Hiden Analytical Ltd.
420 Europa Boulevard
Warrington WA5 7UN
England

T +44 [0] 1925 445 225
F +44 [0] 1925 416 518
E info@hiden.co.uk
W www.HidenAnalytical.com

Control of $Ti_{1-x}Si_xN$ nanostructure via tunable metal-ion momentum transfer during HIPIMS/DCMS co-deposition

Low-energy inert-gas ion irradiation of the film surface during refractory transition-metal (TM) nitride growth by conventional DC magnetron sputtering has been used extensively to overcome the characteristically underdense microstructures with rough surfaces of layers deposited at low temperatures ($T_s / T_m < 0.30$, in which T_s is the film growth temperature and T_m is the melting point in K).[i] We recently demonstrated that high-power pulsed magnetron sputtering (HIPIMS) provides an alternative route for ion-assisted TM nitride film growth via the use of substrate bias, synchronized to the *metal-rich* portion of the plasma pulse. Stresses can be dramatically reduced, or even eliminated, since *metal* (as opposed to inert-gas) ions are components of the film.[ii,iii]

In this project we use a hybrid HIPIMS/DCMS two-target co-sputtering configuration, in which one target (either Ti or Si) is powered by HIPIMS while the other is powered by DCMS, for growth of $Ti_{1-x}Si_xN$ films with compositions $0 \le x \le 0.26$. Markedly different film growth pathways are obtained depending upon which target is powered by HIPIMS with, in both cases, a substrate bias applied in synchronous with the HIPIMS pulse. The observed divergence in film nanostructure, phase content, and mechanical properties between layers grown in Ti-HIPIMS/Si-DCMS and Si-HIPIMS/Ti-DCMS configuration is due to distinctly different metal-ion irradiation conditions, Ti^+/Ti^{2+} *vs*. Si^+/Si^{2+}, during film growth, as determined by the ion mass spectrometry analyses performed at the substrate position with a **Hiden Analytical EQP 1000 instrument** (see Fig. 1(a)-(b)).

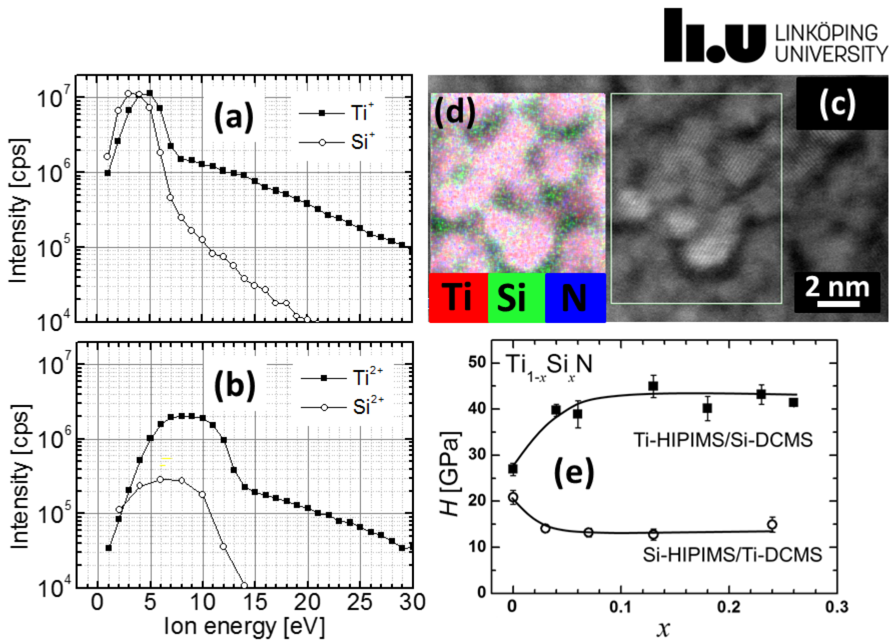

Figure 1. *Ion energy distribution functions measured at the substrate position for (a) singly-charged Ti^+ and Si^+ ions, and (b) doubly-charged Ti^{2+} and Si^{2+} ions during Ti-HIPIMS and Si-HIPIMS pulses; (c) plan-view STEM micrograph, and (d) plan-view EDX/STEM elemental maps of a $Ti_{0.74}Si_{0.26}N$ Ti-HIPIMS/Si-DCMS film, showing spatial distributions, acquired from the area outlined in panel (c); (e) nanoindentation hardnesses H(x) of Ti-HIPIMS/Si-DCMS and Si-HIPIMS/Ti-DCMS $Ti_{1-x}Si_xN$ films grown on Si(001) substrates at T_s = 500°C.*

A better mass match between incident Ti^+ ions and the average film atomic mass, higher metal-ion/metal-atom ratios, and a high fraction of doubly-ionized species results in an average momentum transfer per deposited atom $\langle p_d \rangle$ ~20 times higher for Ti-HIPIMS/Si-DCMS than during Si-HIPIMS/Ti-DCMS. As a consequence, adatom mean free paths are increased leading to the segregation of smaller Si atoms to column boundaries and the formation of a nanocomposite structure consisting of TiN-rich nanocolumns encapsulated in SiN_x tissue phases (cf. plan-view STEM micrograph in Fig.1(c), and EDX/STEM elemental maps in Fig. 1(d)). Ti-HIPIMS/Si-DCMS $Ti_{1-x}Si_xN$ films are superhard over a composition range that is significantly wider than reported previously, $0.04 \le x \le 0.26$, with a maximum hardness, H = 45 GPa, for layers with x = 0.13 (see Fig. 1(e)). However, residual stresses are also high with an average value of -7±1 GPa.

In sharp contrast, during Si-HIPIMS/Ti-DCMS $Ti_{1-x}Si_xN$ film growth, the flux of doubly-ionized metal ions is lower which, together with the lower mass of Si, low metal-ion/metal-atom flux ratio during HIPIMS pulses, and poorer mass match between incident Si^+ ions and average film atomic mass results in relatively low $\langle p_d \rangle$ values. As a consequence, Si is trapped in the metastable $Ti_{1-x}Si_xN$ NaCl structure to form solid solutions over the highest compositional range yet reported, $0 \le x \le 0.24$.

Project summary by:
G. Greczynski
Thin Film Physics Division
Department of Physics (IFM)
Linköping University
SE-581 83 Linköping
Sweden

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Hiden Product:
EQP

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