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# Behavior of nitrogen species in TiN-HiPIMS

Takayuki Ohta, Keigo Takeda
Department of Electrical and Electronic Engineering, Meijo University, Japan
e-mail (speaker): tohta@meijo-u.ac.jp

TiN (Titanium Nitride) thin film has been used for hard coating materials in many mechanical components such as cutting tools or dies due to its excellent mechanical properties (high hardness and abrasion resistance). Io order to realize high film density of TiN film, high ion-to-neutral ratio of the sputtered species is necessary. High power impulse magnetron sputtering (HiPIMS) is an attractive method which is a pulse sputtering with peak power density of higher than 0.5 kW/cm$^2$ and pulse width of around 100μs, to obtain high ionization degree of sputtered species and a production of high energy ions. We have reported that the high-energy sputtered-carbon ions were produced in carbon HiPIMS and contribute to the film density of diamond-like carbon films.

The behavior of atomic nitrogen or nitrogen ions is crucial factors to characterize the film property as well as sputtered-species in reactive-TiN-HiPIMS. In this study, the density of ground-state atomic-nitrogen was measured by using vacuum ultra violet absorption spectroscopy(VUVAS). In addition, positive ions of nitrogen atom or nitrogen molecule were measured by using an energy-resolved mass spectrometry.

Figure 1 shows schematic diagram of HiPIMS chamber equipped with VUVAS system. 2-inch titanium target was used in this study. A negative pulse voltage with frequency of 200Hz, pulse duration of 28μs was applied to the target. The applied voltage was varied from 600V to 850V. The total gas flow rate of Ar /$N_2$ mixed gas was 5sccm, nitrogen gas flow rate ratio $N_2/(N_2 + Ar)$ was 50% and the total pressure was kept at 0.5Pa. The VUV light from micro discharge hollow cathode lamp was introduced into the chamber. The VUV light was passed through the plasma at 5.2cm away from the Ti target and was detected by a photomultiplier tube of a VUV monochromator. The transition lines used for the absorption measurements were around 120.0nm at ground-state of nitrogen atom.

IEDF were measured with an energy-resolved mass spectrometer (EQP 1000 Hiden Analytical). The orifice (diameter of 0.1 mm) of the mass spectrometer was set at opposite of the Ti target, and the distance between the target and the orifice was 84mm.

Figure 2 shows the time-averaged density of N atom as a function of $N_2/(N_2+Ar)$ flow rate ratio. N atom density increased from $1.9\times10^{11}$ to $1.8\times10^{12}$ cm$^{-3}$ with increasing $N_2/(N_2+Ar)$ flow rate ratio and then saturated. When the dissociation of $N_2$ molecule is assumed to be dominant for the production of N atom, the time-averaged dissociation fraction of $N_2$ molecule was estimated to be from 3.2 % to 7.6 %.

Figure 3 shows IEDFs of $N^+$ and $N_2^+$. High-energy $N^+$ around 80eV was observed. The IEDF of $N^+$ was comparable to that of $Ti^+$. On the other hand, the IEDF of $N_2^+$, which is produced from an electron impact of ionization of nitrogen molecules, shows low energy. These results showed $N^+$ is produced via the electron impact ionization of nitrogen atom sputtered from the poisoned target.

Reference
Kazunori Iga, Akinori Oda, Hiroyuki Kousaka, Takayuki Ohta, Thin Solid Films, vol.672, pp. 104 - 108 (2019).

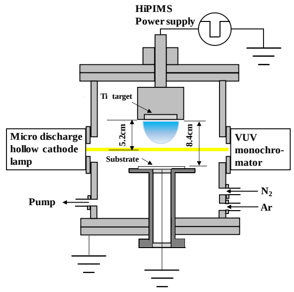


Figure 1 Schematic diagram of HiPIMS chamber with VUVAS system.

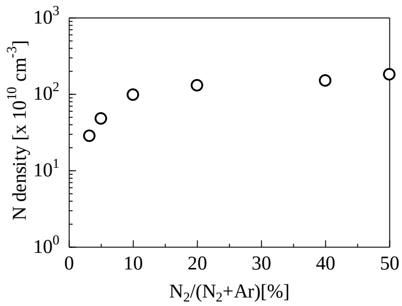


Figure 2 Nitrogen atom density as a function of $N_2/(N_2+Ar)$.

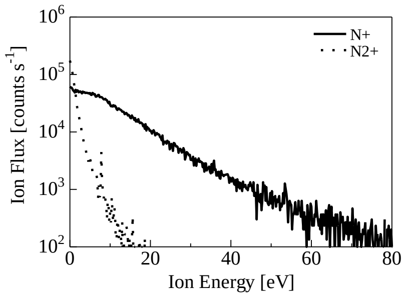


Figure 3 IEDFs of $N^+$ and $N_2^+$.