ZrN and TiN formed by Plasma Based Ion Implantation & Deposition

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Physical vapour deposition (PVD) is an established technology to obtain individually tailored surface coatings on various substrates. One of the most important parameters is the average energy per incoming particle. Correspondingly, changes in the surface morphology and texture are observed with higher energies leading to films with larger grains and less defects while the momentum of the incoming particles can align or orientate the growing crystallites. Plasma based ion implantation & deposition (PBII&D) is ideally suited for a regime where energy deposition is decoupled from the layer growth as the ion bombardment occurs only during the intermittent high voltage pulses with a duty cycle of a few percent at typical voltages around 3 to 10 kV. Thus, the self-sputter limitation, which leads to rapidly decreasing film growth rate at higher energy and particles fluxes for continuous processes, is removed.

In this report, a comparative study of TiN and ZrN films produced from a metal plasma, created by a cathodic arc in nitrogen atmosphere, by applying high voltage pulses to the substrate is presented. The emphasis is on separating the influence of the plasma generation at the cathode from the influence of the energy flux at the substrate. The elemental nitrogen profiles measured for ZrN thin films after 5 minutes of deposition are shown in Fig. 1. Slightly substoichiometric ZrN was obtained with a nitrogen concentration of 45%, independent of the pulse voltage. At the same time, a reduction in the growth rate by about 30% is observed when switching on the high voltage pulses. In contrast, a different influence of the pulse voltage was observed for TiN across the energy range, with the growth rate is actually slightly increasing from 0 to 3 kV pulse bias. The absolute rate itself is about a factor 2 higher for TiN than for ZrN. The N/Ti ratio of 0.9 corresponds to a nitrogen content of 47 at.% in the films.

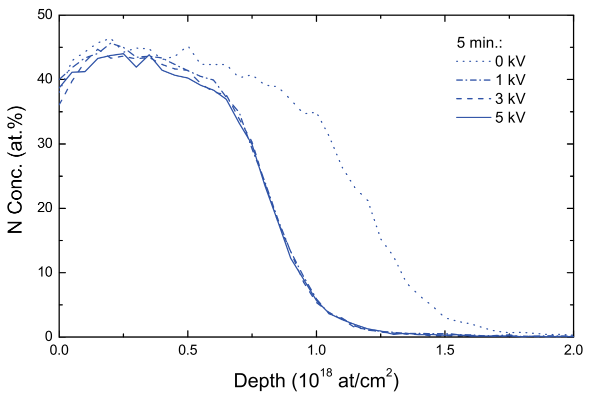

Fig. 1: Nitrogen concentration as a function of depth, measured with ERDA for ZrN films deposited at different pulse bias.

Beside influences of the plasma composition, a different surface reactivity can lead to these results. Saturation at slightly substoichiometric films is observed in both cases. Apparently, the sticking coefficient, which must be close to unity for low nitrogen concentrations, decreases rapidly at a nitrogen concentration of about 45% in both systems. The completely different behaviour under ion bombardment, slight increase in the deposition rate for TiN and a significant decrease for ZrN could be explained by a similar argument. In the case of TiN, nitrogen is preferentially sputtered, which is readily replaced by adsorbing nitrogen from the gas phase, while the plasma sheath width and hence the effective capture cross-section of the substrate increases with increasing pulse bias. In contrast, Zr + N is sputtered in the case of ZrN, leading to reduced deposition rate.

As a result, chemical and physical sputtering should be active to different degrees in both systems. A dense columnar growth for TiN and ZrN is observed in all investigated films. At the same time, a slight increase in the grain size with increasing energy flux is visible in both systems. At high magnifications, minor contaminations with macroparticles smaller than 1 μm are visible for TiN films. On a closer inspection, a nucleation layer next the substrate, followed by the columnar structure, can be seen. This nucleation layer becomes thinner for ZrN for higher pulse voltages. It has to be mentioned that no adhesion problems were observed in any film.

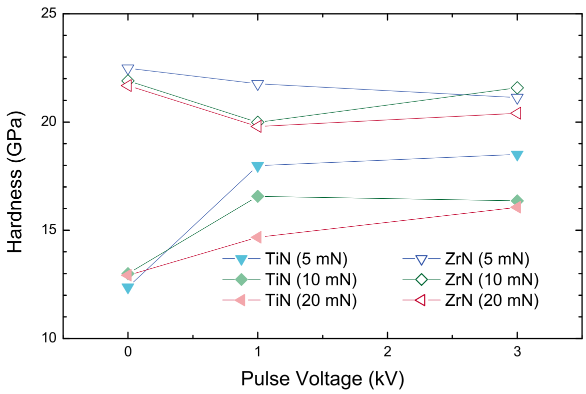

Fig. 2: Dynamic hardness, as measured with a Berkovich nanoindenter, as a function of applied load and deposition conditions.

The hardness of the obtained films is presented in Fig. 2 with TiN showing a markedly increased hardness with higher pulse voltages while ZrN depicts a small decrease. Beside different textures observed in these films, intrinsic stress variations are proposed to cause this effect.

References

[1] S. Heinrich, S. Schirmer, D. Hirsch, J.W. Gerlach, D. Manova, W. Assmann and S. Mändl, Surf. Coat. Technol. **202** (2008) 2310