HIPIMS and MPP Sputtered Tantalum Films Using I-PVD Technology

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ABSTRACT

HIPIMS (high power impulse magnetron sputtering) process utilizing I-PVD technology can produce high ionization, high flux, and high intensity plasma. The metal ions from the target can be used for substrate etching and for the deposition of improved quality coatings. MPP (modulated pulse power) is a variation of HIPIMS that increases the deposition rate through modulation of the pulse shape, intensity, and duration. In MPP, the pulse shape and duration and plasma perturbations affect the degree of ionization of the plasma. In this work, HIPIMS and MPP techniques were investigated to deposit tantalum coatings on steel substrates. The film properties, including topography, microstructure, hardness, phase, residual stress and adhesion were characterized. A phase transformation from hard tetragonal tantalum to soft bcc tantalum was observed as a function of substrate bias voltage.

INTRODUCTION

Refractory metal tantalum has been considered for high temperature wear and erosion applications. Tantalum was deposited from high temperature molten salt solution onto 45 mm riffled liners with excellent wear and erosion performance [1,2]. Tantalum was deposited on 45 mm inside-diameter rifled cylinder using a triode sputtering system [3-4] and the coatings properties were characterized [5,6]. DC magnetron sputtered Ta coatings with bcc and tetragonal phase were investigated in a series of papers quoted in [7]. An *in situ* DC magnetron sputtering system with real time XRD was constructed to study phase and texture evolution of sputtered tantalum thin films [8]. DC cylindrical magnetron systems have been constructed to deposit tantalum coatings up to 200 µm on the interior surfaces of 120 mm inside-diameter using a thin electroplated HC chromium interface layer [9-11]. Tantalum alloys have also been deposited on the interior surfaces of cylindrical structure of 45 mm inside-diameter using explosive bonding technology [12].

An enhanced DC magnetron sputtering technique was developed using an external electron source to generate intense secondary plasma in addition to magnetron generated plasma [13]. The increased ion bombardment from the higher intensity plasma and biasing deposited dense, adhesive, quality tantalum coatings directly on A723 steel [14]. Plasma enhanced tantalum coatings up to 286 µm deposited on A723 steel were tested. The coatings demonstrated superior wear and erosion performance compared to electroplated chromium coatings under the same testing conditions. A plasma-enhanced cylindrical magnetron was constructed to apply the technique in cylindrical geometry [15].

HIPIMS or HPPMS (high power pulsed magnetron sputtering) methods utilizing I-PVD technology was introduced in recently years [16,17]. The technique is being considered to improve DC magnetron sputtered tantalum coatings for potential high temperature wear and erosion applications. The new technology utilizes high power pulses of short duration to ionize the target, and target ions along with gas ions and neutrals can deposit coatings with improved properties. Tantalum coatings were deposited in a trench with high depth to width aspect ratio using this technology [18]. While DC magnetron deposited tantalum film was porous, rough, and directional, HIPIMS deposited tantalum was dense, uniform, adhesive, and with good microstructure.

The MPP method is a variation of the HIPIMS-HPPMS process, allowing full control of magnetron plasma parameters at high power level. The long pulse duration and modulation of the cathode voltage during high power pulsed sputtering gives a high sputter deposition rate, which can exceed DC magnetron with the same average power level [19]. HIPIMS and MPP using I-PVD technology can deposit dense, hard, oxidation-resistant, low friction coatings to improve service life of coated components, and the technology is on the way to commercialization [20].

In this work, the HIPIMS and MPP methods using I-PVD technology were applied to deposit tantalum coatings on steel substrates. It was shown that significant amount of tantalum and Ar ions were generated in the process compared to DC magnetron sputtering process. The coatings properties were characterized and were found to be a sensitive function of the process parameters, such as the substrate bias voltage.

EXPERIMENTAL PROCEDURE

Flat A723 steel was cut into 2.5 cm x 1.2 cm x 2.3 cm samples, cleaned in alcohol and acetone and polished using 1 µm diamond paste. The Chemfilt SINEX 2.0-AS14 on a balanced magnetron was used to etch the steel surfaces and to deposit

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Table 1: MPP Tantalum Deposition Parameters and Characterization Results.

Sample	Deposit Time (min)	Bias Voltage (V)	Pulse Shape	Thick (µm)	Ta Phase	Residual Stree (MPa)	Hardness (HK50)
S1	180	-30	1	20	$\beta + \alpha$	-980 ± 312	
S2	180	-40	1	17	$\alpha + \beta$	-1,382 ± 158	504
S4	180	-50	1	16	α	-1,516 ± 183	581

tantalum coatings [21]. The target-to-substrate distance was 8 cm. Target diameter was 155 mm and 6 mm thick.

The steel samples were cleaned ultrasonically for 5 minutes in acetone and 5 minutes in 2-isopropanol, prior to Ar and Ta etching: Argon gas pressure was 2 mTorr during Ta etch and Ta deposition; and 50 mTorr during Ar etch. Parameters for etching and deposition were: peak voltage 900V, pulse length 50 µs, frequency 300 Hz; 510-520W for etching and 550-570W for deposition.

HIPIMS #4 used 10 min Ar, 30 min Ta etch at 1000V; HIPIMS #6 and HIPIMS-Slanted used 30 min Ta etch at 1000V. Tantalum depositions were made with negative bias of 50V for 60 minutes. Two serial TCR 600V/3A DC power supplies were used to provide the bias voltage. The deposition rate of tantalum films using this process was around 2 µm/hr.

For the MPP tantalum depositions, Table 1 lists the deposition parameters along with the characterization results. The substrate to magnetron distance was 10 cm, MPP power supply was an Axia-100 with a 100 kW peak pulse power. The surface of the substrate steel was cleaned with RF sputter etch process (RF power, ~200W, substrate bias, 700V, sputter etch process time ~ 20 min). The magnetic field of the magnetron was ~300G. Argon gas flow was 200 sccm that correspondent to 5 mTorr sputtering pressure. Target power density was approximately 0.37 kW/cm^2.

MPP tantalum deposition was first tested on silicon substrate in comparison with conventional DC magnetron sputtering at -30 volt bias using pulse shape 1. The same pulse shape was then used to deposit S1, S2, and S4 on tool steel samples at varying substrate bias voltage. The average power for MPP

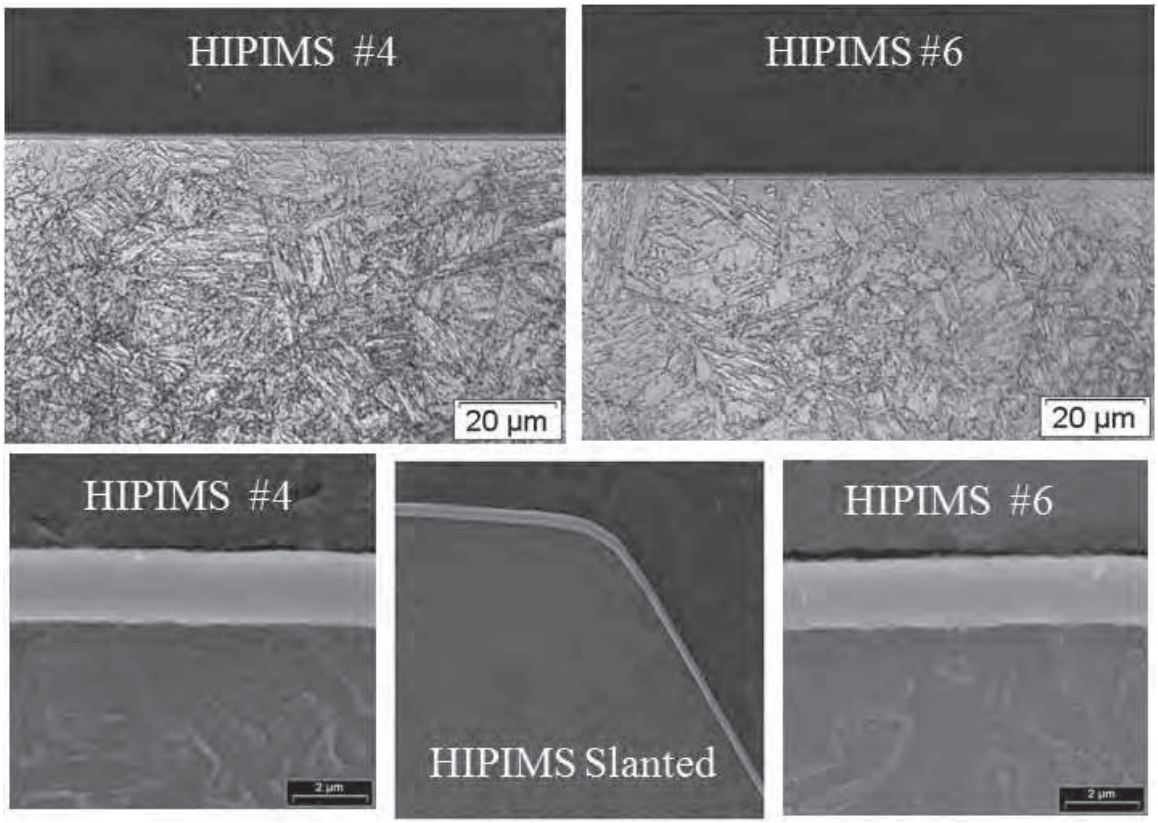


Figure 1: SEM microstructure of HIPIMS Ta films of ~2 µm thickness showing dense and uniform coatings on A723 steel. The depositions were performed using a using Chemfilt SINEX power supply, with pre-deposition etching using tantalum and argon ions [22].

deposition was 1.5kW. The MPP deposition rate of tantalum films was around 18 μm/hr.

RESULTS

HIPIMS Tantalum Depositions

Figure 1 shows the cross section of tantalum depositions using a Chemfilt SINEX 2.0-AS14 HIPIMS power supply on a balanced magnetron. The coatings with ~2 μm thickness were shown in two magnifications. Dense and uniform tantalum coatings deposited directly on A723 steel were observed. The coatings also showed good near featureless microstructure. The deposition on the slanted A723 sample was performed to test the potential to deposit coatings on an object of complex geometry. It showed uniform coatings with slight thickness variation on the slanted edge. The slight difference in etching conditions for the samples (HIPIMS #4 at 10 min Ar, 30 min Ta, 1000V) and HIPIMS #6 and HIPIMS-Slanted (30 min Ta etch at 1000V) did not produce any difference in coatings microstructure. XRD phase and texture analysis was performed, but not presented here. The XRD data showed bcc α-Ta crystalline structure with Ta (110) preferred orientation in all coated A723 steel samples under this investigation. No difference in crystalline structure was observed due to the different etching conditions.

Table 1 shows that tantalum films were deposited using Pulse 1, as a function of bias voltage. Figure 2 shows the Pulse shape 1 used in the tantalum films deposition. The voltage pulse consisted of two stages. The low power stage was -500V discharge voltage, and 16A discharge current for 500 μs duration, the total power was 8 kW. In high power stage, the discharge voltage was -600V and discharge current 48A. The total power was 28.8 kW. The time duration for the high power stage was 1000 μs. The ion current during high power stage was about 1 A that correspondent to 143 mA/cm^2 in the experiment.

Figures 3a and 3 show the OES spectrums for MPP Ta sputtering process in comparison with DC Ta deposition process. The conventional DC magnetron sputtering process with average power 2 kW did not show the presence of Ta ions (line 1) in the magnetron discharge. But MPP sputtering process shows the presence of Ta ions and Ar ions (line 2). The data show that the intensity of Ta lines reduced in pulsed process compare with DC process, but the intensity of Ta + increased in pulsed sputtering process compared with DC process.

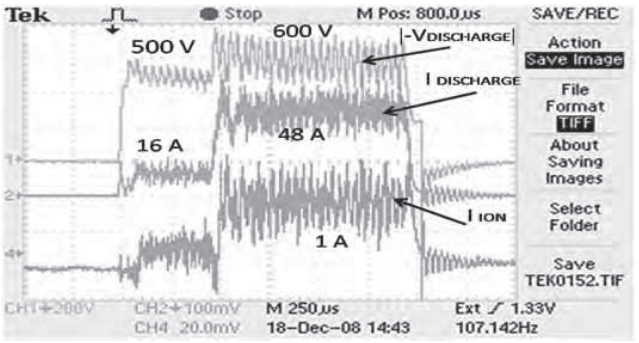
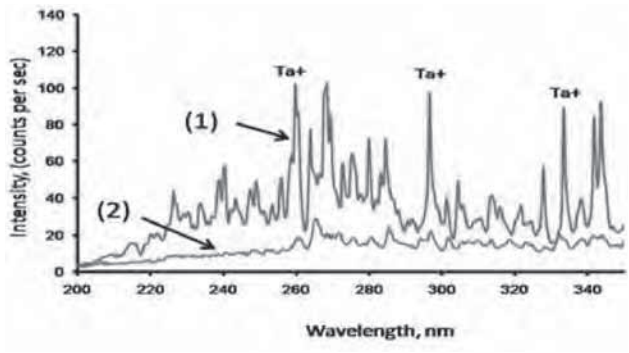
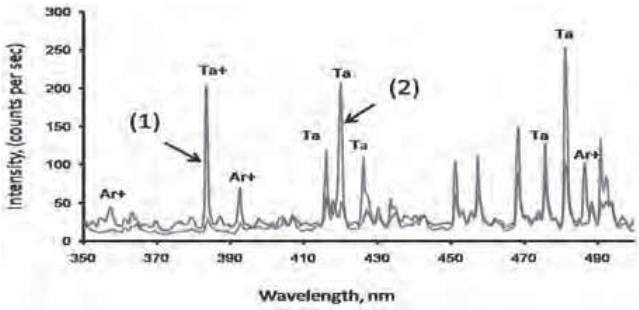


Figure 2: Waveform characteristics of Pulse 1 used in the MPP deposition of Ta films, showing: 1) discharge voltage (top line), 2) discharge current (middle line), 3) substrate ion current (bottom line). The deposition was performed using a Zpulser Axia-100 power supply.



a.

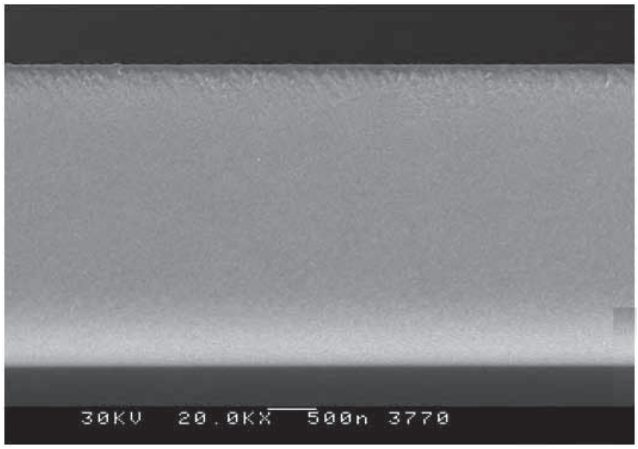


b.

Figure 3: Comparison of Optical Emission Spectrum (OES) for high power pulsed sputtering (Line 1) and conventional DC sputtering (Line 2). Figure 3a shows OES for wavelength range 200 nm to 350 nm and Figure 3b shows OES for wavelength range of 350 nm to 500 nm.

Figures 4a and b show the SEM microstructure comparison of tantalum depositions on silicon substrates using MPP method, compared to DC magnetron sputtering deposition. During the sputtering process, DC bias -30V was applied to the substrate in both the MPP and conventional DC sputtering

processes. It was observed that as DC magnetron sputtered tantalum film had a more porous and columnar microstructure, while the MPP film was very dense with near featureless microstructure.



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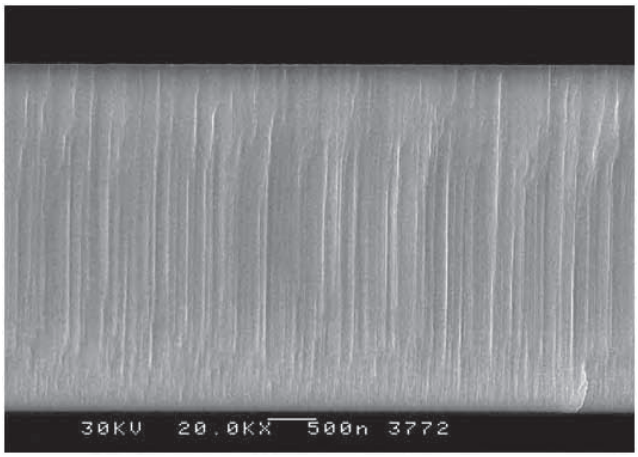


b.

Figure 4: SEM microstructure comparison of Ta depositions using the MPP process using Pulse 1 and conventional DC sputtering process at -30V substrate bias: Figure 4a shows MPP deposited Ta film; Figure 4b shows DC magnetron deposited Ta film on silicon.

In Table 1, film thickness, deposition time, hardness and residual stress measurements are listed. It took an hour to grow tantalum films 16-20 μm thick. The residual stresses were measured using a two-dimensional XRD technique. Hardness and compressive residual stress increased with substrate bias voltage as expected. Moderately high hardness and compressive residual stress levels were observed in the films. Figures 5a and b show respectively the microstructure and topography of tantalum films as a function of substrate bias voltage. The samples were etched to show the microstructure detail. Figure 5a is the SEM for- 1) Sample S1 deposited at -30V is on the top, 2) Sample S2 deposited at -40V is in the middle, 3) Sample S4 deposited at -50V for two sections of the tantalum film are the bottom two figures. Harder β-Ta is shown in shown lighter color, as softer α-Ta is shown in darker color in the films. Samples S1 shows severely cracked β-Ta in α-Ta coatings due the high residual stresses. The crack lines were lateral indicating possible high shear stresses. S2 shows α-Ta mixed with β-Ta in the film. S4 shows predominately α-Ta coatings, with a trace of β-Ta near the film-substrate interface. The films were dense, adhesive, and have a columnar microstructure. In Figure 5b, SEM topography is shown for S4: The left figure is S4 at 15,000X, showing very dense and smooth coatings. The middle figure is S4 deposited by MPP at 8,000X. The right figure is DC magnetron sputtered tantalum coatings with no bias at 8,000X [10]. MPP show dense, smooth, small- grained tantalum films compared to DC magnetron deposited tantalum film with no bias.

Figure 6 shows the 2-D XRD comparison for S1, S2, and S4, revealing that sample S1 consisted of textured α-Ta (110) reflection on the left, and highly textured β-Ta (002) ring section on the right. Samples S1 and S2 show only α-Ta (110) reflection. Fig. 6b shows the diffraction patterns, confirming S1 with mixed α-Ta and β-Ta coatings, and that samples S2 and S4 with predominately α-Ta coatings.

DISCUSSIONS

Plasma enhanced magnetron system using secondary plasma generated by an external filament increased the current density by 25 fold compared to DC magnetron. Coatings deposited using the system showed superior wear and erosion performance compared to electroplated chromium in high temperature wear and erosion testing [14]. This is due to the fact that increased ion bombardment in the new process produced dense, adhesive, crack-resistant coatings. However, in order to implement the technology in the cylindrical geometry, a filament or an antenna to generate the external plasma may cast a shadow on the substrate surfaces. HIPIMS and MPP methods using I-PVD technology are investigated, since the technology does not require a filament to generate the intense plasma. High ionization, high flex, high current density are generated by high power pulsed magnetron power supplies. HIPIMS and MPP I-PVD technology will be implemented in the cylindrical geometry to deposit bore coatings for high temperature wear and erosion applications.

In this work, HIPIMS and MPPS methods using I-PVD technology have been shown to deposit very dense, smooth, small-grained tantalum films with reduced columnar microstructure compared to DC magnetron sputtered tantalum films. This is due to the increased tantalum and argon ions in the plasma can produce high quality coatings. However, the higher concentrations of metal and argon ions in the plasma can also increase residual stresses. High residual stresses can cause buckling, cracking, peel-off, and coating delamination. On the other hand, ion sputtering or etching using argon or metal ions can effectively clean the surfaces to provide strong bonding

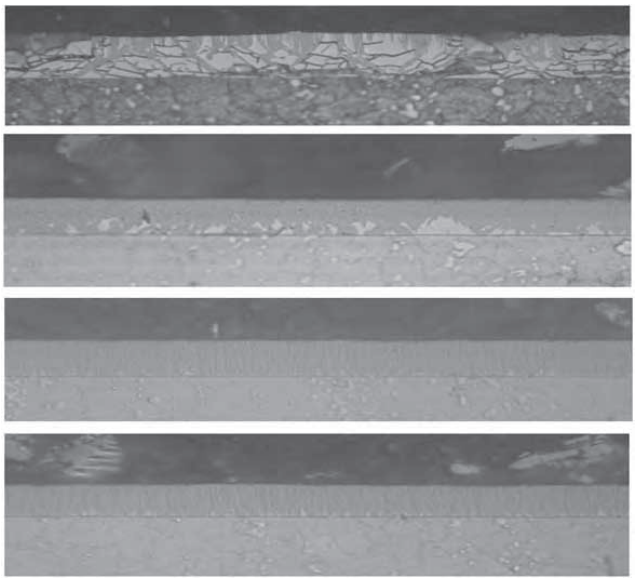
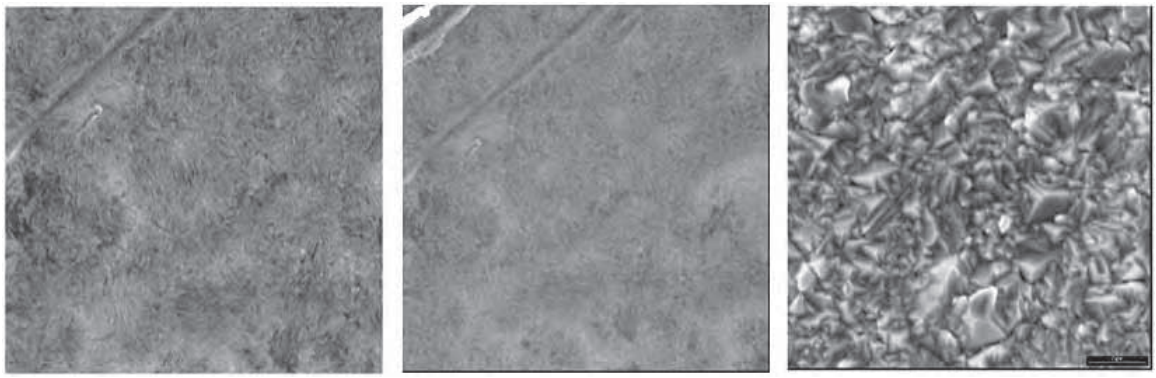


Figure 5a (left): SEM microstructure of MPP Ta depositions showing effect of substrate bias voltage on taltalum phase formation using Pulse 1: 1) Sample S1 deposited at -30V (top); 2) Sample S2 deposited at -40V (middle); 3) Sample S4 deposited at -50V showing two coating areas (bottom 2 figures).

Figure 5b (below): SEM topography of MPP Ta depositions compared to DC magnetron deposition with no bias: S4 at 15,000X (left); S4 at 8,000X (middle); DC magnetron sputtered Ta on A723 steel with no bias at 8,000X (right).



between the film and the substrate. The good bonding can overcome the residual stresses to deposit adhesive films.

Proper choices of deposition parameters are critical to improving the coatings properties. In this work, it was shown that substrate bias significantly affected the tantalum phase formation, and that increasing bias voltage increased the bcc α-phase tantalum contents in the coatings. Tantalum phase was under extensive investigation, and it is believed that tantalum phase is related to ion bombardment energy [23]. It was shown that when pre-heating the substrate to ~300°C temp prior to deposition, all bcc α-Ta coatings can be deposited [10,11,24]. This may be due to increased adatom mobility. Substrate biasing without substrate heating may provide an alternative technique to deposit α-Ta films.

CONCLUSIONS

1. HIPIMS and MPP methods using I-PVD technology can generate significant more tantalum and argon ions in the plasma in comparison to DC magnetron generated plasma.
2. The increased ions can be used to deposit dense, uniform, small-grained, bcc phase tantalum films on steel with improved microstructure compared to DC magnetron sputtered tantalum films.
3. In the MPP deposition, crystalline phase of the tantalum films is a function of bais voltage. The films changed from mixed α- and β- Ta to predominately α-Ta as substrate bias increased from -30V to -50V.
4. Deposition parameters control the film properties. In HIPIMS and MPP sputtered films, process parameter can be optimized to deposit superior films compared to DC magnetron.

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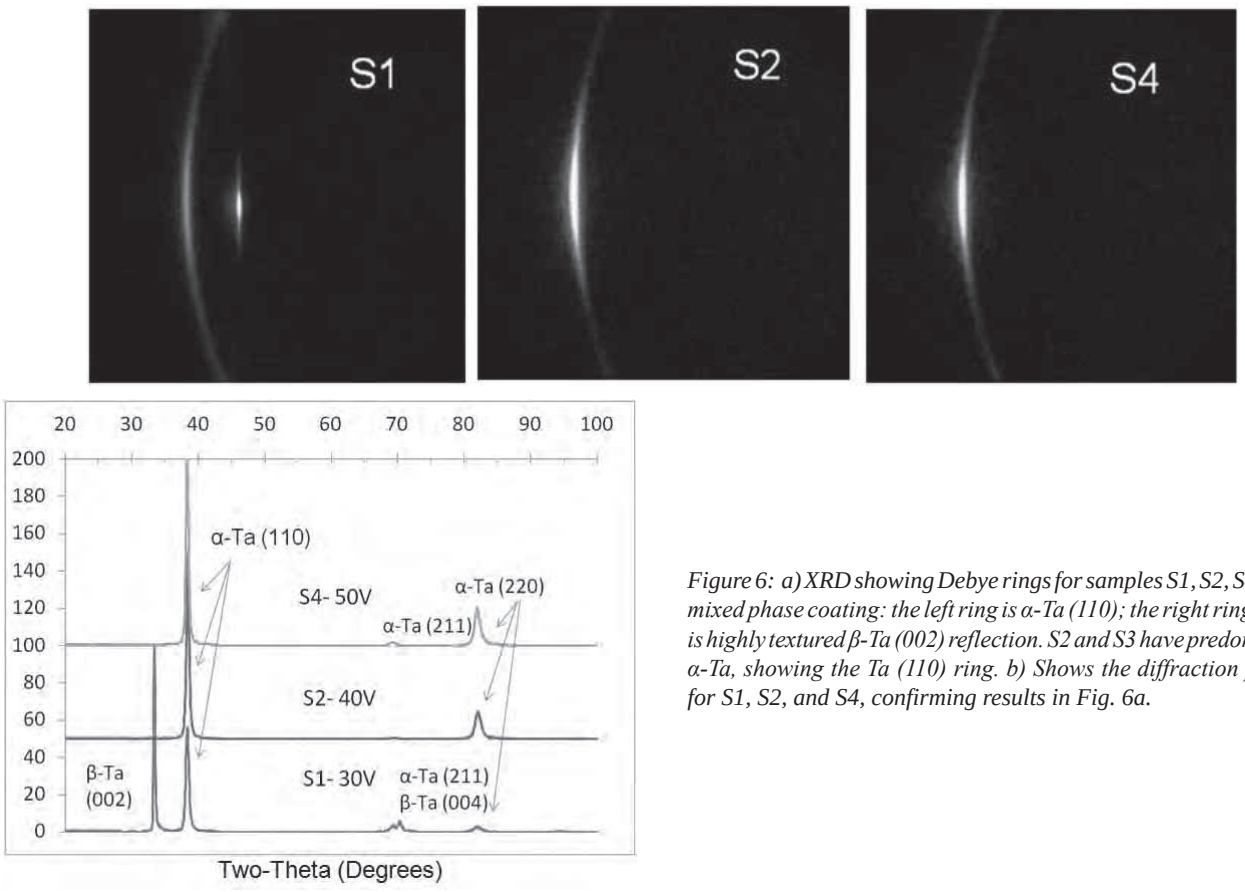

Figure 6: a) XRD showing Debye rings for samples S1, S2, S4. S1 is a mixed phase coating: the left ring is α-Ta (110); the right ring section is highly textured β-Ta (002) reflection. S2 and S3 have predominately α-Ta, showing the Ta (110) ring. b) Shows the diffraction patterns for S1, S2, and S4, confirming results in Fig. 6a.

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