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Substantial difference in target surface chemistry between reactive dc and high power impulse magnetron sputtering

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Abstract
The nitride layer formed in the target race track during the deposition of stoichiometric TiN thin films is a factor 2.5 thicker for high power impulse magnetron sputtering (HIPIMS), compared to conventional dc processing (DCMS). The phenomenon is explained using x-ray photoelectron spectroscopy analysis of the as-operated Ti target surface chemistry supported by sputter depth profiles, dynamic Monte Carlo simulations employing the TRIDYN code, and plasma chemical investigations by ion mass spectrometry. The target chemistry and the thickness of the nitride layer are found to be determined by the implantation of nitrogen ions, predominantly \( \text{N}^+ \) and \( \text{N}_2^+ \) for HIPIMS and DCMS, respectively. Knowledge of this method-inherent difference enables robust processing of high quality functional coatings.

Keywords: HIPIMS, HPPMS, TiN, XPS, magnetron sputtering, target poisoning, target chemistry

As the latest development in the field of magnetron sputtering, high power impulse magnetron sputtering (HIPIMS) [9] is mostly known for the ability to provide significant ionization of the sputtered material flux [10–14]. In contrast to conventional dc magnetron sputtering (DCMS), where the target state in the reactive process is to a large extent determined by the applied power and the supply of the reactive gas, HIPIMS offers an additional means of control by tuning the pulse length and pulsing frequency, which can potentially lead to new phenomena at the target surface. For example, it was reported recently that a \( \approx 500 \) nm thick compound layer formed on a Ti target surface operated in an oxygen-containing atmosphere by HIPIMS [15], while the typical thickness of the reacted film during DCMS is only a few nm [16, 17].

Experimental studies of the target surface chemistry [18, 19] have been limited by a lack of \textit{in situ} analytical...
probes capable of operating under the harsh plasma process conditions used for film growth. An additional snag is that x-ray photoelectron spectroscopy (XPS), used for bonding assignments of magnetron sputtered thin films, is typically performed ex situ, which implies complications arising from the sample oxidation during transport to the spectrometer. Commonly used surface cleaning by Ar⁺-ion etching is not a remedy, as it has other destructive effects [20]², like preferential sputtering, surface roughening, and redeposition of sputtered materials.

Here, we compare the chemical state of a Ti target operating in Ar/N₂ atmospheres using DCMS and HIPIMS, with gas composition optimized to yield stoichiometric TiN films at the substrate. The targets are in situ capped immediately after each film deposition experiment with a few-nm-thick photoelectron-transparent metal-protective layers [21] and subsequently transferred from the growth chamber into the XPS instrument. This new method enables ex situ studies of native target chemistry [22, 23]. High-energy resolution core-level photoelectron spectra recorded from native surfaces, together with sputter-depth profiles reveal essential differences between the two sputtering techniques. HIPIMS operation results in a factor of 2.5 thicker nitride layer than in the case of conventional DCMS, despite the lower N₂ partial pressure pN₂ used. Even if operated at pN₂, too low to result in stoichiometric TiN films on the substrate, the target surface region is fully nitrided during HIPIMS, which is in clear contrast to DCMS [24].

Experiments are conducted in a multi-cathode CC800/9 CemeCon AG magnetron sputtering system [25], employing a rectangular 8.8 × 50 cm² Ti target. A 2 × 4 cm² section of the target, positioned in the middle and across the race track, is made to be detachable to allow for transfer to the XPS system. The background pressure prior to sputtering is 0.2 mPa (1.5 × 10⁻⁶ Torr). The total pressure of Ar/N₂ gas mixture is kept constant at 0.4 Pa (3 mTorr), with pN₂ set at 92 mPa for DCMS experiments, while pN₂ = 45 mPa for HIPIMS. In both cases, pN₂ is the lowest N₂ partial pressure to yield stoichiometric TiN films at the substrate. DCMS is operated at a 2 kW average power, resulting in a target voltage of −351 V. The same target power is used for HIPIMS, together with the 200 µs pulse width and the frequency of 200 Hz. Such experimental conditions result in the incorporation of oxygen from the residual gas [26] causing a bulk oxygen content in the DCMS and HIPIMS films of 0.2 and 0.9 at%, respectively, as assessed by time-of-flight elastic recoil detection analysis. Prior to each experiment, the target is conditioned for 5 min in pure Ar behind closed shutters to reset the target history. For each gas mixture studied, the target is operated for 10 min to assure steady-state conditions.

To prevent target surface oxidation by atmosphere exposure during transport to the XPS instrument [27], Al-caps are deposited following the sputtering tests. First, the Al target, intended for cap layer deposition, is sputter-cleaned in Ar for 120 s at 2 kW behind closed shutters. We do not expect any chemical reactions on the target side during this time, as previous studies indicate that the post-deposition exposure of freshly-grown films to residual gases, including oxygen and water vapor, does not significantly affect the surface chemistry [27]. After that, the Al target power is reduced to 0.4 kW and a capping overlayer is deposited on the Ti target with a thickness of 50 ± 5 Å, as estimated from the attenuation of core level signals [28]. Subsequently, the detachable Ti target fragment is transferred to the load-lock chamber of the UHV XPS system. The total air exposure time is shorter than 2 min.

XPS is performed in an Axis Ultra DLD instrument from Kratos Analytical (UK) employing a monochromatic Al Kα source (hv = 1486.6 eV). The base pressure during spectra acquisition is better than 1.5 × 10⁻⁷ Pa (1.1 × 10⁻⁹ Torr). All spectra are collected at a normal emission angle from a 0.3 × 0.7 mm² target.

Figure 1. Target voltage and target current waveforms recorded during HIPIMS of Ti target in Ar/N₂ mixture with N₂ partial pressure of 45 mPa.

Figure 2. Ti 2p XPS spectra obtained from Al-capped Ti target operated with DCMS at pN₂ = 92 mPa, as well as, with HIPIMS at pN₂ = 45 mPa. N₂ partial pressures are optimized to yield stoichiometric films at the substrate. Included for the reference is the Ti 2p spectrum from TiN thin film sputter-cleaned with 0.5 keV Ar⁺ ions incident at 70° from the surface normal. Satellite peaks on the high BE side of the primary signals are commonly observed, however, beyond the scope of this paper.

For more detailed treatment see, e.g. [20] and references therein.

¹ It was established in a control experiment that the sputtering rate from the Ti target is not lower than 54 nm min⁻¹ × kW. Hence, we estimate that the target cleaning procedure applied in this work results in removing the surface layer which is about 2 orders of magnitude thicker than the compound layer formed during reactive operation.

² For more detailed treatment see, e.g. [20] and references therein.
area centered in the middle of the target race track. The BE scale is calibrated against the Fermi level cut-off [29], using the procedure described in detail elsewhere [23] in order to avoid BE referencing problems resulting from the fact that C 1s BE depends on the type of surface oxides formed during the venting procedure [27], and to remove ambiguities related to the use of C 1s as the BE [30]. For depth profile experiments, Ar$^+$ ions with an energy of 0.5 keV incident at a 70° angle from the surface normal are used to clean a 3 $\times$ 3 mm$^2$ area in the middle of the race track. The sputter rate is calibrated by etching through a 700 V at $-\lambda$ energy-averaged nitrogen implantation profile. The target during HIPIMS of Ti target, which are used below to derive the target current increases to a maximum value 140 V with $-\lambda$ during HIPIMS of Ti target, which are used below to derive the target current increases to a maximum value 140 V with $-\lambda$.

Figure 3 shows voltage and current waveforms recorded during HIPIMS of Ti target, which are used below to derive the energy-averaged nitrogen implantation profile. The target voltage is $-700$ V at $t = 0$ $\mu$s and decreases rapidly with time, due to the size of the capacitor bank with respect to the target area, to reach $-140$ V with $t = 70$ $\mu$s. After plasma ignition at $t = 5$ $\mu$s, the target current increases to a maximum value 1280 A at 32 $\mu$s and decays to zero within the next $\sim 45$ $\mu$s.

Normalized Ti 2p spectra recorded from Al-capped Ti targets after sputtering in (i) DCMS mode with $p_{N_2} = 92$ mPa, and (ii) HIPIMS mode with $p_{N_2} = 45$ mPa are shown in figure 2. In both cases, $p_{N_2}$ is adjusted to grow stoichiometric TiN films. In addition, the Ti 2p spectrum obtained from a polycrystalline TiN thin film surface, deposited in the HIPIMS mode with the exact same settings as specified above, and previously sputter-etched with 0.5 keV Ar$^+$ ions, is included for reference. There is a very clear difference in the appearance of Ti 2p spectra depending on whether the target was operated in DCMS or in HIPIMS. In the case of the target operated under DCMS conditions, the Ti 2p spectrum changes rapidly with increasing depth. The TiN component at 455.0 eV decreases, while the metal-peak at 454.0 eV increases in intensity, such that after first removing12 Å, both contributions are approximately equal. However, the steady state is not reached until the top 28–32 Å are removed and the spectrum contains one metallic peak at 454.0 eV with an asymmetric tail on the high BE side characteristic of a metallic Ti [34]. Hence, there is a very good agreement between the present result and the nitride thickness of 29 Å.

The probing depth is defined as the surface layer that yields 95% of the signal intensity, and is equal to $3 \times \lambda$, in which $\lambda$ stands for the inelastic electron mean free path for Ti 2p electrons excited with Al K$\alpha$ radiation and penetrating through Ti. Values of $\lambda$ are taken from [28].

Figure 3. Ti 2p$_{3/2}$ XPS depth profiles obtained from Ti target surface after (a) DCMS at $p_{N_2} = 92$ mPa, and (b) HIPIMS at $p_{N_2} = 45$ mPa. N$_2$ partial pressures are optimized to yield stoichiometric films at the substrate.

￥See for instance chapter 1 in [29].
The energy-averaged N implantation profiles based on TRIDYN results obtained for specific ion energies assuming: (open circles) $E_{Ar^+} = 350\,\text{eV}$ together with $E_N = 175\,\text{eV}$, and (filled circles) $E_{Ar^+} = E_N$. In the latter case, results are shown as a function of N\(^+\) fraction in the ion flux incident on the Ti target.

The corresponding depth profile performed under the same conditions on the target previously operated in HIPIMS fully confirms that a much thicker compound layer is formed (see figure 3(b)). First, after removing 12 Å, which in the case of the DCMS target results in a Ti 2p\(_{3/2}\) spectrum with equal Ti and TiN peak intensities, the core level signal from the HIPIMS target is still completely dominated by the TiN contribution, with only a small indication of a metallic peak at 454.0 eV. It is not until the 36 Å material is removed that both the Ti and TiN peaks become equally intense. Interestingly, the gradual change between two consecutive spectra is significantly smaller in the case of a HIPIMS-exposed target, indicative of a more diffuse nitride/metal interface than observed for a DCMS target, which likely results from the fact that the amplitude of the target voltage (hence, incident ion energy) varies in a wide range during the HIPIMS pulse (see figure 1).

The steady-state condition, corresponding to the metallic Ti spectrum, is reached at the depth of 72–76 Å, which is ~2.5 times deeper than for the DCMS target. Thus, at the reactive gas partial pressures that ensure stoichiometric film growth at times deeper than for the DCMS target. The steady-state condition, corresponding to the metallic Ti spectrum, is reached at the depth of 72–76 Å, which is ~2.5 times deeper than for the DCMS target. Thus, at the reactive gas partial pressures that ensure stoichiometric film growth at times deeper than for the DCMS target.

Importantly, previous ion mass spectrometry measurements, conducted during Ti HIPIMS in Ar/N\(_2\) atmosphere in the same deposition system as used for the present experiments, revealed that gas ion fluxes at the substrate are dominated by N\(^+\) rather than N\(_2^+\), with Ar\(^+\), N\(_2^+\), and N\(^+\) contributions amounting to 36, 17, and 47%, respectively [38]. This is also consistent with other reports on reactive HIPIMS of transition metal targets [43, 44]. Therefore, in the following simulations we assumed that the population of reactive gas ions during HIPIMS is dominated by N\(^+\) implying $E_{Ar^+} = E_{N^+}$. Figure 4 shows the calculated N/Ti implantation profiles for a N\(^+\) fraction in the Ar\(^+\)/N\(^+\) flux incident on the Ti target varying between 20 and 100%. The lower limit corresponds to the N/Ar atomic ratio for the N\(_2^+\) partial pressure of 45 mPa. Interestingly, the minimum N\(^+\) fraction necessary to explain the XPS results is 50%, which corresponds very well to the relative N\(^+\) population during HIPIMS discharge analyzed in [40].

The source of N\(^+\) can be (a) electron-impact induced dissociation of N\(_2\), and (b) N sputtered from the poisoned target surface. An additional effect, which may further increase the N\(^+\)/Ar\(^+\) ratio in the ion flux incident on the Ti target is Ar rarefaction [45]. With a better mass match to Ti atoms, resulting in a more effective momentum transfer, Ar is diluted more than N\(_2\) and N.
To complement the above results, we also analyzed the HIPIMS target chemistry for \( p_{NI} \) lower than 45 mPa. The N/ Ti ratio, as determined by the XPS (not shown), hence reflecting the average N and Ti concentrations within the 54 Å thick surface layer [28], was at 0.98 and 0.88 for \( p_{NI} = 27 \) and 9 mPa, respectively. Thus, in the HIPIMS mode, the Ti target surface region remained severely nitrided, while corresponding films were understoichiometric in nitrogen.

In summary, during the deposition of stoichiometric TiN thin films by HIPIMS, the formation of a 2.5× thicker nitride layer in the center of the race track was observed, as compared to conventional dc processing. The ~50 Å thick target surface region is nitrided during HIPIMS, even at \( p_{NI} \) values too low to yield stoichiometric TiN films on the substrate, which is in clear contrast to conventional DCMS. The differences between the nitride layer thickness during reactive DCMS and HIPIMS can be understood based on correlative plasma chemical investigations and TRIDYN simulations. N\(^+\) ions that dominate nitrogen ion flux during HIPIMS arrive at the target with significantly higher energy than molecular N\(_2\) present in DCMS discharge, resulting in much longer implantation depths. Based on the excellent agreement between TRIDYN simulations and XPS analyses, we conclude that the formation of the compound layer is entirely caused by the implantation of nitrogen ions.

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