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# PEMOCVD of Ti(C,N) Thin Films on D2 Steel and Si(100) Substrates at Low Growth Temperatures

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Titanium nitride (TiN) thin films have useful properties including high hardness, good electrical conductivity, high melting point, and chemical inertness. The applications have included wear-resistant hard coatings on machine tools and bearings, decorative coating making use of the golden color, thermal control coatings for windows, and erosion resistant coatings for spacecraft plasma probes. For all these applications, as feature sizes shrink and aspect ratios grow, the issue of good step coverage becomes increasingly important. It is therefore essential to manufacture conformal coatings of TiN. The growth of TiN thin films by chemical vapor deposition (CVD) is of great interest for achieving conformal deposition. The most widely used precursor for TiN is $TiCl_4$ and $NH_3$. However, chlorine impurity in the as-grown films and relatively high deposition temperature (> 600 ℃) are considered major drawbacks from actual device fabrication. To overcome these problems, recently, MOCVD processes including plasma assisted have been suggested.

In this study, therefore, we have deposited Ti(C,N) thin films on Si(100) and D2 steel substrates in the temperature range of 150 - 300 ℃ using tetrakis diethylamido titanium (TDEAT) and titanium isopropoxide (TIP) by pulsed DC plasma enhanced metal-organic chemical vapor deposition (PEMOCVD) method. Polycrystalline Ti(C,N) thin films were successfully grown on either D2 steel or Si(100) surfaces at temperature as low as 150 ℃. Compositions of the as-grown films were determined with XPS and RBS. From XPS analysis, thin films of Ti(C,N) with low oxygen concentration were obtained. RBS data were also confirmed the changes of stoichiometry and microhardness of our films. Radical formation and ionization behaviors in plasma are analyzed by optical emission spectroscopy (OES) at various pulsed bias and gases conditions. $H_2$ and $He+H_2$ gases are used as carrier gases to compare plasma parameter and the effect of $N_2$ and $NH_3$ gases as reactive gas is also evaluated in reduction of C content of the films. In this study, we found that He and $H_2$ mixture gas is very effective in enhancing ionization of radicals, especially $N_2$ resulting is high hardness. The higher hardness of film is obtained to be ca. 1700 HK 0.01 but it depends on gas species and bias voltage. The proper process is evident for $H_2$ and $N_2$ gas atmosphere and bias voltage of 600 V. However, $NH_3$ gas highly reduces formation of CN radical, thereby decreasing C content of Ti(C,N) thin films in a great deal. Compared to PVD TiN films, the Ti(C,N) film grown by PEMOCVD has very good conformability; the step coverage exceeds 85% with an aspect ratio of more than 3.