

Observation of Ti^{4+} ions in a high power impulse magnetron sputtering plasma

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Significant amounts of multiply charged titanium ions including Ti^{4+} were observed in high power impulse magnetron sputtering discharges. Mass/charge spectrometry was used to identify metal ion species. Confusion of Ti^{4+} with carbon ions was ruled out by comparing the isotope widening of the Ti^{4+} signal with the corresponding C^+ signal. Additionally, a copper target was used to rule out a possible C^+ signal from carbonaceous contamination of the vacuum chamber. Ti^{4+} ions have high potential energy enabling high yield of secondary electrons, which in turn is likely to be responsible for the generation of multiply charged states.

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Sputtering of a metallic target using ions from a gas discharge is a well-known technique to deposit thin films. In conventional magnetron sputtering, the main depositing species are neutrals and the vast majority of ions are those of the sputter gas. However, metal ions are attractive for film synthesis since they allow efficient tailoring of the film properties through energy and momentum transfer.¹ Metal ions are of special interest when used for ion etching of the substrate, which is generally facilitated by a high bias voltage at the substrate. Interfaces for highly adherent coatings have been engineered with the approach.² By increasing the power density of the magnetron discharge, more metal ions can be generated but cooling of the target sets a limit.

In high power impulse magnetron sputtering (HIPIMS), very high peak power density sputtering is permissible due to a very low duty cycle.³ With this approach, sputter plasmas dominated by metal ions have been created. Mass spectrometry⁴ as well as optical spectroscopy^{5,6} have established the presence of even doubly charged metal ions in HIPIMS discharges. Recently it was argued that multiply charged metal ions enable the self-sputtering runaway observed for relatively long HIPIMS discharges.⁷⁻⁹

To investigate the ion charge states in a long-pulse HIPIMS discharge running with a titanium target, an energy-resolving mass spectrometer (EQP by HIDEN Ltd.) was used. Since the HIPIMS discharge is a highly dynamic phenomenon and the highest metal ion content is formed in the later, high current part of the discharge,¹⁰ the detector of the mass spectrometer was gated to sample ions only from this part (Fig. 1). The sputter target was a 2'' (5 cm) high purity titanium disk on a nominally balanced magnetron, and the sampling orifice of the spectrometer faced the target at a distance of 10 cm. Pulsed power was supplied by a SPIK 2000A power supply (Melec GmbH) which

in turn was charged by a switch mode DC supply (Pinnacle by Advanced Energy Inc.). The cryogenically pumped chamber had a background pressure of about 10^{-4} Pa and the process was run in 4N purity argon at a pressure of 0.6 Pa. 150 μ s constant voltage pulses of 875 V were applied at a rate of 100 pulses per second resulting in a peak current of about 65 A (Fig. 1). Due to the time of flight for ions to reach the mass/charge detector, the real time gate was delayed with respect to the discharge pulse. The delay time was determined to be 85 μ s by measuring the time difference between current onset and first detection of an ion signal. A 50 μ s gate was set such that the end of the gate corresponded to the end of the current pulse (Fig. 1).

Mass/charge scans showed distinct peaks at 50, 49, 48, 47, 46, 40, 24, 20, 16 and 12 amu/charge, possibly corresponding to Ti^+ and its isotopes, Ar^+ , Ti^{2+} , Ar^{2+} , Ti^{3+} and Ti^{4+} . To see such high charge states in a sputter plasma is very surprising and signals at 16 and 12 amu/charge could correspond to singly charged oxygen and carbon, respectively. On the other hand, it would be strange if large quantities of oxygen and carbon appeared during the high current part of the HIPIMS discharge when sputtering a high purity titanium target with high purity argon.

To gain further information on the nature of the 16 and 12 amu/charge signals, all the titanium peaks were scanned with a very high mass/charge resolution at an energy setting of 7.3 eV, corresponding to the maximum of the titanium energy distribution. The scans in Fig. 2 show the gradual progression from the clearly resolved titanium isotopes of Ti^{1+} around mass/charge 48 to the overlapping (not resolved) isotope peaks forming shoulders for Ti^{4+} at mass/charge 12. Those shoulders indicate that the 12 peak is indeed due to the presence of Ti^{4+} .

The system was operated with an oil-free cryopump and therefore no significant contamination due to hydrocarbons was expected. However, to further rule out the possibility that some carbon contamination is responsible for the peak at $m/q = 12$, the experiment was reproduced with a carbon target and a copper target at the same base pressure. The signal of the Ti experiment was compared with the signals obtained by the C and Cu experiments (Fig. 3). The copper target was run at a current similar to the titanium discharge to see what potential carbon contamination could be in the system. Clearly, there is almost no signal at $m/q = 12$ indicating that the residual carbon from the vacuum system is negligible. It was not possible to run the carbon target at 65 A – the highest stable current attainable was 13 A. Nevertheless, we can see that the C^{1+} signal has a very different shape: there is complete lack of the “shoulders.” With support from the presented experimental results, it was concluded that there were indeed Ti^{4+} ions in the high power density titanium HIPIMS discharge.

One might be tempted to use the count rates for the different Ti ions to obtain charge state ratios; however, different amplifications on the detector of the mass spectrometer were used for the different species during the investigation, and therefore no quantification of the ratios should be made. Yet, the strong signal for the Ti^{4+} let us state that those ions constitute at least a few percent of the total metal ion content. Additionally, by comparing with the corresponding Ar^+ and Ar^{2+} signals, we can say that metal ions are the vast majority of ions in the late stage of the discharge.

Given this finding, the questions are: How are those multiply ions formed? What are the implications for ion etching and film deposition?

One needs to appreciate that the energy needed to form multiply charged ions is provided by sequential collisions with energetic (“hot”) electrons. Secondary electrons emitted from the target are the main source of energy because they were accelerated in the sheath near the target.

At the relatively low kinetic ion energies used in magnetron discharges (~ 1 keV), secondary electrons are provided predominantly by potential electron emission,¹¹ i.e. emission caused by impact of ions having high potential energy (ionization and excitation energy). Therefore, the appearance of multiply charged ions is related to the self-sputtering runaway: the formation of multiply charged (i.e. high potential energy) ions in HIPIMS causes more secondary electrons to be emitted, which gain high energy and enable the production of a larger number of and more highly charged ions.⁹

Significant amounts of multiply charged ions will form only under certain conditions, namely (i) the power density is high enough to produce HIPIMS discharges with appreciable metal ion content, (ii) the discharge is sufficiently long as to allow for the runaway process to develop, (iii) the self-sputtering yield is not too high (unlike the case of copper), because too many metal neutrals would cool electrons and intensify charge exchange, (iv) the ionization energy for each ionization step is not too high, which implies that high ionization of low-Z materials is unlikely, and (v) the power supply is able to deliver the necessary current while keeping the voltage at a high level. In the case of our titanium discharge, traces of charge state 5+ could be detected but the signal was very small because the ionization energy from 4+ to 5+ is much higher (99.3 eV) than the ionization energies for the previous ionization steps.

High charge states are especially desirable for the application of metal ion etching: the charge state is a multiplier to produce ion energy for impact. This makes sputtering of the substrate surface by multiply charged metal ions very efficient in producing an engineered interface gradient for subsequent deposition of metal. Thus a lower bias voltage can be used, which reduces the risk of arcing on the substrate, to produce coatings with high adhesion strength.

For the coating process one would reduce the applied bias voltage. Both the potential and kinetic energy of the condensing ions need to be taken into account. A large fraction of the cumulative ionization energy (sum of all ionization steps) provides atomic scale heating,¹² which is very substantial for Ti^{4+} ions (91.3eV) compared to Ti^{1+} ions (6.83eV) or Ar^+ ions (15.76 eV). The kinetic energy brought by multiply charged ions greatly depends on the sheath voltage of the substrate. One has to be careful because too high bias may lead to undesirable sputtering and ion damage of the growing film. At low bias, even a small percentage of multiply charged ions can provide an effective self-ion assistance, which can have a significant influence on film properties like density, stress and texture.

In summary, it was shown that under certain conditions, HIPIMS discharges can produce significant amounts of multiply charged ions, and specifically at least a few percent of Ti^{3+} and Ti^{4+} ions for long pulses when using a titanium target. Possible misinterpretation due to oxygen and carbon contamination was ruled out. The ion formation can be explained through successive ionization by energetic electrons. The results are primarily relevant for HIPIMS applications in ion etching and film deposition.

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Figure Captions

Fig. 1 (Color online) Discharge current pulse and timing of the gate of the analyzer: the real time gate is delayed to account for the time-of-flight of the ions, and therefore the physical sampling corresponds to the last phase of the discharge, as indicated.

Fig. 2 (Color online) High resolution mass/charge scan for a titanium HIPIMS discharge around the mass 48, 24, 16 and 12, corresponding to charge state 1 to 4, at an energy setting of 7.3 eV. (Note: the absolute counts should not be compared due to the different detector voltage settings).

Fig. 3 (Color online) Mass/charge scans around 12 at the optimum energy setting for carbon (3.9 eV) for HIPIMS discharges using a Ti, C, and Cu target. As is evident from the carbon signal, each isotope signal is instrument-broadened.

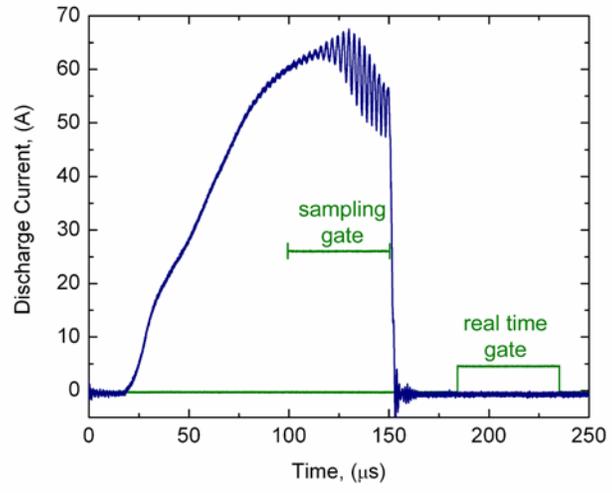


Fig. 1

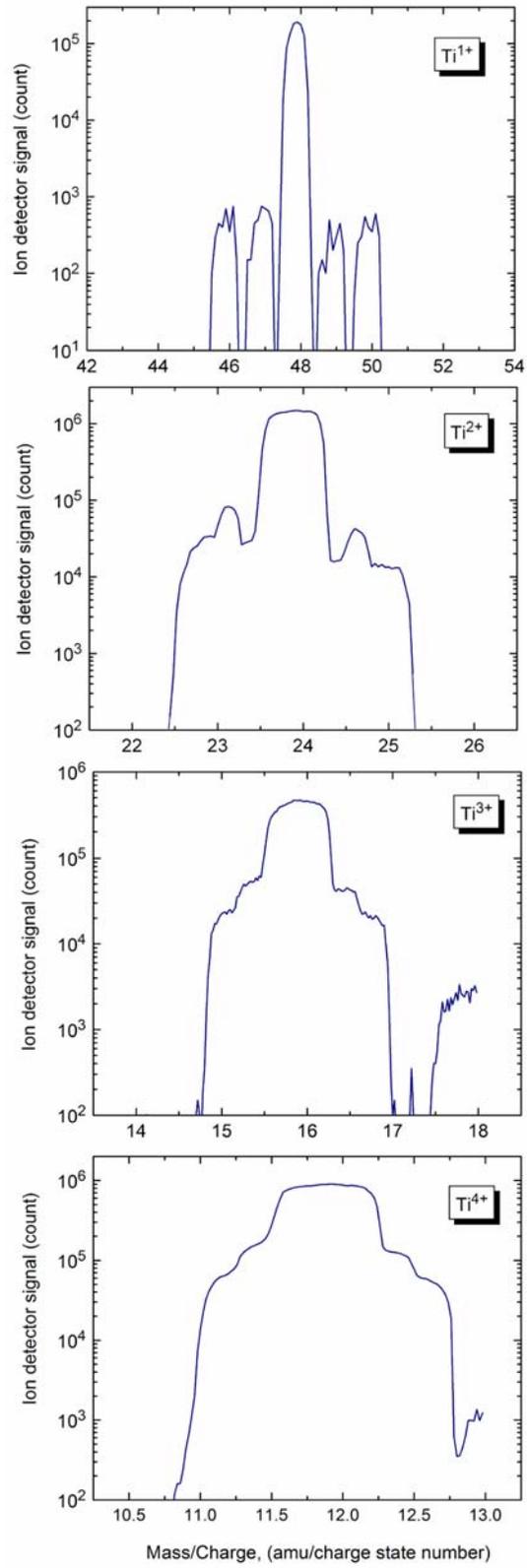


Fig. 2

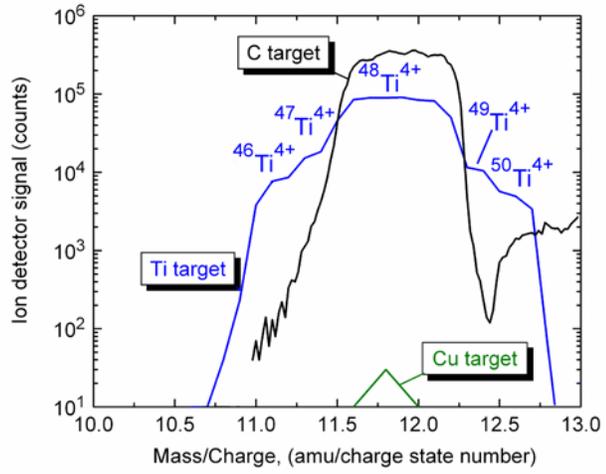


Fig. 3