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# Effect of an optical emission spectrometer feedback-controlled method on the characterizations of nc-TiC/a-C:H coated by high power impulse magnetron sputtering

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ABSTRACT

An optical emission spectrometer (OES) feedback-controlled high power impulse magnetron sputter deposition system was used to deposit nc-TiC/a-C:H thin films in a reactive mode. The plasma emission intensity of $Ti^{2+}$ ions at the emission wavelength of 365 nm was monitored and the amount of reactive $C_2H_2$ gas was precisely controlled to maintain stable emission intensity during the deposition process. By controlling the $C_2H_2$ input flow rate and different $Ti^{2+}$ ion optical emission intensities, various nc-TiC/a-C:H thin films were obtained at a fixed duty cycle of 2% and repetition frequency of 500 Hz at 75 °C. The characteristics and mechanical properties of the obtained films were also investigated. As the OES set point was 40%, the phase changing from TiC to nc-TiC/a-C:H films was clearly identified. The highest hardness of 26 GPa was obtained at the OES set point of 40%, where the film was composed of TiC. In addition, the lowest friction coefficient of 0.08 was obtained at the OES set point of 7%, which represented the nanocomposite structure of nc-TiC/a-C:H films.


## 1. Introduction

Hydrogenated nc-TiC/a-C:H composite films have been widely used in cutting and tribological applications because of their properties of high hardness (over 40 GPa) and low friction coefficient (around 0.1) [1–5]; these properties are largely determined by the volumetric fraction and size distribution of TiC nanocrystallites [6–8] or by the concentrations of titanium and carbon in the film [9–15]. Hydrogenated nc-TiC/a-C:H composites is mostly synthesized by sputtering (or cathodic arc evaporation) of a Ti target in hydrocarbons containing plasma by a hybrid PVD–PECVD process [16]. Hydrocarbons such as Methane [17] and acetylene [3,5,9,10,18] are most often used by controlled reactive gas flow using mass flow meters in deposition system However, conventional reactive sputter deposition often leads to target poisoning, and undesirable hysteresis effect [19].

High power impulse magnetron sputter (HiPIMS) deposition, developed by Kouznetsov et al., represents a relatively new deposition technique that provides high gas dissociation and highly ionized plasma by delivering high power in a short pulse to the target [20,21]. The target materials are, therefore, not only sputtered but also ionized during the deposition process [22]. A plasma density in the order from $10^{17}$ $m^{-3}$ to $10^{19}$ $m^{-3}$ can be achieved in the HiPIMS process [20,23]. Other advantages of HiPIMS include low process temperature, well-adherent coatings, superior film quality, and a droplet-free coating process [24,25].

Although the use of HiPIMS has been reported to reduce target poisoning [26,27], some improvements are still required, for example, the use of optical emission spectrometer (OES) feedback control of the reactive gas [28–30]. An optical emission spectrometer signal from the sputtered material, ion intensity of the reactive gas, or a cathode voltage have been used as feedback signals in conventional reactive sputter deposition systems [31,32]. However, in this study, we used a proportional integral derivative (PID) controller to precisely control a piezoelectric valve of the reactive gas. It is noted that the PID controller is typically used in temperature control. The intensity of $Ti^{2+}$ ions at an emission wavelength of 365 nm from the plasma is used as the feedback signal. The phase change of nc-TiC/a-C:H film was studied in order to evaluate the feasibility of this technique. As a result, the variation of film characteristics with respect to the $Ti^{2+}$ ion emission intensity is addressed and discussed. A phase changing process at a specific deposition condition is also demonstrated. We also found that the film property was not influenced by the substrate.

## 2. Experimental details

The deposition of nc-TiC/a-C:H film was performed in a modified STAR-2 PVD system, manufactured by Daedalus Precision Engineering Co., Ltd. in Taiwan. The substrates including silicon wafer (area of

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5 ∗ 5 $cm^2$) and WC-Co plates (area of 2.5 ∗ 2.5 $cm^2$) were used. A TruPlasma Highpulse Series 4002 (TRUMPF Hüttinger GmbH + Co. KG) was used to power the Ti target to 1 kW. The target was 6 in. in diameter and had a purity of 99.99%. Effect of pulse frequency on the hysteresis curve of target poison in the HiPIMS process was preceded first. Five frequency values of 150, 200, 300, 400 and 500 Hz with fixed 2% duty cycle and various pulse on-time of 133, 10, 67, 50 and 40 μs were selected, respectively, for the HiPIMS power supply to obtain the hysteresis curves for Ti target poisoning experiments.

A uni-polar mode with a constant pulse on-time of 40 μs and a duty cycle of 2% at a fixed frequency of 500 Hz was applied, while the target-to-substrate distance was fixed at 150 mm. The substrates were rotated in a speed of 4 rpm to keep the uniformity of coatings within 5% thickness deviation. The OES feedback controlled HiPIMS deposition system is shown elsewhere [30]. The emission intensity of $Ti^{2+}$ ions (emission wavelength of 365 nm) during the deposition process was monitored by a collimator of optical emission spectroscopy (OES, Plasus Emicon system), which was placed 50 mm away from the target. Closed-loop optical emission spectroscopy was used to control the dynamic flow of reactive gases of $C_2H_2$. The OES detected the optical emission of the metal plasma excited by magnetron sources during the reactive sputtering process. The emission measurement proceeded with the aid of a fiber optics system and a matched photomultiplier. An electronic package (proportional integral derivative (PID) controller) connected to the measuring unit controlled a piezoelectric valve as a process-specific regulating element for reactive gas admission. The OES reading indicated the ratio of the plasma intensity of $Ti^{2+}$ ions emitted during the reactive sputtering process with respect to its full emission intensity in metallic sputtering mode. The chamber was evacuated to a background pressure of approximately $1.2 \times 10^{-3}$ Pa. A fixed Ar flow rate of 20 sccm was controlled by a regular mass flow meter. The effect of the relative OES intensity of various $Ti^{2+}$ ions during the deposition was investigated in this study.

At the beginning of the deposition, an adhesion interlayer of pure Ti was first deposited for 15 min at a working pressure of $1.33 \times 10^{-1}$ Pa, and the substrate was grounded. The nc-TiC/a-C:H film was deposited for 30 min at the same working pressure and substrate bias without additional heating. The final film thickness was in the range of 720 to 1016 nm depending on the OES set points. The substrate temperature was measured near the substrate surface by a thermocouple. For all deposition conditions, the substrate temperature was below 75 °C.

During the deposition of nc-TiC/a-C:H film, the ions and neutrals in the discharge were identified by optical emission spectroscopy (OES, EMICON). The signal collector was placed 50 mm away from the target center. The cross-sectional view and high resolution transmission electron microscopy (HRTEM) images of the thin films deposited on Si wafer were observed by a spherical-aberration corrected field emission transmission electron microscope (TEM, JEOL, JEM-ARM200FTH). A focused ion beam system (Quanta 3D Dual Beam, FEI, USA) operated at 30 kV was employed to prepare the TEM samples. The composition and chemical bonding state of the film surface grown on Si wafer were analyzed using X-ray photoelectron spectroscopy (XPS, ULVAC-PHI PHI-5000 VersaProbe) with a monochromatic Al Kα X-ray beam (energy = 58.71486 eV and power = 25 W) after surface cleaning by ion bombardment. The crystallinity and microstructures of coating deposited on Si substrate were investigated using a grazing incident X-ray diffractometry (GIXRD, PANalytical-X'Pert PRO MRD) with an incident angle of 0.5°. The X-ray source was CuKα radiation (λ = 1.5418 Å) operated at 45 kV and 40 mA. The nc-TiC/a-C:H films grown on Si substrate were examined by a Raman spectroscopy (Ranishaw System 2000). The hardness and elastic modulus of coatings deposited on WC-Co substrates were measured using a nanoindenter (Nano Hardness Tester, CSM) equipped with a Berkovich 142.3° diamond probe tip at a maximum applying load of 700 μN. The friction coefficient of coating grown on WC-Co substrate was measured to use a CSM tribometer with a ball-on-disk configuration at 30 cm/s sliding speed and 1 N normal load, which were performed to use a standard WC-Co ball having a diameter of 6 mm at room temperature under dry condition. The sliding rotational radius of the ball was 5 mm.

## 3. Results and discussion

### *3.1. Effect of pulse frequency on the hysteresis curve of target poison in the HiPIMS process*

Before deposition, the effect of pulse frequency on the hysteresis curve of target poison by flowing $C_2H_2$ reaction gas, as seen in Fig. 1, was obtained in order to define the target poison performance in the HiPIMS process. It can be seen that the hysteresis recorded at 150 Hz is the smallest and that at 200 Hz is the largest, and the rest three are medium and comparable to each other. These results clearly showed that target poisoning occurred no matter the pulse frequency increased from 150 Hz to 500 Hz. Therefore, HiPIMS technology still cannot fully prevent the target poison phenomenon. Consequently, a frequency of 500 Hz was selected for the following nc-TiC/a-C:H deposition in this study.

### *3.2. Effect of OES set points on the I-V characterizations of the target in the HiPIMS process*

The OES set points of 100% and 0% by monitoring the OES signal of $Ti^{2+}$ ions at 365 nm were regarded as the pure metallic mode deposition and fully poisoning mode deposition, respectively. A set point between 0% and 100% represents the percentage of the reduced $Ti^{2+}$ OES intensity. For example, at an OES set point of 20%, a typical time-OES intensity plot for nc-TiC/a-C:H thin film deposition using the OES feedback-controlled HiPIMS process is shown in Fig. 2. It shows that the OES set point intensity of 100% can be obtained at 550 counts/s during the first step of the deposition of an adhesion interlayer of pure Ti. Then, as the deposition of nc-TiC/a-C:H starts, the OES set point of 20% was input in a very short time; the $Ti^{2+}$ intensity decreased quickly to the desired value of 110 counts/s, and the step remained stable during the following deposition process. At the same time, a reactive curve signal intensity of neutral C atom at 473 nm was obtained, which also changed with OES set points. This result demonstrates that the OES feedback-controlled HiPIMS process is accuracy and stable, especially in reactive poisoning deposition.

The average target input power was kept constant for all depositions at 1 kW with a fixed duty cycle of 2% and a pulse frequency of 500 Hz. The peak current, peak voltage, peak power, peak power density, and arc counts with respect to the changing of OES parameter are given in Table 1. As the OES set point was decreased from 100% to 7%, both the peak current and the peak voltage gradually increased from 154 A to

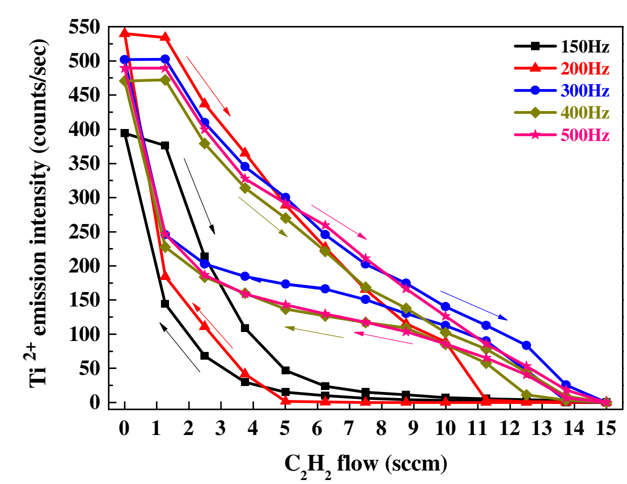


**Fig. 1.** Effects of frequency on the hysteresis curve of target poison by flowing $C_2H_2$ reaction gas.