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Effect of the Degree of High Power Impulse Magnetron Sputtering Utilisation on the Structure and Properties of TiN Films

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Abstract

TiN films were deposited using High Power Impulse Magnetron Sputtering (HIPIMS) enabled four cathode industrial size coating system equipped with HIPIMS power supplies. The standard version of this system allows control over the ion bombardment during coating growth by varying the strength of the electromagnetic field of the unbalancing coils and bias voltage applied to the substrate. The coatings were produced in different coating growth conditions achieved in combined HIPIMS - direct current (DC) unbalanced magnetron sputtering (HIPIMS/UBM) processes where HIPIMS was used as an additional tool to manipulate the ionisation degree in the plasma. Four cathode combinations were explored with increasing contribution of HIPIMS namely 4UBM (pure UBM), 1HIPIMS+ 3UBM, 2HIPIMS+2UBM and 2HIPIMS (pure HIPIMS) to deposit TiN coatings. Optical emission spectroscopy (OES) measurements were carried out to examine the plasma generated by the various combinations of HIPIMS and UBM cathodes. The micro-structural study was done by scanning electron microscopy (SEM). X-ray diffraction (XRD) technique was used to calculate the residual stress and texture parameter. It has been revealed that the residual stress can be controlled in a wide range from - 0.22 GPa to -11.67 GPa by intelligent selection of the degree of HIPIMS utilisation, strength of the electromagnetic field of the unbalancing coils and the bias voltage applied to the substrate while maintaining the stoichiometry of the coatings. The effect of the degree of HIPIMS utilisation on the microstructure, texture and residual stress is discussed. Combining HIPIMS with dc-UBM sputtering is also seen as an effective tool for improving the productivity of the deposition process.

Keywords: Effect of HIPIMS; TiN films; Optical emission spectroscopy; Microstructure; Texture; Residual stress

1. Introduction

High Power Impulse Magnetron Sputtering (HIPIMS) is a fast developing technology, which utilises extremely high power impulses (short pulses) to ionise the sputtered metal atom flux. It is characterised with power densities of about 3 $kWcm^{-2}$ and current densities of about 2 Acm^{-2} applied at low duty cycle of < 0.25% [1]. Each power impulse undergoes a cycle of breakdown-ignition, gas sputtering and self-sputtering and produces highly dense plasma of the order of 10^{13} cm^{-3}. This has the effect of ionising and activating reactive and inert gases in the plasma while sputtered metal atoms traversing the plasma are ionised with a high probability and charge states of 2^+ or higher are observed for many target materials. The resulting deposition flux is rich in metal ions and highly activated gas ions which results in Me^+/Me^0 (metal ion to metal neutral) and G^+/Me^+ (gas ion to metal ion) ratios of 1 near the substrate. The mean energy of metal and gas ions of approximately 6 eV is factor 3 greater than in conventional sputtering in the same conditions [2]. The high ion-to-neutral ratios, high degree of metal ionisation and gas activation in the deposition flux are prerequisites for the build-up of a dense microstructure and specific preferred orientation of the coatings. Thus HIPIMS coatings have improved wear, corrosion and oxidation resistance. Oxide coatings have improved optical and electrical properties [3]. The HIPIMS has also been used for pre-treatment of the substrate prior to coating deposition to improve adhesion by intensive sputter-cleaning of impurities and metal ion implantation [1]. Extensive reviews on the sputter-cleaning process and technology can be found in the literatures [3, 5].

However, one of the drawbacks of HIPIMS is the lower deposition rate when compared to the conventional magnetron sputtering. Major contribution to the reduction is the back attraction of the positively charged metal ions to the cathode, an effect observed and described already with the arc discharges [6]. One way to improve the deposition rate is to use lower strength magnetic fields, for example lower than 40mT as suggested in [7], which reduces the magnetic confinement of the plasma and allows more positive ions to reach the

substrate. Following this approach, deposition rates reaching 90% of the deposition rate of the conventional magnetron sputtering were achieved for Nb and other metals [7, 8]. With deposition systems equipped with multiple and different plasma sources however, there is a possibility to run combined processes where only parts of the sources are operated in HIPIMS mode. A schematic cross section of a Hauzer system equipped with one HIPIMS source and three conventional unbalanced magnetrons was published already in 2004, soon after the up scaling of the HIPIMS technology [9]. In such configuration HIPIMS was made available to be used for surface pre-treatment to enhance the coating- substrate adhesion and also to deposit the coatings, either as a single source or in combination with the standard unbalanced magnetrons with improved microstructure due to the higher ionisation of the sputtered material. Indeed, highly dense TiN coatings with excellent mechanical properties deposited by HIPIMS can be seen elsewhere in the literature [10-12]. Nanoscale multilayer coatings of CrN/NbN with enhanced wear and corrosion resistance [13], CrN/TiN with improved wear resistance [14] and CrAlYN/CrN with improved high temperature oxidation resistance [15] were produced by the combined HIPIMS and conventional direct current (DC) - unbalanced magnetron (UBM) sputtering technology. The performance enhancement of the above said coatings was attributed to the fully dense microstructure with reduced multilayer waviness and sharp interfaces resulting from the higher ad atom mobility (energy) of the condensing species provided by HIPIMS.

Furthermore, the penalty due to the lower deposition rate of HIPIMS is expected to be significantly reduced with combined HIPIMS/UBM sputtering. However, the contribution, the extent of the HIPIMS utilisation in such combined processes needs to be well understood and carefully considered. The answer to the question: "how much HIPIMS is needed in the process for the production of high quality coating" is not straightforward. The answer to this question has also implications on the physical vapour deposition (PVD) system manufacturers as well as HIPIMS power supply manufacturers who shall consider the design and the specifications of the next generation of systems enabled to deliver the combined technology.

The aim of this research is to shed more light on the effect of combining HIPIMS with UBM sputtering in one process by studying the ionisation degree in the plasma, coating microstructure and the deposition rate. TiN has been chosen as a model coating, which presents a simpler case to study the above mentioned effects in the HIPIMS/UBM combination. The authors however, believe that the conclusions of this study will be transferable to other more sophisticated coatings too.

2. Experimental Details

2.1. Deposition of TiN Coatings

TiN coatings were deposited in an industrial size PVD coating machine (chamber volume - 1 m^3, HAUZER 1000 - 4 HTC, Hauzer Techno Coating, The Netherlands) enabled with HIPIMS technology at Sheffield Hallam University. The original system was equipped with four dc-unbalanced magnetrons with target area of 1200 cm^2 each. In the modified version of the HTC 1000 - 4 system, two of the magnetrons were connected to HIPIMS power supplies allowing operation selectively either in UBM or in HIPIMS mode (Fig. 1). The HMP2/1 generators manufactured by Huettinger Electronic Sp. z.o.o., Poland were used to energise the HIPIMS magnetrons. The power supply was capable of supplying power pulses with duration in the range 0 - 200 μs at a frequency of 0 - 100 Hz (10 ms) equivalent to a duty cycle of 2%. The power supply was capable of delivering peak currents of up to 3000 A and at a voltage of 2000 V. In this study, the HIPIMS power supplies were operated in a non-synchronised mode. Arcing energy was minimized by arc suppression design that allowed switch off of the power supply even at the maximum current. The unbalancing effect was achieved by external magnetic field generated by electromagnetic coils surrounding the cathodes and arranged in such a way to achieve close field magnetic configuration. Schematic cross section of the vacuum chamber is shown in Fig. 1. All cathodes were furnished with 99.99% pure Ti targets manufactured by GfE, Germany. The coatings were deposited on mirror polished (1 μm diamond paste) 30 mm diameter, 6 mm thick coupons from hardened M2 high-speed steel (HRC 62), 25 × 25× 0.2 mm, bright annealed 304 stainless steel coupons

and 20 × 10 × 0.2 mm, silicon wafer samples. Prior to the deposition, the substrates were cleaned in an automated cleaning line comprising a series of alkali solutions and de-ionised water baths followed by a vacuum drying furnace. The base pressure for all the coatings was 0.006 Pa. Four different cathode combinations were exploited as follows: 4 cathodes in conventional dc-UBM mode to deposit pure UBM coating, 1HIPIMS+3UBM and 2HIPIMS+2UBM cathodes to deposit combined HIPIMS/UBM coatings and 2HIPIMS cathodes to deposit pure HIPIMS coatings. During the conventional UBM sputtering the targets were operated with average power density of about 0.006 $kWcm^{-2}$ whereas high peak power density of about 0.180 $kWcm^{-2}$ was applied during HIPIMS, which results in equal average power in the range of 7 - 9 kW applied on all the four magnetrons. The substrate pre-treatment was done by bombarding the substrate with highly ionised mixture of Ti^{+}/Ar^{+} plasma generated from a HIPIMS discharge maintained on the Ti target in an Ar atmosphere. Fundamentals and technical details of the metal ion etching procedure using HIPIMS are given in the literature [1,2, 5]. The coating deposition was carried out in a reactive $Ar+N_2$ atmosphere at 400 °C. To maintain a stable bias voltage in both surface pre-treatment and coating deposition processes, a specialised HIPIMS compatible bias power supply model HBP (Hüttinger Electronic Sp. z o.o.) was used [16].

2.2. Characterisation Techniques

Various surface analysis techniques were employed to characterize the microstructure, texture and residual stress in the coatings. Optical emission spectroscopy (OES) measurements have been done to analyse the plasma in order to examine the influence of various combinations of HIPIMS and UBM plasma generation. OES spectra of TiN plasma were recorded by HORIBA Jobin Ivon Triax 320 monochromator with quartz optical fibre and collimator in time - averaged mode *in vacuo*. The quartz fibre capable of transmitting in the ultraviolet spectral region was kept in the substrate region during the measurements to analyse the plasma near the substrate as illustrated in Fig. 1. The orifice of the quartz fibre was facing downward to be able to see the mixed plasma and not only certain target areas as

targets were on opposing sides. Table 1 lists the emission lines used in this study. The chosen Ti species lines have similar wavelengths, similar upper excitation energies and similar oscillator strengths. Further the Ti neutral is a transition to the ground sate. Considering the intensity ratio of these lines is ideal for a qualitative statement on the effect of HIPIMS utilisation on the ionisation of metal. The intensity ratios of Ti^{1+}, Ar^0 and $N_2{}^0$ to intensity ratios of all Ti species (Ti^{1+}+ Ti^0) in the plasma are considered to extract information about the 'weighted emission intensity' of Ti^{1+}, Ar^0 and $N_2{}^0$. To improve the accuracy of the estimates, the oscillator strengths for Ar^0 and Ti^{1+} were used in the calculation, assuming that the line intensity $I \sim f_{ik}*n$, where f_{ik} is the oscillator strength and n is the density of species. The following relations were used to estimate the 'weighted emission intensity' of Ti^{1+}, Ar^0 and $N_2{}^0$.

$$\{\mathbf{Ti^{1+}}\} = \frac{\frac{\mathbf{Ti^{1+}}}{\mathbf{f_{ik}^{Ti^{1+}}}}}{\left(\frac{\mathbf{Ti^{1+}}}{\mathbf{f_{ik}^{Ti^{1+}}}}+\frac{\mathbf{Ti^{0}}}{\mathbf{f_{ik}^{Ti^{0}}}}\right)} \quad (1)$$

$$\{\mathbf{Ar^{0}}\} = \frac{\frac{\mathbf{Ar^{0}}}{\mathbf{f_{ik}^{Ar^{0}}}}}{\left(\frac{\mathbf{Ti^{1+}}}{\mathbf{f_{ik}^{Ti^{1+}}}}+\frac{\mathbf{Ti^{0}}}{\mathbf{f_{ik}^{Ti^{0}}}}\right)} \quad (2)$$

$$\{\mathbf{N_2^0}\} = \frac{\mathbf{N_2^0}}{\left(\frac{\mathbf{Ti^{1+}}}{\mathbf{f_{ik}^{Ti^{1+}}}}+\frac{\mathbf{Ti^{0}}}{\mathbf{f_{ik}^{Ti^{0}}}}\right)} \quad (3)$$

where Ti^{1+}, Ti^0, Ar^0 and $N_2{}^0$ is the emission line intensity of Ti^{1+} ions, Ti^0 neutrals, Ar^0 neutrals and $N_2{}^0$ neutrals respectively. $f_{ik}^{Ar^0}$, $f_{ik}^{Ti^0}$ and $f_{ik}^{Ti^{1+}}$ is the oscillator strength of Ar^0, Ti^0 and Ti^{1+} respectively. Due to the use of oscillator strength, the 'weighted emission intensity' is proportional to the density of species in the plasma. However, the coefficient of proportionality could not be measured. Therefore the 'weighted emission intensity' is only a qualitative measure of the density of species. The excitation energies for Ar and N_2 are significantly higher than Ti^0 and Ti^{1+} and as such the ratios are dependent on the electron temperature. Calculating these ratios for $N_2{}^{1+}$ which has similar excitation energy as Ti^0 and Ti^{1+} yielded similar trends as the ones observed for $N_2{}^0$ (not shown). This was confirmed

when changing the deposition process, unbalancing coil current and nitrogen flow. This indicates that the main effect observed was that of the change in density and the influence of electron temperature is secondary.

X - ray diffraction (XRD) technique was utilized (Philips X'Pert MPD) for the texture, T* (Bragg-Brentano, BB) and stress, σ (Glancing angle (GA) geometry) calculations. Texture coefficient (T*) was calculated using the following equation [17]:

$$T^* = [I_{(hkl)}/R_{(hkl)}]/[n^{-1}(\Sigma\, {}^0{}_n I_{(hkl)}/ R_{(hkl)})] \quad (4)$$

where $I_{(hkl)}$ & $R_{(hkl)}$ are the intensities from the (hkl) reflections in the specimen and a random powder respectively and n is the number of reflections considered. The residual stress was determined by X-ray omega diffractometer using $\sin^2\Psi$ method [17]. Stress (σ) was calculated from the slope of the least-squares fit of the plot of a_Ψ versus $\sin^2\Psi$ and using the following expression [17]:

$$\sigma = (\text{Slope } E)/ [a_0 (1+\nu)] \quad (5)$$

Stress dependence of the lattice parameter a_Ψ related by the following equation [17]:

$$a_\Psi = \sigma a_0 \left(\frac{1+\nu}{E} Sin^2\Psi - \frac{2\nu}{E}\right) + a_0 \quad (6)$$

where Ψ= θ-γ (Bragg angle (θ) – Angle of incidence(γ) of the X-ray beam relative to the specimen surface), a_0 is the unstressed lattice parameter, E is the elastic modulus determined in this study by nanoindentation test and ν is the Poisson's ratio (in this study=0.3). A nano hardness tester (CSM Instruments SA) with a Berkovich indenter was used to evaluate the elastic modulus using Oliver and Pharr method. The applied load for all of the elastic modulus measurements was 10 mN. A scanning electron microscope (FEI NOVA - NanoSEM 200) was used for microstructure imaging and thickness measurements. TiN coated silicon fracture was used for this purpose. Surface roughness measurement of the coatings was done using a profilometer. The energy dispersive X-ray spectroscopy (EDX) analysis of the films has been carried out using a scanning electron microscope (FEI NOVA - NanoSEM 200) equipped with an EDX detector. Stoichiometric TiN film deposited by chemical vapour deposition

(CVD) and characterised by Rutherford back scattering (RBS) techniques was used to calibrate the EDX module.

3. Results and Discussion

3.1 OES Measurements:

3.1.1. Effect of different HIPMS/UBM source combination:

The effect of various HIPIMS/UBM source combinations on $\{Ti^{1+}\}$ and $\{N_2{}^0\}$ is illustrated in Fig. 2. All the measurements were carried out with coil current (I_{coil}): 3 A, bias voltage (U_b): 0 V and working pressure: 0.3 Pa.

The $\{Ti^{1+}\}$ starts at a low value of 0.13 for the pure UBM process and rises continuously as more HIPIMS cathodes are energised; reaching a maximum of 0.75 for the pure HIPIMS process. This increase is related to the increased production of Ti^{1+} ions in the high peak power HIPIMS process. The pure HIPIMS process generates a factor of ~7.5 higher metal ionisation ratio than the pure UBM process.

The $\{N_2{}^0\}$ is high for the pure UBM process and reduces when HIPIMS is involved. Emission from $N_2{}^{1+}$ at 391.4 nm (not shown) was observed to follow the trend for $N_2{}^0$. The amount of nitrogen in the working atmosphere was constant given that the partial pressure of N_2 was controlled to be constant and the resulting variation in flow rates was <10% between all cases. Additionally, according to the EDX studies (not shown), the film composition was similar (stoichiometric) within the error of the measurement. Combining these and the plasma observations, we deduce that the lower $\{N_2{}^0\}$ in the plasma could be attributed to ionisation and subsequent dissociation of the molecular gas due to the HIPIMS process generating high density of electrons that are responsible for the above processes [18]. Such observations are consistent with studies of discharge composition found in pure HIPIMS sputtering of Ti in Ar and N_2 atmosphere [2], where the content of dissociated nitrogen ions was found to be higher than that of molecular nitrogen. In summary, the implementation of HIPIMS in this process has led to highly activated conditions of deposition, in particular dissociation of nitrogen and ionisation of Ti. In principle these results show that all the

combinations where HIPIMS is involved such as 1HIPIMS+3UBM, 2HIPIMS+2UBM and 2HIPIMS provide favourable conditions for depositing films with stoichiometric composition. Therefore the optimum combination of sources should be selected accounting also for the effect on coating microstructure and compressive stress.

3.1.2. Effect of Unbalancing and Closed Field Confinement

In order to illustrate the effect of unbalancing coil current on the chemistry of the ion flux generated, the 2HIPIMS+2UBM cathode combination has been considered. This combination appears to be the best one in this research as it provides a large bias voltage range where relatively low stress highly dense coatings can be produced as explained in sections 3.3 and 3.5. The degree of magnetic unbalancing of the cathode and the strength of closed field confinement in the system were varied using the electromagnetic coil current. In this system the coil current increases the degree of magnetic unbalancing of the magnetron and increases the closed field confinement whilst reducing the width of the race track. The bias voltage (U_b) and working pressure were 0 V and 0.3 Pa respectively during these measurements.

Fig. 3 shows $\{Ar^0\}$, $\{N_2{}^0\}$ and $\{Ti^{1+}\}$ in relation to the applied coil current. The $\{Ar^0\}$ rises for coil currents up to 3.5 A. This can be attributed to the increase of the effective excitation volume for argon (Ar) due to an enhanced electron transport away from the cathode. For coil currents of 4 - 6 A, the Ar^0 ratio reduces significantly. This may be caused by increasing ionisation of Ar and rarefaction due to narrowing of the racetrack and the resulting increase in power density. The $\{Ti^{1+}\}$ also increases with increasing coil current. The $\{N_2{}^0\}$ decreases monotonically with coil current. This behaviour may be due to prevalent dissociation (see Section 3.1.1) rather than excitation processes for nitrogen, which in this case is fuelled by a local enhancement of plasma density near the target on account of reduced racetrack width and target power density. In comparison, Ar has a smaller ionisation cross section that requires higher plasma density to shift the balance from excitation to ionisation

and the shift in balance and corresponding drop in intensity is only observed for coil currents above 4 A.

3.1.3. Effect of Target Poisoning

OES measurements with increasing Nitrogen flow from 0 to 180 sccm (total pressure from 0.24 Pa to 0.36 Pa) were done to understand the effect of target poisoning with 2HIPIMS+2UBM cathode combination. The bias voltage (U_b) and coil current (I_{coil}) was kept at 0 V and 3 A respectively during these measurements.

Fig. 4 shows peak discharge current, Ti^0, Ti^{1+} intensities and $\{Ti^{1+}\}$ and $\{N_2{}^0\}$ as a function of N_2 flow. The trend is very similar to the classical poisoning case observed for magnetron sputtering (reduction of the amount of metallic species with increasing reactive gas flow rate). It was found that the intensity of Ti^0 and Ti^{1+} decreases rapidly with increasing N_2 flow, which can be attributed to the development of the target poisoning effect. It is well understood that during reactive sputtering a thin layer of TiN is formed due to the chemisorption or physisorption of neutral N_2 molecules on the target and the target bombardment by molecular or atomic nitrogen ions. As a consequence, the deposition rate of TiN (not shown in Fig. 5) will reduce with increasing the nitrogen flow rate. Ti^0 and Ti^{1+} emission intensities are diminished due to lower sputtering yield of TiN and the involvement of more nitrogen ions in the sputtering process compared to the non-reactive sputtering case where Ar ions are used [19]. The effective gas ionisation rate is increased as observed from the increase in the peak discharge current [Fig. 4]. The increase in current may be attributed partially to the enhanced probability of ionisation of the process gas through the addition of N_2 which has a higher collisional cross section than Ar and Ti. As Magnus et al [20] point out, N^{1+} ions may play an important role in being able to extract secondary electrons from a TiN-covered target surface along with Ar^{1+}, $N_2{}^{1+}$ and Ti^{2+}. The rich variety of reaction pathways for N_2 predispose the production of high fluxes of N^{1+} ions detected near the substrate, [2] indicating an extensive build up of N^{1+} ions in the dense plasma region near the target as well. Increasing N_2 partial pressure would increase the probability of collisions thus producing N^{1+}

at higher rate even though the electron temperature is reduced as observed from Ti line ratios (not shown). Thus it appears that in HIPIMS, the creation of an additional ion that is able to induce secondary emission outweighs the reduction of the secondary emission yield that results from covering a Ti target surface with a TiN compound during poisoning. Above 120 sccm of N_2 flow, the target poisoning is complete and the intensities of Ti^0 and Ti^{1+} are constant. The $\{N_2{}^0\}$ is below the detection limit for nitrogen flows up to 90 sccm as the nitrogen is completely absorbed while reacting with titanium. For flows between 90 - 120 sccm, the $\{N_2{}^0\}$ rises sharply, as excess nitrogen is introduced. The $\{Ti^{1+}\}$ remains stable for all nitrogen flows in both poisoned and sub-stoichiometric regimes due to the constant peak power. A small reduction near the stoichiometric point can be attributed to fluctuations in peak power near the point where metal-rich plasma is replaced by gas-rich plasma.

3.2. Effect of HIPIMS utilisation on deposition rate

The TiN coatings deposited on silicon substrate were used for the thickness measurements. The coated silicon samples were fractured and investigated under a scanning electron microscope. All the HIPIMS/UBM combined processes were carried out with bias voltage (U_b) - 50 V, coil current (I_{coil}) - 3 A and working pressure - 0.3 Pa. For pure UBM coating, bias voltage (U_b), coil current (I_{coil}) and working pressure was - 75 V, 6 A and 0.3 Pa respectively. The deposition time was 4 hours for all the coatings. Fig. 5 shows the TiN coating thickness as a function of the degree of HIPIMS utilisation. For completeness, a 4 HIPIMS case derived by extrapolating the results from the 2HIPIMS experiment is also added. Deposition rate loss due to increased HIPIMS utilisation is found to be 1.37% for 1HIPIMS +3UBM, 13.7% for 2HIPIMS +2UBM, 60.7 % for 2HIPIMS (due to the reduced number of targets) and only 21.3% for 4HIPIMS (extrapolated value). These experiments clearly demonstrate that combined HIPIMS+UBM processes bear a high potential for improved productivity. Furthermore, if followed, this approach might lead to a reasonable reduction of hardware costs as high quality coatings could be produced with smaller number

of HIPIMS sources involved in the process provided that they deliver the necessary high plasma ionisation.

3.3. Microstructure analysis

Cross-sectional SEM studies were carried out on TiN coatings deposited on Si substrates with various HIPIMS/UBM combinations to reveal the coating microstructure. These experiments were done to demonstrate the microstructure 'structural densification' achieved by the incorporation of HIPIMS in the process. Therefore coatings deposited with different combinations of bias voltage, coil current and working pressure are considered and listed in Table 2. The average surface roughness (R_a) values of the coatings are listed in Table 3.

Fig. 6 a - e shows SEM cross section images of TiN coatings deposited with various HIPIMS/UBM cathode combinations with different process parameters. The microstructure was columnar for all the coatings but with distinct differences as the HIPIMS contribution in the process increased. Coarse microstructure with pronounced open column boundaries and rough coating top surface was observed for both the pure UBM [Fig. 6(a)] and the UBM dominated 1HIPIMS+3UBM coatings [Fig.6 (b)] which is a clear indication for insufficient ion bombardment leading to inter-columnar fracture mechanism. The lower $\{Ti^{1+}\}$ [0.13 and 0.47] in the plasma as shown by the OES measurements for both the cases supports this claim. The R_a for pure UBM and 1HIIPIMS+3UBM coatings was 0.05 µm and 0.043 respectively. It is interesting to note that in the case of 1HIPIMS+3UBM, even for a small reduction in the bias voltage and coil current from U_b= -75 V to U_b = - 50 V and I_{coil} = 3 A to I_{coil} = 0 A respectively, the structure of 1HIPIMS+3UBM ,shown in Fig. 6(b) converts to fully open highly under dense structure with sharp column tops [Fig. 6(e)] which resembles the structure of pure UBM coating deposited at floating potential [21]. One can conclude that when HIPIMS is strongly “diluted” in UBM or operated in “weak” ionisation conditions it will produce inferior structures and therefore inferior performance. Of course the structure in such

cases can be densified by applying higher bias voltages which however, is at the expense of increased compressive stress in the coating.

In contrast when HIPIMS or HIPIMS/UBM combinations maintaining conditions of sufficiently high metal ionisation [{Ti^{1+}} for 2HIPIMS+2UBM & pure HIPIMS: 0.55 & 0.75 respectively] are used, highly dense and very smooth coatings are produced [Fig. 6 (c & d)]. The fracture morphology is smooth, glassier, with column width increasing with HIPIMS contribution in the deposition process. The R_a for 2HIPIMS+2UBM and pure HIPIMS coatings was 0.04 μm and 0.037 respectively. The low R_a values 2HIPIMS+2UBM and pure HIPIMS coatings confirm that these coatings are relatively smoother compared to pure UBM and 1HIPIMS+3UBM coatings. The wide columnar structure with very smooth column tops as in Fig. 6d was first described for HIPIMS deposited CrN and explained by the high ad atom mobility and re-sputtering effect due to the high metal ion fracture and energy in the condensing flux [22]. The glassy morphology is believed to form via trans-columnar fracture mechanism, which results from the equal strength of the material at the column boundaries and within the column. Previous research using atomic resolution TEM has shown that HIPIMS can produce TiN coatings with almost bulk material density with atomically tight grain boundaries and columns bonded on atomic level thus creating the "equal strength" structure [2].

3.4. Texture evolution

The texture evolution of different combined HIPIMS/UBM TiN coatings analysed by X - ray diffraction (θ-2θ, BB geometry) is shown in Fig. 7. For 1HIPIMS+3UBM, 2HIPIMS+2UBM and pure HIPIMS combinations, the working pressure was 0.3 Pa and the coil current was 3 A. It was found that the 1HIPIMS+3UBM coating exhibited strong [111] texture which switched to strong [200] with increasing number of HIPIMS cathodes involved in the process. Many studies have shown that the most important parameters defining nitride coating texture are molecular or atomic nitrogen, ionized or neutral metal species and the ion-to neutral flux ratio [2, 23-24]. For HIPIMS-deposited TiN it was demonstrated that increase

of the peak discharge current above a specific threshold value produced a texture switch from (111) to (200) due to increased amount of atomic nitrogen and Ti^{1+} ions [18].

According to Ehisarian et al. [2] (111) oriented grain growth is promoted when mostly Ti atoms and N_2 molecules are involved in the deposition process which is evident from 1HIPIMS+3UBM process in this study. Moreover (200) oriented grain growth is promoted under deposition conditions in which the incident particles are primarily Ti^{1+} ions and atomic nitrogen typical for the pure HIPIMS process. It has been shown that HIPIMS plasmas were found to be a highly efficient source of atomic nitrogen and metal ions capable of producing fluxes with N^{1+}: $N_2{}^{1+}$ >1 and Ti^{1+}: Ti^0>1 [2]. Thus this study revealed that the texture can be manipulated by the amount of HIPIMS utilisation in the process as this changes the plasma chemistry and ionisation degree as shown by the OES analyses discussed in Section 3.1.1.

It is interesting to note that the switch in texture is observed at relatively low power densities of 0.180 $kWcm^{-2}$ compared to laboratory-scale HIPIMS studies [18] with 0.3 $kWcm^{-2}$. This could be attributed to the large plasma volume in industrial scale sources which is more efficient in dissociating the gas. The closed field configuration and unbalancing of the cathode are also responsible for enhancing the activation of plasma near the substrate. The exact correlation is subject to further studies. The results reported here however, are in a good agreement with those published elsewhere in the literature. [2,11].

3.5. Residual stress measurement

Magnetron sputtered coatings experience compressive stress when deposited in conditions of high energy ion bombardment of the surface which creates lattice defects [25, 26]. This is particularly critical and higher for HIPIMS due to higher energetics in this process [2,12]. GA XRD was done to calculate the compressive stress generated by high energy ion bombardment. The behaviour of the residual stress (σ) as a function of the substrate bias voltage was studied for the following three configurations: 1HIPIMS+3UBM, 2HIPIMS+2UBM and 2HIPIMS and the results are summarised in Fig. 8. For all the three source combinations the working pressure was 0.3 Pa and the coil current was 3 A for the

1HIPIMS+3HIPIMS and 2HIPIMS+2UBM combinations. It was 0 A in the case of 2HIPIMS (pure HIPIMS) coatings.

The advantage of HIPIMS compared to UBM is that the bombarding flux in HIPIMS is strongly dominated by metal ions. The presence of metal ions of the same descent as these of the condensing metal creates better conditions for recombination of the ion bombardment induced lattice defects, therefore lower stress, provided that the ion energy (bias voltage) stays below a material specific threshold limit. In contrast, when bombarding predominantly with gas (Ar^{1+}) ions as in the UBM case, the lattice defect density mainly increases with ion energy due to gas entrapment.

Analysis of the slope of the stress (σ) - bias voltage curves in Fig. 8 shows that the steepest slope is achieved by the 1HIPIMS+3UBM process where the metal ion content in the plasma is the smallest. This is the worst scenario, as in this case mostly neutrals take part in the growth process bombarded mainly by gas ions, whereas the recombination effect is not that pronounced due to the relatively small number of metal ions. This combination leads to a steep increase of stress with bias voltage. The very low stress, σ = - 0.22 GPa measured for the coating deposited at low bias, (U_b = -50V) is due to the formation of a very open columnar structure as shown in Fig. 6(e) where stress relaxation takes place during the coating growth via crack and voids formation mechanisms. Further details on the stress generation in PVD coatings can be found in Ref. 27. The open columnar structure however, is not recommendable for practical applications. Therefore, for the 1HIPIMS+3UBM combination, conditions leading to even lower ion bombardment during coating growth as provided at 0V bias voltage were not included in the experiment.

Fore pure HIPIMS coatings, the stress increases with bias voltage, however, at a lower rate compared to the 1HIPIM+3UBM process due to the presence of a large amount of film forming metal ions, as shown by the OES analysis in section 3.1.1. Coatings with lower stress (σ = -3.28 GPa) can be deposited with this technique by applying lower bias voltages or even deposited at floating potential without deteriorating the coating structure.

The 2HIPIMS+2UBM source combination appears to be the best one in this research as this provides a large bias voltage range where relatively low stress (σ = -3.5 GPa), highly dense, Fig. 6(c), coatings can be produced. This is believed to be due to the more optimal $\{Ti^{1+}\}$, 0.55 achieved with the process. Furthermore the 2HIPIMS+2UBM combination is advantageous as the large bias voltage window allows for better process and therefore better tuning of coating properties.

4. Conclusions:

Combining high power impulse magnetron sputtering with dc - unbalanced magnetron sputtering in one deposition process in a multiple source deposition system such as Hauzer 1000/4 is an effective approach which allows manipulation of the ionisation degree in the plasma therefore widens the process window for coating structure, texture, residual stress and properties control. The OES measurements revealed that the $\{Ti^{1+}\}$ in the deposition flux was found to be increased with increasing number of HIPIMS sources involved in the process as follows: pure UBM : 0.13; 1HIPIMS+3UBM : 0.47; 2HIPIMS+2UBM: 0.55 and 2HIPIMS (pure HIPIMS): 0.75. This shows combined HIPIMS/UBM processes generate more metal ions than neutral metal atoms compared to pure UBM process. The thickness measurements by SEM showed that combining HIPIMS with UBM is seen as an effective tool for improving the productivity of the deposition process. Deposition rate losses due to utilisation of HIPIMS were found to be as follows: 1.37% for 1HIPIMS+3UBM process; 13.7% for 2HIPIMS+2UBM process and 21.3% for pure HIPIMS process when extrapolated to four HIPIMS sources. The residual stress in TiN coatings can be varied in a wide range from -0.22 GPa to -11.67 GPa and film texture can be altered from strong (111) to random to (200). High dense coatings can be produced by intelligent selection of the degree of HIPIMS utilisation, the strength of the electromagnetic field produced by the unbalancing coils of the machine as well as the bias voltage applied to the substrate. The combination of 2HIPIMS+2UBM appears to be the most advantageous in this research as this provides a large bias voltage range where relatively low stress (σ = -3.5 GPa) and highly dense (Fig. 6c) coatings can be

produced at reasonably high deposition rates. This is believed to be due to the more optimum $\{Ti^{1+}\}$, 0.55 achieved with the process.

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I. List of emission lines used

Species	Oscillator strength (f_{ik})	Wavelength (nm)	Upper excitation energy (eV)	Lower excitation energy (eV)
Ti^{1+}	0.0035	367.968	4.05	1.58
Ti^{0}	0.0053	364.6196	3.4	0
Ar^{0}	0.24	763.511	13.2	12.3
N_2^{0} $C^3\prod_u - B^3\prod_g$; (0-2)*	-	380.49	11.18	7.92
N_2^{1+} $B^2\Sigma_u^+ - X^2\Sigma_g^+$; (0-0) *	-	391.4	3.31	0.14

* Spectroscopic notation of the excited and ground state energy bands of N_2^{0} and N_2^{1+} species

II. List of experiments considered to demonstrate microstructure evolution

Fig. No.	Source Combination	Bias voltage (U_b) (V)	Coil Current (I_{coil}) (A)	Working Pressure (Pa)
6 a	UBM	- 75	6	0.33
6 b	1HIPIMS + 3UBM	- 75	3	0.30
6 c	2HIPIMS + 2UBM	- 50	3	0.30
6 d	2HIPIMS	- 50	3	0.30
6 e	1HIPIMS + 3UBM	- 50	0	0.30

III. Surface roughness of TiN coatings deposited by combined HIPIMS/UBM sources

Source combination	Average surface roughness (μm)
Pure UBM (4 UBM)	0.05
1HIPIMS+3UBM	0.043
2HIPIMS+2UBM	0.04
Pure HIPIMS (2HIPIMS)	0.037

Figure Captions:

Fig. 1: Schematic of industrial size sputtering machine equipped with HIPIMS/UBM sources and Optical Emission Spectrometer setup.

Fig. 2: $\{Ti^{1+}\}$ and $\{N_2^0\}$ calculated by using the respective intensity ratios as a function of source combination. $\{N_2^0\}$ is multiplied by 1000 for better visibility.

Fig. 3: Effect of coil current on $\{Ti^{1+}\}$, $\{N_2^0\}$ and $\{Ar^0\}$. Normalisation factor for $\{Ti^{1+}\}$, $\{N_2^0\}$ and $\{Ar^0\}$ was 1.83, 1197.65 and 55.92 respectively.

Fig. 4: Effect of N_2 flow on peak discharge current, $\{Ti^{1+}\}$, $\{N_2^0\}$ and $\{Ar^0\}$ and emission intensity of Ti^{1+} & Ti^0 species. $\{N_2^0\}$ is multiplied by 1000 for better visibility.

Fig. 5: Coating thickness as a function of source combination: Pure UBM, 1HIPIMS+3UBM, 2HIPIMS+2UBM, 2HIPIMS, 4HIPIMS (Extrapolated result). Deposition time - 4 hours.

Fig. 6: Effect of bias voltage on the microstructure of TiN coatings deposited with different source combinations: (a) Pure UBM, U_b= - 75 V (b) 1HIPIMS+3UBM, U_b = - 75 V (c) 2HIPIMS+2UBM, U_b = -50 V (d) Pure HIPIMS, U_b = -50 V, (e) 1HIPIMS +3UBM, U_b = - 50 V.

Fig. 7: Texture coefficient as a function of source combination.

Fig. 8: Effect of bias voltage on the residual stress of TiN coatings deposited with different source combinations.