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ARTICLE

Effect of Target Current of Dual-stage HPPMS on the Microstructure and Corrosion Resistance of TiN Coatings

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Abstract: A dual-stage high power pulsed magnetron sputtering (HPPMS) technique, which has two continuous and independently adjustable steps in one pulse period, was developed in order to solve low deposition rate of traditional HPPMS. Through the reasonable allocation of electric field of dual-stage HPPMS, a fine and dense structure of TiN coating was prepared. The effects of target current of dual-stage HPPMS on the microstructure and corrosion resistance of TiN coating were studied. It is found that the morphology of target surface changed from small pits to large-area craters when target current increased to 20 A. It indicated that the leave-target mode of deposited particles changed from sputtering to sublimation or evaporation. Additionally, when target current was 10 A, the TiN coating exhibited pyramid-shaped particles with average grain size of 11 nm. When target current increased to 25 A, the TiN coating showed a circular shape particles with average grain size of 18 nm and dense columnar structure. This microstructure gave rise to a better corrosion resistance.

Key words: dual-stage HPPMS; target current; deposition rate

TiN coating is widely used in the fields of mechanical engineering, aerospace and semiconductor due to its good mechanical properties, low electrical resistivity and superior chemical and thermal stability[1]. In addition, unique optical properties of brown to golden of TiN coating make it suitable for application in luxury goods and decoration fields[2]. The magnetron sputtering technique has been widely employed to deposit TiN coating, which has the advantages of low deposition temperature, multicomponent deposition and fabricating smooth coating[3,4]. However, low density plasma of magnetron sputtering results in loose structure and poor adhesion of TiN coating[5]. High power pulsed magnetron sputtering (HPPMS) was developed by Kouznetsov[6]. It creates a high density plasma of a high degree of ionization of the deposited particles using a pulsed high peak target power density (e.g.1~3 kW/cm^2) for a short period of time (e.g. 5~150 μs)[7]. HPPMS technique has been proved to improve the coating structure and properties, and enhance coating adhesion as compared to traditional magnetron sputtering[8]. However, the extremely high peak target power causes overheating of target, resulting in a significant reduction in duty cycle (<5%). Moreover, the ionized deposited particles can be attracted back toward the cathodic target with high voltage, which reduces the deposition rate of coating[9,10].

As an alternative HPPMS technique, dual-stage HPPMS has been developed after the development of HPPMS. The dual-stage HPPMS technique uses two continuous and independent adjustable pulse stages in one pulse period. Fig.1 shows the waveform of target current of dual-stage HPPMS. The first stage is the weakly ionized stage. In this stage, low voltage, current and power are loaded on the target to ignite plasma. The second stage is strongly ionized stage with high voltage, current and power. The weakly ionized stage allows for the formation of a stable discharge prior to entering the strongly ionized stage, which is beneficial for suppressing the arc formation during the high power mode of operation. Additionally, when the target current is greatly increased through current control mode in the strongly ionized stage, the number of Ar^+ bombardment on the target surface can be increased. The temperature of target surface will rise due to Ar^+ bombardment and resistance heat. When the temperature

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exceeds the melting point of target material, the number of deposited particles can be increased by sublimation or evaporation process[11,12]. Consequently, the dual-stage HPPMS technique can produce higher density of plasma and deposited particles than traditional magnetron sputtering.

Based on the above analysis, it could be inferred that target current is a very important factor, which affects the leave-target mode and deposition of deposited particles. In this study, the correlations between microstructure, deposition rate and corrosion resistant properties of TiN coatings deposited by dual-stage HPPMS technique with different target currents in strongly ionized stage were studied. In addition, the leave-target mode of deposited particles was discussed in detail in accordance with the morphology of target surface evolution.

1 Experiment

All TiN coatings were reactively deposited by a closed unbalanced magnetron sputtering system in a mixture atmosphere of Ar and N_2. The deposition system is a cylindrical chamber that contains two unbalanced magnetrons of alternating reversed magnetic polarities installed on the chamber wall to form a closed magnetron field. Ti target was circle with the diameter of 100 mm, thickness of 7 mm and purity of 99.9%. The substrates are P-type (100) Si wafer and M2 high-speed steel. The substrates were ultrasonically cleaned in acetone and alcohol for 15 min separately. After drying with N_2 gas, the substrates were installed into the sample holder. The substrates were parallel to the target surface, and the distance between target and substrate was 130 mm. The rotating speed of sample holder was set to 5 r/min. The diagram of coating deposition system is shown in Fig. 2.

The substrate was cleaned by plasma sputter etching in a pure Ar plasma using a pulsed dc substrate bias voltage of −500 V for 10 min before all deposition. Then the Ti transition layer was deposited for 10 min to enhance adhesion between the coating and substrate. Finally, TiN coatings were deposited at different target currents using dual-stage HPPMS power supply for 40 min. The specific experimental parameters are shown in Table 1. It should be noted that T_{on} in the weakly and the strongly ionized stages of dual-stage HPPMS was set to 8 and 6 ms respectively, and T_{off} was 6 ms. The duty cycle was 70%.

The crystal structure of TiN coatings was determined by X-ray diffractometry (XRD-7000s, Shimadzu limited Corp.). The scanning electron microscope (JSM-6700F, JEOL Ltd) was used to characterize the surface and cross-section morphology of coatings. The three-dimensional morphology of target surface was characterized by laser confocal microscope (LEXT OLS4000, OLYMPUS Inc.). The corrosion resistance of coatings was characterized by electrochemical test system (CS350, Wuhan Corrtest Instruments Co., Ltd). The polarization curve of TiN coatings in 3.5% NaCl corrosion medium was measured by potentiodynamic scanning, which was analyzed by the software of C-View.

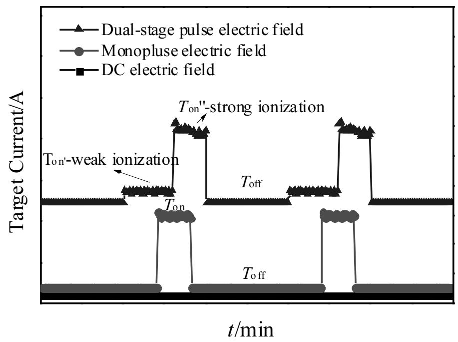

Fig.1 Target current waveform at different electric fields

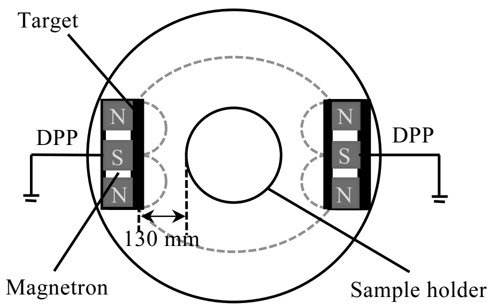

Fig.2 Diagram of coating deposition system

Table 1 Parameters of TiN coating deposited at different target currents by dual-stage HPPMS

Sample No.	I_p/A	T_{on}/ms	T_{off}/ms	f/Hz	U_t/V	U_s/V	Ar Flow/mL·min^{-1}	N_2 Flow /mL·min^{-1}	P/Pa	T_s/°C	T/min
1#	2.0/10	8/6	6	50	220/523	−60	60	20	0.8	50	40
2#	2.0/15	8/6	6	50	220/548	−60	60	20	0.8	56	40
3#	2.0/20	8/6	6	50	220/556	−60	60	20	0.8	68	40
4#	2.0/25	8/6	6	50	220/570	−60	60	20	0.8	80	40

Note: I_p-target current of the weakly and strongly ionized stages; T_{on}-pulse length of the weakly and strongly ionized stages; T_{off}-pulse turn-off length; f-frequency; U_t-target voltage; U_s-bias voltage; P-deposition pressure; T_s-deposited temperature; T-deposition time

2 Results and Discussion

2.1 Microstructure analysis

Fig.3 shows the XRD pattern of TiN coatings. All TiN coatings exhibit a NaCl-type face centered cubic (fcc) structure, which contains diffraction peaks of (111), (200), (220) and (311). The diffraction peaks of Ti or Ti_2N are not detected in XRD pattern. It is evident that the TiN is the main component of these coatings. The preferred orientation changes significantly, in which the (111) diffraction peak of TiN coating first increases and then decreases in intensity with target current increasing from 10 A to 25 A, and the intensity of (220) diffraction peak continues to increase. The preferred orientation gradually changes from (111) to (220) with the target current increasing.

Formation of preferred orientation during TiN film growth is dependent on competition between strain energy, surface energy and stopping energy[13,14]. For TiN coating with fcc structure, (200) plane has the lowest surface energy, (111) plane has the lowest strain energy and (220) plane has the lowest stopping energy. In this study, increasing plasma density improves ion bombardment and increases adatom mobility and strain energy in coatings, resulting in the production of (111) orientation which has the lowest strain energy plane. When the target current continuously increases to 25 A, the growth of (111) plane is restricted and (220) plane with the lowest stopping energy becomes preferred orientation since the TiN coating possesses the highest deposition rate.

The average grain size of TiN coatings was calculated from the full width at half maximum (FWHM) of diffraction peak according to Scherrer's equation[15]. When target current increases from 10 A to 25 A, the average grain sizes of TiN coating are 11, 13, 16 and 18 nm, respectively. It can be seen that the grain size increases slightly with increase of target current. The nucleation and growth process of TiN coating are mainly affected by plasma density, substrate temperature, and deposition rate. The high plasma density can be obtained by the dual-stage HPPMS technique at high target current, and the substrate temperature is enhanced by increasing the plasma density. High plasma density and high substrate temperature improved adatom mobility and diffusivity but reduced undercooling of phase transformation[16,17]. The critical radius of nucleation was increased and the grain growth was enhanced. Thus, higher target current can obviously increase the average grain size of TiN coating. It is noted that the increasing average deposition rate under high target current can reduce the critical radius of nucleation and increase nucleation number. Therefore, the average grain size of TiN coatings is controlled at the nanometer scale which is less than 20 nm.

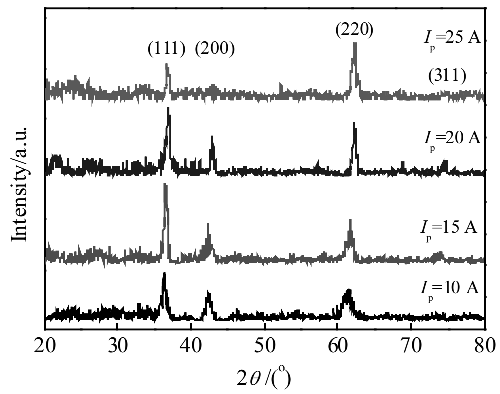

Fig.3 XRD patterns of TiN coatings

The surface and cross-sectional morphologies of TiN coatings are shown in Fig.4 and Fig.5, respectively. When the target current is 10 A, the TiN coating exhibits pyramid-shaped particles, and some voids exist between particles. When target current is increased to 15 A, the TiN coating still exhibits pyramid-shaped particles, but the number of voids obviously decreases. When target current continuously increases to 20 and 25 A, the surface morphology of TiN coatings changes from pyramid shape to circular shape, and the voids between particles disappear, indicating that the coating compactness has been improved. Fig.5 shows all the TiN coatings exhibit columnar structure.

The microstructure of TiN coating is mainly related to deposition characteristics. As the target current increases, the number of plasma and deposited particles increases. It

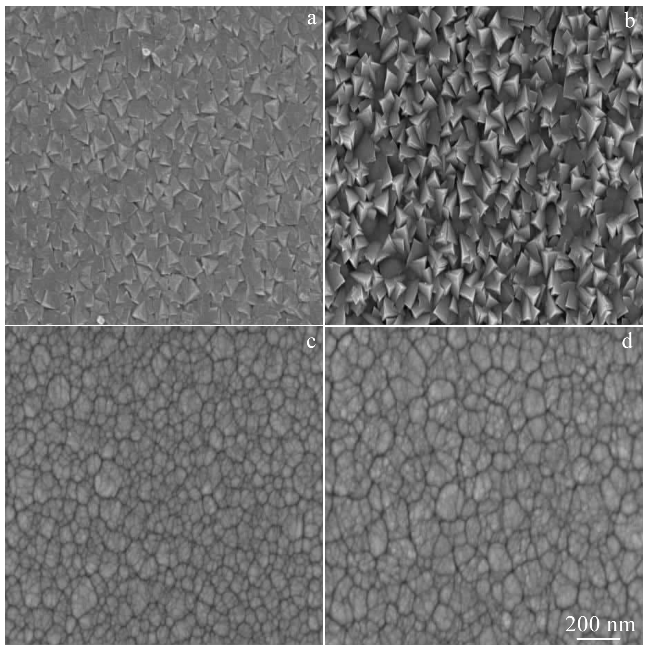

Fig.4 Surface SEM images of TiN coatings deposited at different target currents by dual-stage HPPMS: (a) 10 A, (b) 15 A, (c) 20 A, and (d) 25 A

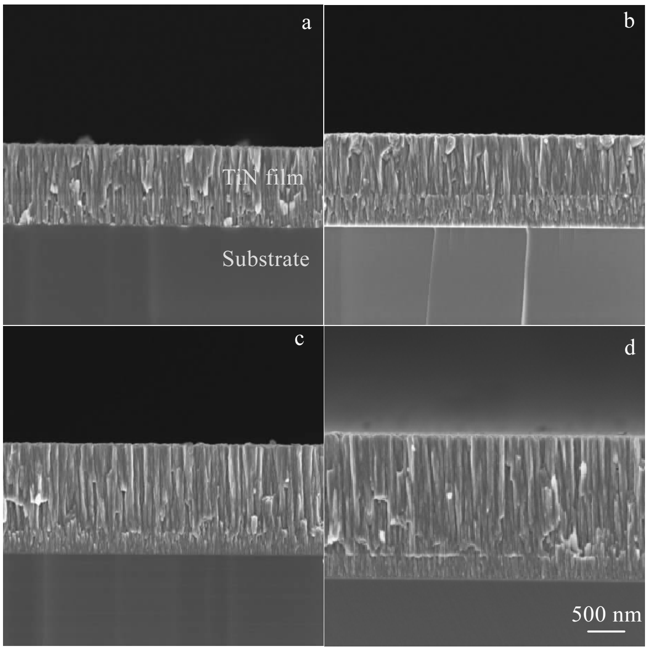

Fig.5 Cross-sectional SEM images of TiN coatings deposited at different target currents by dual-stage HPPMS: (a) 10 A, (b) 15 A, (c) 20 A, and (d) 25 A

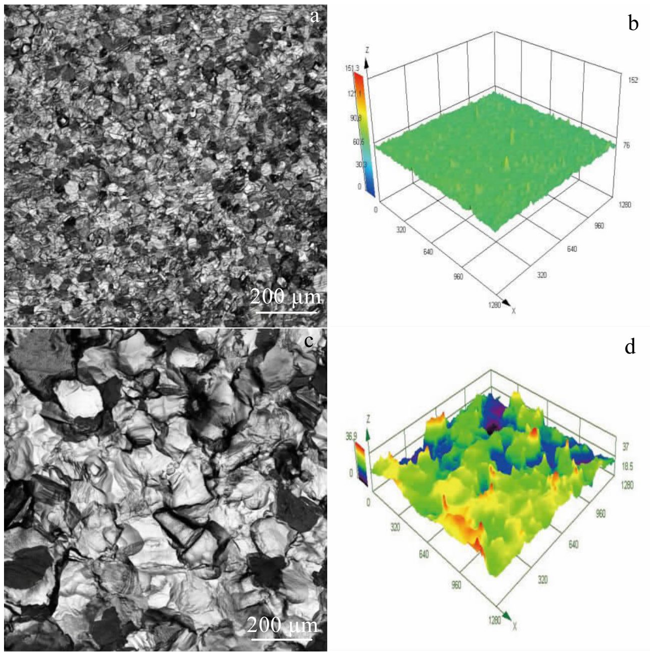

Fig.6 Two-dimensional and three-dimensional morphology of discharge impression on the target surface: (a, b) 15 A and (c, d) 20 A

helps enhance the mobility and diffusivity of adatom on substrate surface. The enhanced mobility is favorable for the diffusion on substrate surface to obtain a coating with dense structure. Additionally, with increase of plasma density, the deposition temperature enhances the plasma bombardment effect on substrate. Higher deposition temperature and mobility of deposition particles contribute to nucleation and growth of the coating. According to Thornton's classic film growth theory [18], this condition enables the TiN coating to grow in a dense columnar structure.

2.2 Leave-target mode of deposited particles

The characteristics of deposited particles mainly depend on leave-target mode and will affect deposition and microstructure of TiN coatings. The laser confocal microscope was used to observe the 2D and 3D morphologies of target surface in order to further study the change of leave-target mode, as shown in Fig.6. The deposited particles leave target in the sputtering mode and the target surface shows a pit-like morphology at low target current (Fig.6a). The size of the pit is 10~50 μm. When target current increases above 20 A, part of deposited particles leave the target by sublimation or evaporation process and a large area of pits can be clearly observed on the target surface. The size and the depth of pits are larger than those under low target current, and the size increases to 50~100 μm. In addition, the grain size of target materials has increased. As the target current increases, the bombardment energy of Ar^+ and the Joule heat can generate a large amount of heat accumulation at the area of grain boundary or defect of target surface with high resistance. The temperature of target can be improved by heat accumulation, which causes the deposited particles to leave target surface by sublimation or evaporation, and the grain growth of target material.

2.3 Deposition rate analysis

The average deposition rate of TiN coatings was calculated by the ratio of coating thickness to deposition time, shown in Fig.7. The average deposition rate increases nonlinearly with increasing of the target current. When the target current is 25 A, the average deposition rate reaches the highest value of 56.3 nm/min. The deposition rate of dual-stage HPPMS is higher than traditional HPPMS rate for an equivalent amount of average target power[19]. Because the inert gas is ionized to form low density plasma by applying low power in the weakly ionized stage during dual-stage HPPMS deposition, the target voltage that induces high density plasma in the strongly ionized stage is reduced. The deposition rate can be increased by effectively avoiding the loss of deposited particles. When the target current is low, the deposited particles leave target by sputtering process, and the target current can directly affect the number of bombardment of Ar^+, so the number of deposited particles should be linearly proportional to the target current. However, when the target current continues to increase to 20 A, deposited particles gradually leave

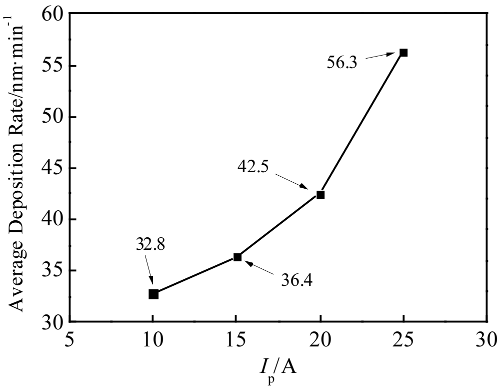

Fig.7 Average deposition rate of the TiN coatings deposited at different target currents by dual-stage HPPMS

target by sputtering, sublimation or evaporation process. The amount of deposited particles is significantly higher than the increment of target current, thus making the deposition rate increase nonlinearly at the conditions of high target current (> 20 A).

2.4 Corrosion resistance analysis

The electrochemical polarization curve of TiN coatings deposited by different target current are studied, as shown in Fig.8. The corrosion potential (E_{corr}), corrosion current density (I_{corr}) and corrosion rate (V_{corr}) are obtained by fitting the electrochemical parameters in the polarization curve with C-View software, as shown in Table 2. With the increase of target current, I_{corr} and V_{corr} decrease first and then increase. This result demonstrates that the corrosion resistance of TiN coating increases first and then decreases slightly. The TiN coating deposited at the target current of 20 A shows the best corrosion resistance. This improvement of corrosion resistance can be mainly attributed to the enhancement of structural compactness and the decrease in abundant crystal boundaries in TiN coating[20-22]. The diffusion paths of the corrosion medium are effectively limited by compact structure of the coating, while the intercrystalline corrosion is prevented by rare crystal boundaries.

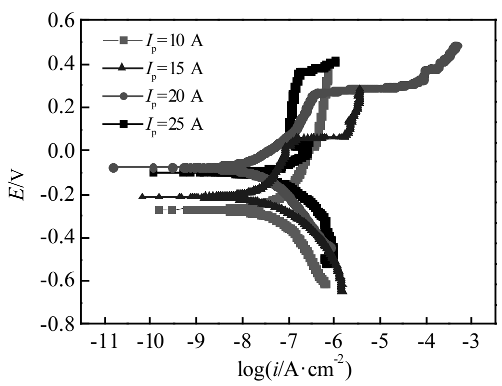

Fig.8 Polarization curves of TiN coatings deposited at different target currents

Table 2 Results of electrochemical tests in 3.5% NaCl solution

I_p/A	E_{corr}/V	I_{corr}/×10^{-8} A·cm^{-2}	V_{corr}/×10^{-4} mm·A^{-1}
10	-0.2411	3.4237	1.7935
15	-0.1954	2.6491	1.5244
20	-0.0982	1.1354	0.59 217
25	-0.1135	2.0689	1.0831

3 Conclusions

1) When the target current increases from 10 A to 25 A, all TiN coatings exhibit a NaCl-type face centered cubic structure. The preferred orientation of TiN coating is changed from (111) to (220). The highest deposition rate of 56.3 nm/min can be achieved.

2) When the target current is 20 A, the leave-target mode of deposited particles changes from sputtering to sputtering and sublimation/evaporation using dual-stage HPPMS technique. And the TiN coating with smooth and dense microstructure exhibits the best corrosion resistance. The "deposition-crystallization-growth" atomic stack thickening mechanism is still maintained.

3) The dual-stage HPPMS technique can improve the deposition rate of TiN coating, which can reduce the cost of coating preparation effectively.

References

1 Chawla V, Jayaganthan R, Chawla A K *et al*. *Journal of Materials Processing Technology*[J], 2009, 209(7): 3444

2 Lin N M, Huang X B, Zhang X Y *et al*. *Applied Surface Science*[J], 2012, 258: 7047

3 Lin J L, John J, Moore J J *et al*. *Surface & Coatings Technology*[J], 2010, 204(14): 2230

4 Lin J, Moore J J, Sproul W D *et al*. *Journal of Vacuum Science & Technology A*[J], 2011, 29: e061301

5 Greczynski G, Mraz S, Hultman L *et al*. *Applied Physics Letters*[J], 2016, 108: e041603-1

6 Kouznetsov V, Macák K, Schneider J M *et al*. *Surface & Coatings Technology*[J], 1999, 122(2-3): 290

7 Bagcivan N, Bobzin K, Grundmeier G *et al*. *Thin Solid Films*[J], 2013, 549: 192

8 Wu Z Z, Tian X B, Gong C Z *et al*. *Surface & Coatings Technology*[J], 2013, 229: 210

9 Brenning N, Huo C, Lundin D *et al*. *Plasma Sources Science & Technology*[J], 2012, 21(2): e025005

10 Anders A. *Journal of Vacuum Science & Technology A*[J], 2010, 28: 783

11 Sidelev D V, Bleykher G A, Grudinin V A *et al*. *Surface & Coatings Technology*[J], 2018, 334: 61

12 Bleykher G A, Borduleva A O, Krivobokov V P *et al*. *Vacuum*[J], 2016, 132: 62

13 Yang C, Jiang B L, Feng L. *Acta Metallurgica Sinica*[J], 2015, 51: 1523
14 Ma C H, Huang J H, Chen H. *Thin Solid Films*[J], 2004, 446: 184
15 Zenoozi S, Agbolaghi S, Poormahdi E *et al. Macromolecular Research*[J], 2017, 25: 826
16 Li G D, Li L H, Han M Y *et al*. *Metals*[J], 2019, 9: e918
17 Shekargoftar M, Jurmanova J, Homola T. *Metals*[J], 2019, 9: e991
18 Alexis D M, Schuster F, Billard A *et al*. *Surface & Coatings Technology*[J], 2017, 330: 241
19 Greczynski G, Hultman L. *Vacuum*[J], 2016, 124: 1
20 Zhang L N, Chen L Y, Zhao C H *et al*. *Metals*[J], 2019, 8: e850
21 Supplit R, Koch T, Schubert U. *Corrosion Science*[J], 2007, 49: 3015
22 Du H, Zhao H, Xiong J. *International Journal of Refractory Metals & Hard Materials*[J], 2013, 37: 60

双级 HPPMS 靶电流对 TiN 镀层微观结构及耐蚀性的影响

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摘 要：为了解决传统高功率脉冲磁控溅射（HPPMS）平均沉积速率低的问题，研究提出一种新型的双级 HPPMS 技术，即在一个脉冲周期内具有两个连续的、独立可调的脉冲阶段。通过对双级 HPPMS 电场的合理调配，可制备得到结构致密的 TiN 镀层，研究了双级 HPPMS 靶电流对 TiN 镀层微观结构及耐蚀性的影响。结果表明，当靶电流增大至 20 A 时，靶面形貌由小凹坑转变为大面积凹坑，说明镀料粒子的脱靶方式由碰撞溅射转变为升华或蒸发。同时，当靶电流为 10 A 时，镀层颗粒呈现三棱锥状结构，平均晶粒尺寸为 11 nm；当靶电流增大至 25 A 时，镀层颗粒呈现光滑致密的圆胞状结构，平均晶粒尺寸为 18 nm，光滑致密的组织结构使镀层具有较好的耐蚀性。

关键词：双级HPPMS；靶电流；沉积速率

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