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 N⁺ and N₂⁺ 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

Advanced functional coatings with applications ranging from wear-resistant layers on cutting tools [1, 2] to diffusion barriers in electronic devices [3, 4] are often produced with the advantage of reactive magnetron sputtering under high vacuum conditions. The presence of a reactive gas, however, leads not only to the desired compound formation at the substrate, but also to a simultaneous chemisorption at the target that is covered with a compound layer by so-called target poisoning. This results in severe reduction of the sputtering rate and large off-sets in the process parameter operating points, because of the change in the secondary electron emission yield and the chemical composition of the sputtered flux, as well as the energy distribution thereof, [5, 6] ion implantation effects, [7] and process hysteresis [8].

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 ~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 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], 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 (hν = 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
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 × 3 mm² area in the middle of the race track. The sputter rate is calibrated by etching through a 300nm thick TiN film grown on Si(001) substrates.

Figure 1 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 µs 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 µs. After plasma ignition at t = 5 µs, the target current increases to a maximum value 1280 A at 32 µs and decays to zero within the next ~45 µs.

Normalized Ti 2p spectra recorded from Al-capped Ti targets after sputtering in (i) DCMS mode with pN₂ = 92 mPa, and (ii) HIPIMS mode with pN₂ = 45 mPa are shown in figure 2. In both cases, pN₂ 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 former case, the Ti 2p spectra possess two distinct contributions, with stronger 2p3/2 spin-split components at 454.0 and 455.0 eV, corresponding to Ti and TiN, respectively [31]. The relative signal variation revealed by the angle-dependent XPS (not shown) indicated a layer-over-layer structure. The thickness of the top nitride layer was estimated to be 29 Å [22], based on the relative peak intensities of metal and nitride components in the fitted Ti 2p XPS spectra supported by TRIDYN simulations [32, 33].

In contrast to the DCMS case, the Ti 2p spectrum acquired after HIPIMS operation exhibits only one 2p3/2 peak, assigned to TiN. The lack of a metallic contribution is direct evidence for a thicker surface TiN layer than during DCMS, clearly exceeding 54 Å, which is the estimated XPS probing depth. The overall spectral envelope is essentially identical to that from the sputter-etched TiN-film reference. The agreement is exceptionally good, given that the Ti 2p spectrum of TiN is prone to exhibit the destructive effects of an Ar ion etch [21]. This can be rationalized by the fact that, in both cases, for the target sputtered in Ar/N₂ atmosphere, as well as the Ar⁺-etched TiN film, the surface is exposed to Ar⁺ ions with similar energy. Good agreement also indicates that the potential influence of a higher surface roughness of the Ti target on the quality of the XPS spectra is negligibly small.

To verify the estimates of compound layer thickness based on Al-capped samples, we performed sputter depth profiles on Ti targets after (a) DCMS and (b) HIPIMS operation. Figure 3 shows the Ti 2p3/2 spectra evolution as a function of sputtering depth. The starting point denoted as ‘0 Å’ corresponds to the sample state after removing the Al capping layer. In the case of the target operated under DCMS conditions, the Ti 2p3/2 spectrum changes rapidly with increasing depth. The TiN component at 455.0 eV decreases, while the metallic 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 × λ, in which λ stands for the inelastic electron mean free path for Ti 2p electrons excited with Al Kα radiation and penetrating through Ti. Values of λ are taken from [28].
The energy-averaged N implantation profiles based on TRIDYN results obtained for specific ion energies assuming: (open circles) $E_{Ar^+} = 350$ eV together with $E_N = 175$ 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 TRIDYN simulations in the case of HIPIMS are more complex since the energy of incident ions is not constant, due to the target voltage $V_T$ varying during the pulse (see figure 1). To handle this effect, we performed TRIDYN for an applicable range of incident ion energies from 100 to 700 eV, in steps of 100 eV. As the ion flux to the target is proportional to the target current, the $I$–$V$ plot can be considered a first-order approximation to the ion energy distribution function, which can in turn be used to derive the energy-averaged N implantation profile based on TRIDYN results obtained for specific ion energies.

In the first case, similar to DCMS, we assumed Ar$^+$ ($E_{Ar^+} = 350$ eV) and N$_2^+$ ions that dissociate upon impact and give rise to two N atoms, each with 350 eV, and $E_N = 175$ eV. As shown in figure 4, the results indicated that the N implantation depths are too short to explain the XPS data. Essentially, no N is found deeper than ~45 Å, which is inconsistent with the XPS findings (see figure 3(b)). 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 atom 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 $p_{N_2}$ 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 $p_{N_2} = 27$ 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, compared to conventional DC processing. The ~50 Å thick target surface region is nitrided during HIPIMS, even at $p_{N_2}$ 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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