of target and gas ions, a significantly higher level of ion bombardment and more effective momentum transfer on the growing Ta film is expected as compared to that in the dcMS condition. Moreover, the kinetic energy and the behaviors of ions and electrons arriving on the growing film strongly depend on the level of the substrate bias. Alami *et al.* [23] investigated the negative substrate bias effect on the phase formation of HiPIMS Ta coatings at a working pressure of 0.67 Pa. They demonstrated that the negative bias voltage promoted the formation of α-Ta due to high Ta ion-to-neutral ratio in the deposition flux. Therefore, it is expected that the enhanced ion bombardment in MPP can also be possibly utilized to tailor the phase structure and improve the structure and properties of Ta coatings.

In the current study, the effects of negative bias voltage on the substrate ion current density, the crystalline phase formation, the microstructure and hardness changes of the MPP sputtered Ta coatings were investigated. We also report on the approach of producing thick α-Ta coatings (up to 100 μm) with high deposition rate and good coating coverage on the substrate's surface placed orthogonal to the target by using the MPP technique.

II. EXPERIMENTAL DETAILS

The depositions were carried out in a closed-field unbalanced magnetron sputtering system equipped with two rectangular shaped unbalanced magnetrons installed opposite and parallel to each other. The schematic configuration of the system was reported earlier [21]. A metal Ta target (300 × 100 mm) with a purity of 99.99% was powered by an MPP power supply (SOLO/AXIS-180 Pulsed DC Plasma Generator, Zpulser LLC).

AISI 304 stainless steel coupons and (100) Si wafers were used as substrates, which were ultrasonically cleaned in acetone and ethylene for 15 min, respectively. The substrates were mounted on a substrate holder with a target to substrate distance of 120 mm. A base pressure of less than 1×10^{-4} Pa was reached prior to all coating depositions. The substrates were sputter-etched by Ar plasma bombardment at a pulsed bias voltage of -450 V (100 kHz and 90% duty cycle) to enhance the coating adhesion using a middle frequency pulsed dc power supply (Pinnacle Plus, Advanced Energy Inc.). During the depositions, high purity Ar (99.999%) was introduced into the system using an MKS mass flow controller with a flow of 62 sccm. The working pressure, as measured by high precision capacitance manometer, was kept constant at 0.67 Pa.

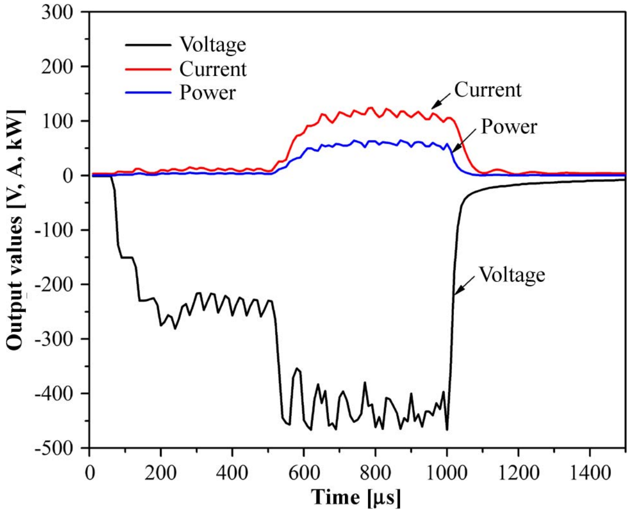


Fig. 1. Target voltage, current, and power waveforms during one modulated pulse used for Ta coating deposition (pulsewidth $= 1000$ μs, $f = 100$ Hz, $P_a = 2.5$ kW).

Ta coatings were deposited at different negative dc bias voltages on the substrate from 0 to 100 V at an average MPP target power (P_a) of 2.5 kW. The pulse shape applied on the target is shown in Fig. 1. It is a 1000-μs pulse which contains a 500 μs weakly ionized stage and a 500 μs strongly ionized stage. The peak power (P_p), peak voltage (V_p), and peak current (I_p) generated during the strongly ionized stage were 50 kW, -430 V, and 100 A, respectively. The repetition rate (f) of the pulse was 100 Hz. The negative bias voltage was controlled by a Zpulser AXIS dc bias power supply which has the capability to handle a maximum of 60 A current with arc suppression to avoid the bias voltage drop during the highly ionized portion of the MPP pulse. The thickness of the deposited coatings exhibited small variations in a range of 4.2–4.5 μm.

Thick Ta coatings with thicknesses up to 100 μm were deposited on AISI 304 stainless steel and A723 tool steel coupons using the same pulse shape with a pulse length of 1000 μs as shown in Fig. 1. However a higher P_p of 56 kW, an I_p of 136 A, and a P_a of 3 kW were utilized to enhance the deposition rate. A -50-dc bias voltage was used for thick coating deposition.

The ion energy distribution (IED) during MPP Ta coating deposition was measured using a Hiden electrostatic quadrupole plasma mass spectrometer (EQP) in an effort to determine the ion energy level in the plasmas. The EQP probe was installed parallel to the target surface through the side of the chamber. The EQP axis was placed exactly along the middle line between the two targets. The distances between the EQP orifice (100-μm diameter) to the target surfaces and the center of the chamber were 120 and 25 mm, respectively, as described in [21]. During the plasma examination, a negative voltage of -20 V was applied on the filament for attracting and sampling the positive ions within the plasma. The IED scans were measured from -5 to 100 V with a step size of 0.5 V and a 100-ms dwell time.

The peak and mean substrate ion current densities (I_{sub}) during the coating depositions were measured by a current monitor which was installed in the bias power supply. The crystal structure of Ta coatings were characterized using monochromatic CuK_α radiation on a Siemens X-ray diffractometer (Model KRISTALLOFLEX-810) operated at 30 kV and 20 mA in the $\theta - 2\theta$ mode. The cross section of the coatings was examined using a JSM-7000F field-emission scanning electron microscope (FESEM) operated at 5-kV accelerating voltage. The thickness of the coatings was determined from the cross-sectional SEM observation. For the thick Ta coatings, the coating thickness was double checked by examining the cross section of the metallographic polished specimen under an optical microscope.

The hardness and Young's modulus of the coatings were measured using a nanoindenter (NanoIndenter XPTM, MTS Systems Corporation) equipped with a diamond Berkovich tip. The indentation depth was controlled to be 10% of the coating thickness to avoid the substrate effect. At least 20 measurements were carried out for each sample to obtain the mean value and the standard deviation.

The residual stress of the thick Ta coating was measured using a TEC (Technology for Energy) X-ray stress analyzer using Cr radiation. The Ta [220] reflection was used to obtain residual stress with psi oscillation angles from $-40°$ to $40°$ at 100 s counting time per angle. The adhesion strength of the thick Ta coating (100 μm) was evaluated using two methods. For the coating deposited on AISI 304 stainless steel, Rockwell-C adhesion (HF) tests were carried out at a 150-kg load using a 200 μm radius Rockwell-C indenter. The indent was examined by FESEM according to the VDI guidelines 3198, (1991) [24]. For the coating deposited on A723 hard tool steel, the adhesion strength of the coating was evaluated by a Teer scratch tester using a Rockwell C indent tip (tip radius $\mathrm{R} = 200$ μm and conical angle $= 120°$). The applied load was increased from 5 to 100 N with an increasing speed of 100 N/min and a scratch length of 6 mm. The friction force change was monitored as a function of the progressive load. The end of the scratch track was examined by FESEM and energy dispersive X-ray spectroscopy (EDS).

III. RESULTS AND DISCUSSION

A. *Ion Energy Distribution of the MPP Ta Coating Deposition*

Fig. 2 shows the IEDs of Ar^+, Ta^+, and Ta^{2+} ions measured during the MPP Ta coating deposition at a 0.67 Pa working pressure, a P_p of 50 kW, and an I_p of 100 A. The IEDs of all ion species exhibited a peak energy of 3 eV. The Ar^+ and Ta^+ ions exhibited a similar maximum tail energy of about 12 eV, whereas the Ta^{2+} ions exhibited a lower maximum tail energy at 8 eV due to its lower m/e ratio [21]. It is evident that the IED of Ta^{2+} ions exhibits good intensity and the Ta^+ IED has a higher peak intensity than that of the gas Ar^+ ion, suggesting that a large fraction of the ion species within the plasma is from the target metal ions. The IEDs during the MPP Ta coating deposition exhibited similar characteristics to those observed previously for the MPP Cr and CrN coating depositions [21], [25].

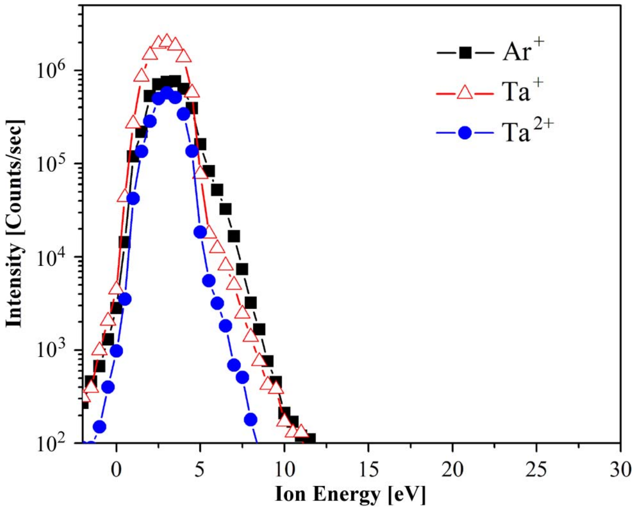


Fig. 2. Ion energy distributions of Ar^+, Ta^+, and Ta^{2+} ions during the MPP Ta coating deposition (working pressure $= 0.67$ Pa, $P_a = 2$ kW, $P_p = 50$ kW, $I_p = 100$ A, and $f = 100$ Hz).

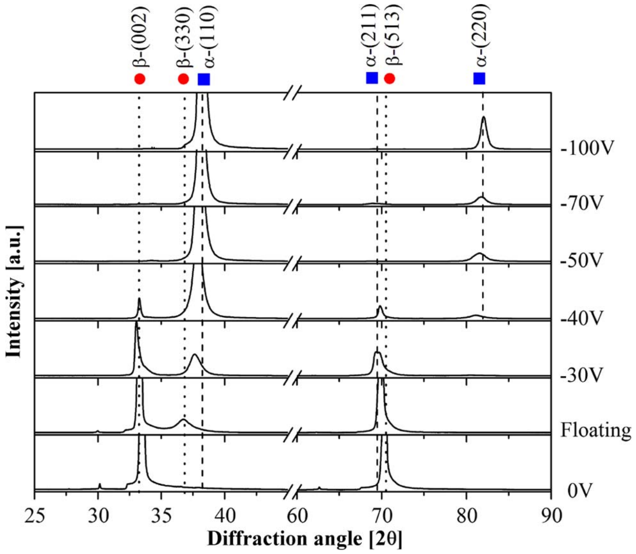


Fig. 3. XRD patterns of the MPP Ta coatings deposited at different negative substrate bias voltages.

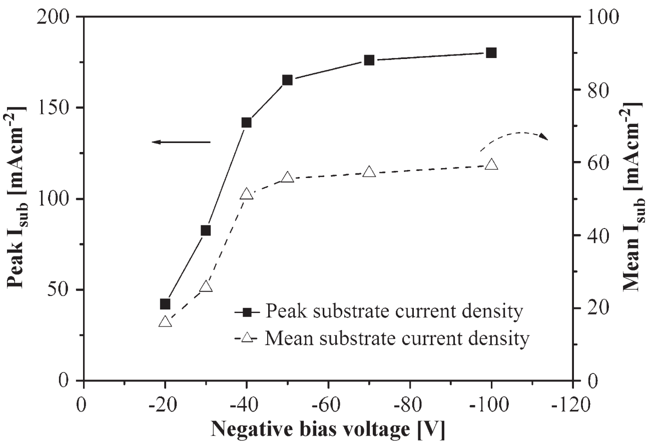


Fig. 4. Peak and mean substrate ion current densities as a function of the negative bias voltage during the MPP Ta coating depositions (working pressure $=$ 0.67 Pa, $P_a = 2.5$ kW, $P_p = 50$ kW, $I_p = 100$ A).

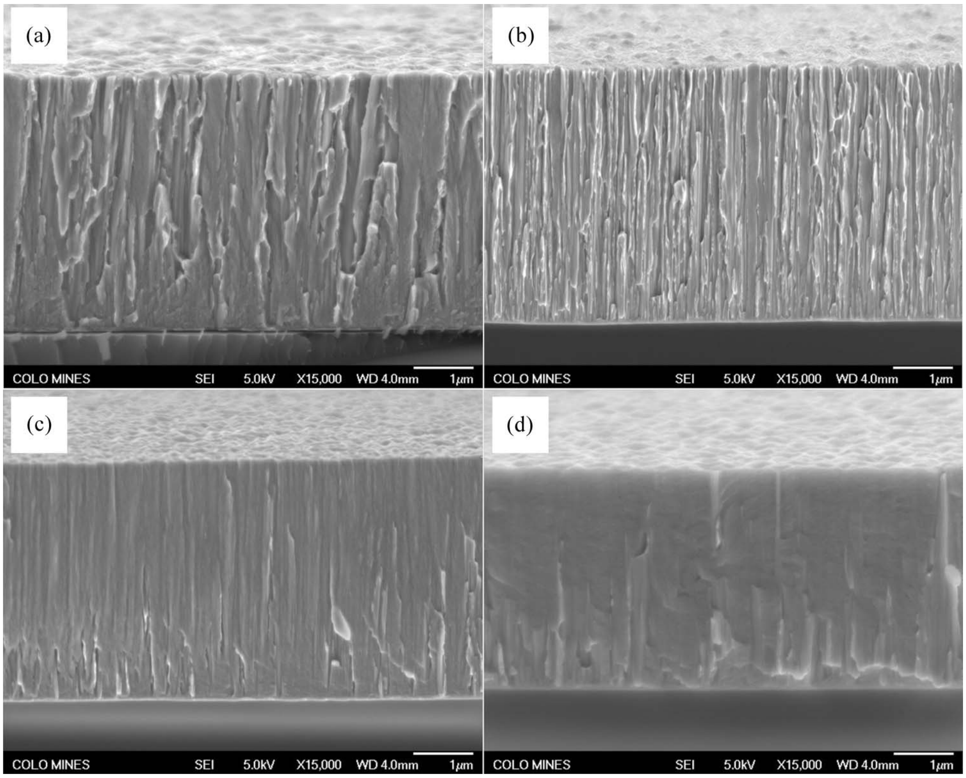


Fig. 5. Cross-sectional SEM micrographs of the Ta coatings deposited at (a) 0, (b) −30, (c) −50, and (d) −70 V negative substrate bias voltages.

The considerably large fraction of ionized target metal species in the MPP plasma is critical for providing high ion flux bombardment during the deposition to densify the film and enhance the adhesion, while the low kinetic ion energy will keep the defect density and residual stress at a low level in the films.

B. Effects of Negative Substrate Bias on the MPP Ta Coatings

Fig. 3 shows the XRD patterns of Ta coatings deposited with different negative bias voltages. The coating that is deposited on the grounded substrate (0 V) exhibited strong tetragonal (002) and (513) reflections (JCPDS 25-1280), corresponding to a pure beta phase structure. The coating deposited at a floating bias voltage also exhibited a beta phase with intense (002) and (513) reflections, while a broad (330) peak appeared, indicating that a polycrystalline structure had developed and a possible decrease in grain size within the coatings. As the negative bias voltage was increased, the phase structure of the coatings gradually changed from a mixed alpha and beta phases at −30 and −40 V bias voltages to an all alpha phase at a −50 V and greater, where the alpha Ta (110), (211), and (220) reflections (JCPDS 04-0788) were identified (Fig. 3). Peak broadening of the diffraction peaks was observed as the negative bias voltage was increased (Fig. 3), suggesting a decrease in the grain size and/or an increase in the residual stress in the coatings from the increased ion bombardment energy.

Since MPP is an alternative HPPMS/HiPIMS technique that generates a large fraction of metal target ions in the plasma as the ion irradiation source for the growing film (as shown in Fig. 2), it is expected that the number of target ions arriving on the substrate/growing film is also critical for the α-Ta phase formation in the MPP/HiPIMS depositions. Therefore, the peak and mean I_{sub} for the MPP Ta coating deposition were measured as a function of the negative bias voltage and are shown in Fig. 4. It can be seen that the negative substrate bias has a pronounced effect on the I_{sub}. Both I_{sub} values increased rapidly when the negative bias voltage was increased from 0 to −50 V and then the increasing rate slowed down as the negative bias voltage was further increased.

The evolution of the substrate current, as shown in Fig. 4, is relevant to the behavior of ions and electrons arriving on the substrate in response to the increase in the negative bias voltage. If the substrate is at a floating potential, which is generally about 15–20 V negatively, it collects an equal number of ions and electrons. If a greater external negative bias was applied on the substrate, the electrons are repelled, and only ions are being collected, and the total current will increase positively. Further increase in the negative bias voltage will give even more current as the substrate holder attracts ions from the surrounding parts of the plasma until saturation occurs.

The peak and mean I_{sub} measured at −50-V substrate bias were 165 and 55 mAcm^{-2}, respectively. These values are much higher than those reported in the conventional dc magnetron sputtering, which is generally in the range of 2–5 $\mathrm{mA/cm}^2$ [26], [27], confirming that a large number of ions arrive on the growing film. Since the peak ion energy in the MPP plasma is low (3 eV), as shown in Fig. 2, these ions have kinetic energy determined by the negative bias voltage applied on the substrate. In the current study, a negative bias of −30 V with a peak I_{sub} of 82 mAcm^{-2} and a mean I_{sub} of 25 mAcm^{-2} already promoted the formation of α-Ta phase in the MPP

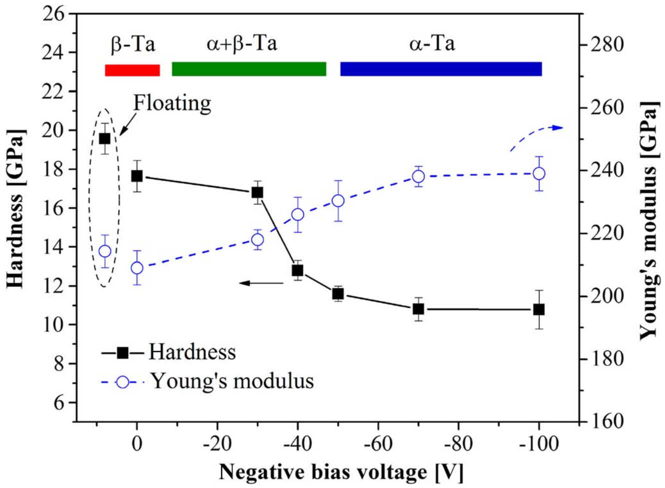


Fig. 6. Hardness and Young's modulus of the MPP Ta coatings deposited at different negative substrate bias voltages.

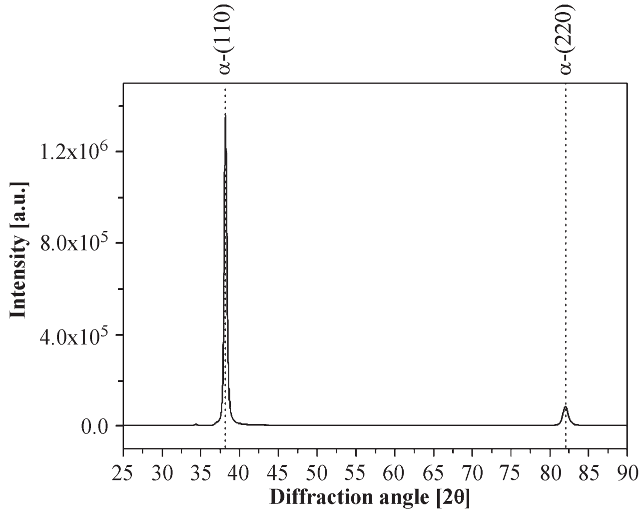


Fig. 7. XRD pattern of a 100-μm Ta coating showing an all alpha phase structure.

technique. Additionally, an all α-Ta phase was formed at a -50 V negative substrate bias with a peak I_{sub} of 165 mAcm^{-2} and a mean I_{sub} of 55 mAcm^{-2}. This study demonstrates that it is possible to control the Ta coating phase formation by optimizing the ion bombardment kinetic energy and the number of metallic ions generated in the plasma by using the MPP technique.

The negative bias voltage also has a significant effect on the microstructure of the MPP Ta coatings. Fig. 5 shows the cross-sectional SEM micrographs of Ta coatings deposited at 0, -30, -50, and -70 V negative bias voltages, respectively. The coating deposited at 0 V exhibited large columnar structure without the effective kinetic ion bombardment [Fig. 5(a)]. A gradual decrease in the size of the columnar grains together with the densification of the coatings was observed as the negative bias voltage was increased from -30 to -70 V [Fig. 5(b)–(d)]. This microstructure change corresponds to the increase in kinetic energy of the incident ions (bias voltage) as well as an increase in the peak I_{sub} from 82 to 170 mAcm^{-2}.

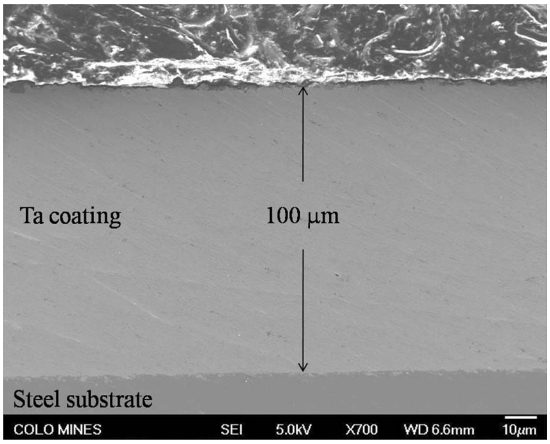


Fig. 8. Cross-sectional SEM micrograph of a 100-μm α-Ta coating deposited at a -50 V substrate bias voltage.

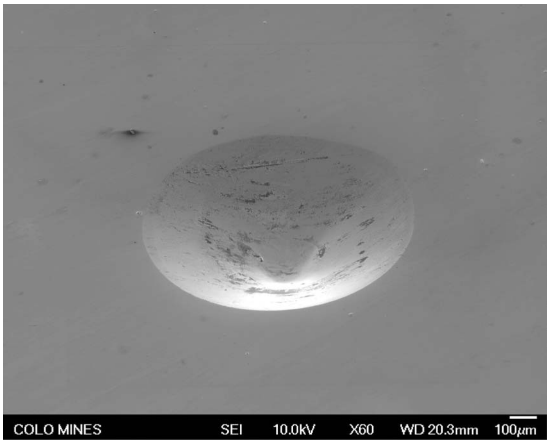


Fig. 9. SEM micrograph of the indent morphology after Rockwell C-Brale indentation of the 100-μm Ta coatings.

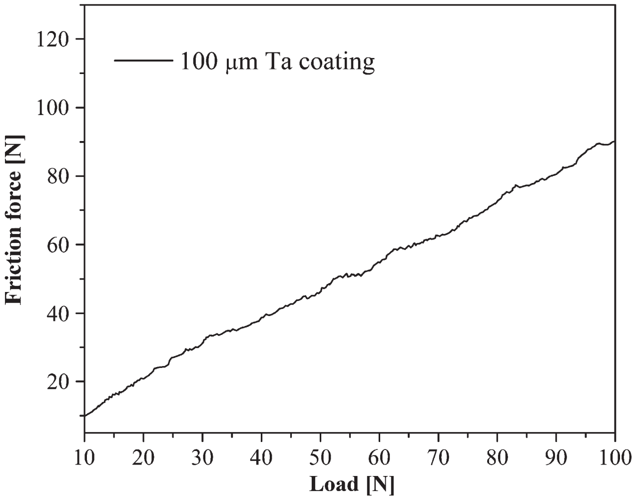


Fig. 10. Friction force versus the applied load for progressive load scratch test performed on the 100-μm Ta coating deposited on A257 steel substrate.

Fig. 6 shows the hardness and Young's modulus of the MPP Ta coatings deposited at different negative bias voltages. The phase structure of these coatings is shown at the top of the figure. It was interesting to see that the Young's modulus values

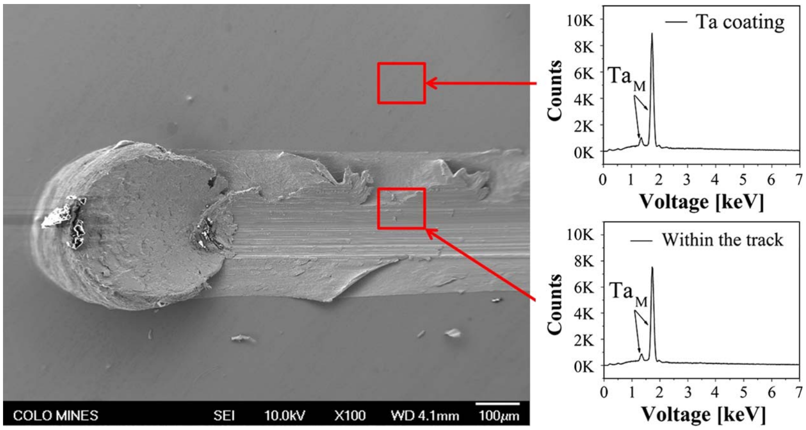


Fig. 11. SEM micrograph of the end of the scratch track on the 100-μm Ta coating and EDS spectra obtained on the coating and within the scratch track.

of the α-Ta coatings are generally higher than the β-Ta coatings. It can be seen that the coatings deposited at 0 V and at a floating bias, which exhibited a pure beta phase structure, showed high hardness of 17.6 and 19.5 GPa, respectively. When the coatings contain a mixture of alpha and beta phases, deposited at -30 and -40 V bias voltages, the hardness of the coatings dropped rapidly as the volume fraction of the α-Ta phase increased (e.g., at -40 V). As the negative bias voltage was increased to above -50 V, the hardness of the coatings are in the range of 10–11 GPa, corresponding to a pure α-Ta phase formation. These results agree well with the previous reports that β-Ta coating exhibits higher hardness than that of the α-Ta coating [1], [2].

C. Structure and Properties of Thick MPP Ta Coating

A Ta coating with a thickness of 100 μm was deposited at $P_a = 3$ kW with a -50 V negative bias voltage. The deposition time is 4.5 h at a large substrate to target distance of 120 mm and a working pressure of 0.67 Pa. It is expected that a shorter substrate to target distance and a higher working pressure can further enhance the deposition rate for the thick Ta coating deposition that will be done in future studies.

The coating exhibited strong α-Ta reflections of (110) and (220) as shown in the XRD pattern (Fig. 7). This result agrees well with the previous results that an all α-Ta phase structure can be obtained by using a -50 V negative bias voltage in the MPP deposition. Fig. 8 shows the SEM image of the cross section of a 100-μm α-Ta coating. The coating exhibited a dense microstructure free of macroparticle incorporation.

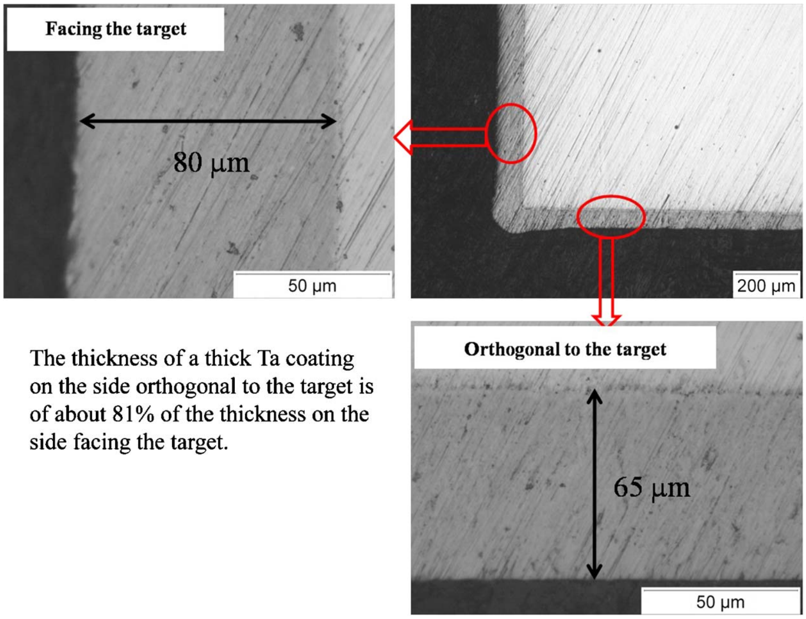
The residual stress of a thick MPP Ta coating deposited on A723 tool steel was measured using a TEC stress analyzer. It was found that the thick MPP Ta coating exhibited a compressive residual stress of -2.1 GPa. The low residual stress in the thick MPP Ta coating can possibly be attributed to the low ion energy bombardment from the MPP plasma and the releasing of the residual stress by the annihilation of the defects as the deposition time and the coating surface temperature were increased.

The adhesion of the 100-μm Ta coating was evaluated using Rockwell-C and scratch adhesion tests. Fig. 9 shows the SEM micrograph of the indent morphology after Rockwell C indentation (150-kg load) on the 100-μm α-Ta coating deposited on AISI 304 stainless steel. The coating exhibited excellent adhesion strength and toughness in that no coating delimination and cracks can be seen along the indent circumference. This adhesion strength is even better than the HF1 adhesion strength quality as described in [24].

For the coating deposited on A723 tool steel, a change in the friction force as a function of the load was recorded during the scratch test, as shown in Fig. 10. In general, a sudden rise of the friction force is related to the coating delimination or failure. It can be seen that there is no sign of coating delimination with an increase in the scratch load up to 100 N. The morphology of the end of the scratch track was examined using FESEM, as shown in Fig. 11. It can be seen that the 100-μm α-Ta coating was ploughed by the tip, and the metal material piled up at the end of the scratch track, indicating its ductile nature. Except for the piling up of the material, the substrate was not revealed at the end of the scratch track, and no cracks along the sides of the track, as confirmed by the EDS analysis within the scratch track (Fig. 11).

As the deposited species are largely ions in the HPPMS/MPP depositions, it is possible to control the metal ion trajectory by biasing the substrate to improve the step coverage and achieve good deposition rate on the surface placed at an angle to the target. Early work conducted by Alami *et al.* [28] showed that the Ta thin films grown on a Si substrate placed along the wall of a 2-cm deep and 1-cm wide trench by HPPMS exhibited a denser microstructure and a higher deposition rate than the film grown by dc magnetron sputtering. Recently, Bobzin *et al.* [29] have also shown that the growth rate of a CrAlSiN coating on the rake side of the cutting tool is only slightly lower than that on the flank side of the substrate by using the HPPMS technique.

In the current study, an 80 μm α-Ta coating was deposited on the steel substrate placed with one side facing the target surface and the other side orthogonal to the target. As shown in Fig. 12, the thickness of the coating on the orthogonal side is 65 μm, which is of 81% of the thickness of the coating deposited on the side facing the target (80 μm). Considering the large thickness of the coating, the good homogeneity achieved by MPP is a direct consequence of the high ion fraction of sputtered species being controlled by the bias on the substrate.



The thickness of a thick Ta coating on the side orthogonal to the target is of about 81% of the thickness on the side facing the target.

Fig. 12. Optical images of an 80-μm-thick α-Ta coating deposited using MPP showing a good homogeneity of the coating coverage on the side orthogonal to the target.

IV. CONCLUSION

Ta coatings were deposited using MPP at different negative bias voltages from 0 to -100 V. The plasma diagnostic showed that the Ta^+ and Ar^+ ions in the MPP plasma exhibited a low peak ion energy of 3–4 eV. The peak and mean substrate ion current densities increased rapidly to 165 and 55 mAcm^{-2}, respectively, as the negative bias was increased from 0 to -50 V and became saturated with further increase in the negative bias voltage. The negative bias voltage has a pronounced effect on the phase structure of the MPP Ta coatings. As the bias voltage was increased negatively from 0 to -70 V, the crystalline phase changed from an all beta phase when the bias voltage was 0 V to a mixed alpha and beta phases when the bias voltage was in the range of -30 to -40 V, and finally to an all alpha phase when the negative bias voltage was -50 V or greater. Thick α-Ta coatings with thicknesses up to 100 μm were successfully deposited using the MPP technique with a high deposition rate. The thick Ta coating showed a low residual stress of -2.1 GPa. Excellent adhesion strength was identified for the thick Ta coating using Rockwell-C indentation and scratch tests. The study also demonstrated the possibility to coat complex-shaped substrates with good coating coverage on the surface placed orthogonal to the target using the MPP technique.

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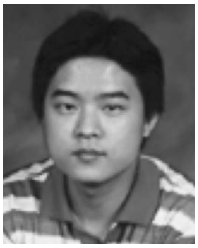

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