# Nanocrystalline titanium films deposited via thermal-emission-enhanced magnetron sputtering

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## ARTICLE INFO

## ABSTRACT

Nanocrystalline titanium films were deposited at ultra-high current density by a direct-current closed-field unbalanced magnetron sputtering technique. The structures and properties of the films were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM) and nanoindentation microscratch. The Ti film deposited at target current density of 0.267 A/cm$^2$ exhibited a polycrystalline microstructure with average grain size of 16 nm, fine columnar structure with no obvious voids and smooth surface, better film thickness uniformity in different parts, and excellent film–substrate adhesion. These results showed that the excellent film structure and performances were primarily achieved by using high ionization rate and energy of target atoms. As current density exceeded 0.175 A/cm$^2$, ionization rate and energy of target atoms were greatly improved owing to the thermally-enhanced spontaneous emission of atoms and electrons from the target by Ar$^+$ bombardment and Joule heating.

## 1. Introduction

Magnetron sputtering ion plating (MSIP) is a typical film deposition technique widely employed in manufacturing semi-conductive and optical thin film [1–4], by which multi-layer gradient or compound films can be deposited on the substrates using cathode targets of different materials and based on precise control of target current [5]. In a MSIP system, argon plasma (Ar$^+$) mechanically knocks out the target atoms and turns them into uncharged low-energy particles [6–8]. Since neutral particles are not subjected to an electromagnetic field, the uncharged particles with low energy are difficult to form uniform, dense and highly-adhesive film on a large-scale and complex-shape substrate surface.

As revealed by former reports, film quality and microstructure are critically determined by two major factors: the ionization rate and the ion energy of target particles [9–11]. To overcome the limitations of uncharged low-energy particles in MSIP, researchers have made great endeavors to improve both ionization rate and ion energy [12–15]. New magnetron configurations (e.g. "Unbalanced" [16,17] and "Closed-field" [18]) are developed based on extending plasma space distribution and increasing plasma density to control target magnetic field, and elevate ionization rate of gas atoms. Nonetheless, in closed-field unbalanced MSIP (CFUBMSIP) plasma, the magnetic fields fail to significantly improve the quantity and energy of the target ions, while most of the ions are gas species (Ar$^+$) [19,20]. Therefore, the existing

magnetron configurations are not able to provide sufficient ion bombardment on the growing film, in which case, a porous microstructure and reduction of the film properties will be resulted.

Thus in this work, we investigated a new approach by altering the mechanism of atom and electron release from the target. At a critical temperature (for most metals the critical temperatures are approximately 1000 °C), electron thermal emission triggers metal atoms to escape from a metal surface along with a hot electron flow [21,22]. This process produces abundant high-energy metal atoms and electrons in the plasma that accelerates the ionization of metal atoms. By increasing the target current density and reducing the target discharge area, we developed a thin-film deposition technique involving both thermal-emission and magnetron sputtering. This technique can greatly increase the ionization rate and energy of target atoms, and improve the film's microstructure, adhesion, and the thickness homogeneity.

## 2. Experimental procedure

A square Ti target (100 × 100 mm$^2$) was mounted in a closed-field unbalanced magnetron sputtering (CFUBMS) system (Fig. 1). Prior to an experiment, the system was pumped down to $3.0 \times 10^{-3}$ Pa and then filled with pure Ar gas at 90 mL/min to 0.8 Pa. The films were deposited on silicon wafers (5 × 5 mm$^2$) and 304$^\#$ stainless steel ($\Phi = 50$ mm) substrates separately by a continuous direct-current (dc) power supply (10 kW, Advanced Energy Inc.) in the current regulation mode. The silicon wafers were placed every 25 mm from 100 to 250 mm away from the target, while the stainless steel was placed at
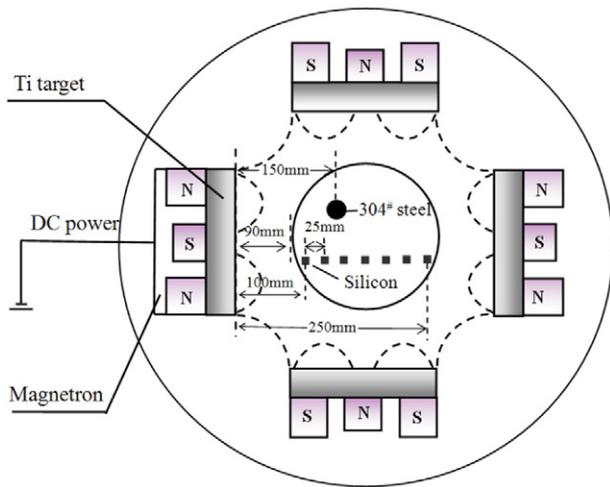
Fig. 1. Schematic of the CFUBMS system and the substrate position from top view.

150 mm from the target. Each substrate was placed into a sample holder, which was located vertically to the target surface.

Each deposition process lasted for 80 min. In the first 20 min, the substrate was sputter-eroded in pure Ar plasma under a pulsed dc substrate bias voltage −450 V (250 kHz and 87.5% duty circle) (Pinnacle Plus, Advanced Energy Inc.). The pulsed dc biasing is able to control unipolar arcing at the substrate, thereby enabling consistent and stable long-period operation and minimizing the deleterious effect on the substrate surfaces [23]. In the following 60 min, the Ti films were deposited under the target current density ($I_d$) of 0.067, 0.150, 0.175, 0.217 and 0.267 A/cm$^2$ respectively. $I_d$ was calculated as the target current divided by the effective sputter track area (60 cm$^2$). The pulsed dc substrate bias voltage was set at −65 V (50 kHz and 92.5% duty circle). The detailed deposition information was listed in Table 1.

The crystal structures of the films were characterized by an XRD-7000S X-ray diffractometer (XRD, SHIMADZU-LIMITED Corp.) from 30° to 80° at an increment of 0.02°. The grain sizes of the films were calculated from the (101) diffraction peak according to Scherrer's equation [24,25]:

$$t = 0.9\lambda/(B\cos\theta) \qquad (1)$$

where $\lambda$ is the X-ray wavelength (0.15406 nm for Cu), $\theta$ is the Bragg angle of the diffraction peak, and $B$ is the full-width-half-maximum (FWHM) of the peak.

The target surface temperature was measured by a Model WRP-130 thermocouple (SAIC Instruments). Specifically, the thermocouple probe was installed 10 mm away from the target surface with a gauge range of 0–1300 °C. The surface morphology and cross-sectional microstructures of the Ti films were observed by a JSM-6700F field-emission scanning electron microscope (SEM, JEOL Ltd.). The film microstructures were examined by a JEM-3010 transmission electron microscope (TEM, JEOL Ltd.). The film thicknesses at different target-substrate distances

**Table 1**
Parameters of Ti film deposition in dc mode.

| Sample ID | Deposition condition | | | | | |
|---|---|---|---|---|---|---|
| | $I_d$ (A/cm$^2$) | $U_t$ (V) | $U_s$ (V) | $I_s$ (A) | $T_t$ (°C) | $T_s$ (°C) |
| A | 0.067 | 346 | −65 | 0.01 | 296 | 54 |
| B | 0.150 | 431 | −65 | 0.07 | 854 | 113 |
| C | 0.175 | 441 | −65 | 0.18 | 1011 | 133 |
| D | 0.217 | 415 | −65 | 0.32 | >1300 | 150 |
| E | 0.267 | 375 | −65 | 0.67 | >1300 | 178 |
| F | 0.267 | 375 | 0 | 0 | >1300 | 136 |

Note: $I_d$: Target current density; $U_t$: Target voltage; $U_s$: Bias voltage of substrate; $I_s$: Bias current of substrate; $T_t$: Target surface temperature; $T_s$: Substrate temperature.

(TSDs) were measured by a laser scanning confocal microscope (LEXT-OLS4000, OLYMPUS Inc.). The film surface roughness was measured by an atomic force microscope (Model Dimension Icon, BRUKER Inc.) at a scanning area of 5 × 5 μm$^2$. Film adhesion was tested by a WS-2005 microscratch tester (ZKKH Instruments Inc.) at the applied load from 0.01 to 40 N. The images of the scratch track and film failure morphology were characterized by a GX71 optical microscope (OLYMPUS Inc.).

## 3. Results and discussion

### 3.1. Volt-ampere characteristics and target surface temperatures

Fig. 2 illustrates the volt-ampere characteristics of target in a dc electric field. The voltage corresponded to a certain current in the capable output of the power source. With the current density rising from 0 to 0.335 A/cm$^2$, the voltage first increased and then fell down, with a knee point at 0.175 A/cm$^2$. In traditional MSIP (current density at 0.1–100 mA/cm$^2$ [26]), generation of ions and electrons between the cathode target and the anode vacuum chamber mainly depends on the impact ionization, which is determined by the potential drop in the plasma sheath on the cathode surface. The functional relationship between the discharge current $j$ and discharge voltage $V$ of the dominant charge carrier is expressed according to Child's law [27–29] as follows:

$$j = (4\varepsilon/9)^2 (e/m)^{0.5} \left(V^{1.5}/d^2\right) \qquad (2)$$

where $\varepsilon$ is the space permittivity, $e/m$ is the charge-to-mass ratio for the dominant species, and $d$ is the sheath width.

In the film deposition process, however, the bombardment of abundant Ar$^+$ not only transmits high energy to the target, but also inflicts structural defects on the target surfaces. Owing to the heat accumulation from Ar$^+$ bombardment and Joule-heating ($Q = I^2Rt$), the target surface temperature rises significantly in the high $I_d$ range ($I_d > 0.175$ A/cm$^2$). The generation of the Joule-heating is caused by the high $I_d$ and the high-resistance structural defects [30]. Meanwhile, low heat dissipation rate can decrease thermal conductivity of Ti (15.24 W/(m·k)). At that moment, the acceleration of atom ionization is probably due to an increasingly effective emission of atoms and electrons when the micro-area temperature on the target surface exceeds the critical level of thermal emission. Thus at high current density, the volt-ampere characteristic curve is changed from an increasing function to a decreasing function (Fig. 2). Posadowski succeeded in conducting this process for copper, silver and tantalum [31,32]. The target surface temperatures of samples A to E during deposition measured by the thermocouple were 296, 854, 1011, >1300 and >1300 °C, respectively
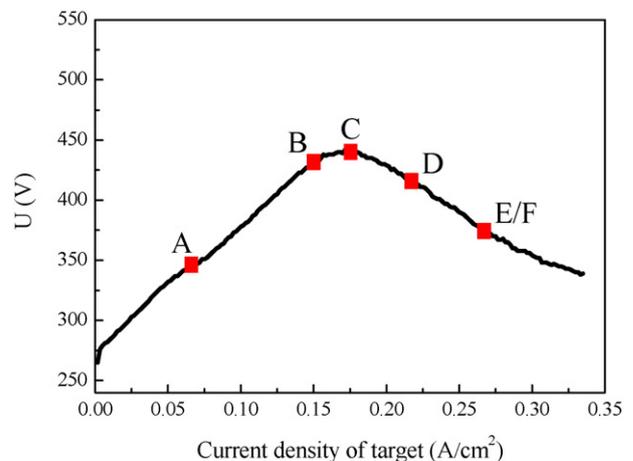


Fig. 2. The volt-ampere characteristics of the target.