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Controlling the Boron-to-Titanium Ratio in Magnetron-Sputter-Deposited TiBx Thin Films via Preferential Ionization of Sputter-Ejected Ti

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TiBx thin films grown from compound TiB2 targets by magnetron sputter deposition are typically highly overstoichiometric, with x ranging from 2.4 to 3.5, due to differences in Ti and B preferential ejections angles and gas-phase scattering during transport between the target and the substrate. We show that the use of highlymagnetically-unbalanced magnetron sputtering of TiB2 target leads to selective ionization of sputter-ejected Ti atoms which are steered via an external magnetic field to the film, thus establishing control of the B/Ti ratio with the ability to obtain stoichiometric TiB2 films over a wide range in Ar sputtering pressures.1 We further demonstrate that stoichiometric TiB2 films can be obtained using high power impulse magnetron sputtering (HiPIMS) in Ar; the B/Ti ratio x is controllably varied from 2.08 to 1.83 by adjusting the length of HiPIMS pulses tau between 100 and 30 μs, while maintaining average power and pulse frequency constant. Energy- and time-dependent mass spectrometry analyses of ion fluxes incident at the substrate position show that the density of metal ions increases with decreasing tau, due to a dramatic increase in the peak target current density and strong gas rarefaction. With tau < 60 $\mu s,$ film growth is increasingly controlled by incident ions rather than neutrals. Thus, since sputter-ejected Ti atoms have a higher probability of being ionized than B atoms due to their lower first ionization potential and larger ionization cross-section, the Ti concentration in as-deposited films increases with decreasing ton as ionized sputtered species are steered to the substrate by the plasma in order to maintain charge neutrality.

1 I. .Petrov. A. Hall, A.B Mei, N. Nedfors, I. Zhirkov, J. Rosen, A. Reed, B. Howe, G. Greczynski, J. Birch, L. Hultman, JE Greene, J Vac Sci Technol A, 35 050601 (2017)

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