Effect of Target Surface Discharge Characteristics on Ionization Rate of Deposited Particles and Deposition Behavior (Postprint)

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Abstract

Based on the principles of gas discharge plasma physics, increasing the current density of the target material introduces the gas discharge on the target surface into the glow-arc discharge transition region between glow discharge and arc discharge. Utilizing the collision kinetic energy from Ar+ bombardment of the target surface and the Joule thermal energy generated by electron transport, the self-emission of electrons and atoms from the target surface is collectively induced, enabling them to overcome the surface work function. This yields deposition particles characterized by high density, high ionization degree, and high energy. In the experiments, two groups of pure Ti thin films were prepared in the glow discharge region and the glow-arc transition region, respectively. The film thickness at different target-to-substrate distances was measured using confocal laser scanning microscopy (CLSM), the microstructure of the films was characterized by XRD, SEM, AFM, and TEM, and the film-substrate adhesion strength was evaluated using a coating adhesion scratch tester. The experimental results indicate that the pure Ti thin films deposited in the glow-arc discharge transition region possess nanoscale grains, dense microstructure, uniform thickness, high deposition rate, and excellent film-substrate bonding strength.

Full Text

Effect of Target Surface Discharge Characteristics on Ionization Rate and Deposition Behavior of Deposited Particles

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Abstract

Based on the physics of gas discharge plasma, increasing the current density of the target material can shift the target surface gas discharge into the glow-arc transition region between glow discharge and arc discharge. By utilizing both the collision kinetic energy of Ar^+ bombardment on the target surface and the Joule heating effect from electron transport, electrons and atoms are induced to spontaneously emit from the target surface by overcoming the work function. This yields deposited particles with high density, high ionization, and high energy. In this study, two groups of pure Ti films were prepared in both the glow discharge region and the glow-arc transition region, respectively. Film thickness at different target-to-substrate distances was measured using confocal laser scanning microscopy (CLSM), while the microstructure was characterized by XRD, SEM, AFM, and TEM. The film-substrate adhesion was evaluated using a coating adhesion scratch tester. The results demonstrate that pure Ti films deposited in the glow-arc transition region exhibit nanoscale grain size, dense structure, uniform thickness, high deposition rate, and excellent film-substrate bonding strength.

Keywords: magnetron sputtering ion plating, volt-ampere characteristic of gas discharge, thermal emission, ionization rate

Introduction

With the rapid development of modern society, increasingly stringent demands have been placed on the ability of various products to withstand harsh environments and maintain long-term operational reliability and stability, particularly under conditions involving high temperature, high pressure, high speed, high automation, and severe working conditions. However, in industrial production, most mechanical components inevitably experience failure under such demanding environments, leading to material scrapping and severe resource waste. This not only significantly affects production efficiency and increases manufacturing costs but also constrains long-term enterprise development. Surface modification technology addresses this challenge by preparing thin films with special composition, structure, and properties on material surfaces, thereby endowing materials with the capability to resist adverse environments and meet harsh service conditions. Consequently, surface modification technology has been widely applied in machining, mold production, material protection, and surface decoration.

Magnetron sputtering ion plating (MAIP) has been extensively utilized in semiconductor, optical, and decorative thin film preparation due to its advantages of low-temperature deposition, ease of multi-element co-deposition or gradient deposition, and ability to produce smooth surfaces. However, constrained by collisional sputtering mechanisms, conventional MAIP primarily produces low-energy neutral atoms as deposited particles. Since neutral particles are unaffected by electromagnetic fields, they exhibit low activity and surface diffusion energy when reaching the substrate, making it difficult to prepare dense films with good adhesion. This limitation has severely restricted the further development of this technology in precision machinery manufacturing. Therefore, obtaining highly ionized and high-energy deposited particles has become crucial for improving coating structure and comprehensive film performance. Over recent decades, researchers have introduced various magnetic field control methods such as "unbalanced" and "closed-field" configurations to expand the plasma region and increase plasma density, aiming to enhance the ionization rate of deposited particles. Nevertheless, conventional MAIP is limited by low sputtering yield and low energy transfer coefficients, resulting in low density and energy of deposited particles in the plasma region, which restricts their collisional ionization with electrons or ions. Consequently, simply altering the magnetic field environment cannot fundamentally resolve the low ionization rate of deposited particles in MAIP.

Only by changing the collisional sputtering mechanism of deposited particles in MAIP can the ionization rate be substantially improved. Based on gas discharge plasma physics, this work introduces gas discharge into the glow-arc transition region by adjusting the cathode magnetic field arrangement and employing a wide-pulse discharge mode. By utilizing the collision kinetic energy of high-density Ar^+ bombarding a narrow annular region on the target surface and the Joule heating effect generated by electron current flowing through the metal target, thermal emission of target atoms and electrons is induced, overcoming the surface work function. This transforms the particle emission mechanism from pure collisional sputtering to a hybrid mode combining collisional heating and thermal emission, thereby obtaining deposited particles with high ionization, high energy, and high density, laying a solid foundation for preparing well-structured and high-performance thin films. Additionally, this study investigates the influence of different discharge characteristics on film microstructure, coating uniformity, and bonding strength.

Experimental Methods

Deposition System and Sample Preparation

The experiments were conducted using an unbalanced closed-field magnetron sputtering system to prepare four groups of pure Ti films at various current densities corresponding to different discharge regimes. A planar magnetron cathode with a 99.9% pure Ti target (100 mm × 100 mm) was employed. The cathode magnet arrangement and magnetic field strength were adjusted to reduce the target discharge area to 60 cm^2, with the discharge area determined by measuring the erosion ring area. The target current density was defined as the ratio of target current to discharge area. P-type (100) Si wafers and 304 stainless steel sheets were used as substrates. Prior to deposition, substrates were cleaned in CH_3COCH_3 and CH_3CH_2OH solutions for 20 min each, dried with pure N_2, and placed in the vacuum chamber. Si wafers were positioned at target-to-substrate distances of 100–300 mm (at 25 mm intervals) to measure film thickness at various positions, with the wafer at 200 mm used for microstructural observation. Stainless steel sheets were placed at 150 mm target-to-substrate distance for adhesion testing. All substrates were oriented perpendicular to the target surface, as shown in [Figure 1: see original paper].

Deposition Parameters

A 40 kHz wide-pulse power supply in constant-current mode was used to prepare two groups of pure Ti films in each discharge region. The deposition process lasted 80 min, comprising 20 min of etching and cleaning of the target and substrate surfaces using Ar^+ bombardment (Ti target current: 0.5 A, substrate bias: -450 V), followed by 60 min of pure Ti film deposition. During deposition, the Ti target current density i was set to 0.083, 0.133, 0.217, and 0.250 A/cm^2, with a substrate bias of -65 V. The current density of 0.083 A/cm^2 falls within the typical range for conventional magnetron sputtering. The Ar gas flow rate was maintained at 150 Pa/s (90 mL/min), and the chamber pressure was kept at 0.8 Pa. Detailed experimental parameters are listed in .

Characterization Methods

Film microstructure was analyzed using an XRD-7000S X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm) over a 2 range of 30°–80° at a step size of 0.02°. Surface and cross-sectional morphologies were examined using a JSM-6700F scanning electron microscope (SEM) and a Dimension Icon atomic force microscope (AFM). Film thickness at different target-to-substrate distances was measured using a LEXT-OLS4000 confocal laser scanning microscope (CLSM). Film-substrate adhesion was evaluated using a WS-2005 automatic coating adhesion scratch tester (diamond indenter, maximum load 40 N, loading rate 60 N/min, scratch length 4 mm). Scratch regions were observed using a GX-71 inverted metallurgical microscope (OM).

Results and Discussion

2.1 Gas Discharge Volt-Ampere Characteristics

The volt-ampere characteristics of the target were measured under 40 kHz wide-pulse electric field conditions by recording target voltage values as a function of target current density, as shown in [Figure 2: see original paper]. Conventional magnetron sputtering ion plating operates at target current densities of 0.1–100 mA/cm^2, where the volt-ampere characteristics in the glow discharge region exhibit a proportional relationship. When the target current density increases above 0.2 A/cm^2, the relationship between cathode target and anode chamber wall gradually transitions from proportional to inversely proportional. In conventional MAIP, electron generation primarily relies on collisional ionization of atoms and electrons in the cathode sheath region. The degree of ionization depends on electron energy, which is mainly influenced by the potential difference between anode and cathode, resulting in a proportional current-voltage relationship. However, when the target current density is increased several-fold or by an order of magnitude beyond conventional sputtering levels, the gas discharge enters the glow-arc transition region between glow and arc discharge. In this regime, the combined effects of high-density Ar$^+$ bombardment kinetic energy on a narrow annular target region and Joule heating from electron current flowing through the metal target cause rapid target surface temperature elevation. Increased temperature enhances the internal energy of surface electrons and atoms, enabling them to overcome the surface potential barrier and emit spontaneously. Since thermal emission does not require maintenance of a high anode-cathode potential difference, the target can achieve current densities several times higher than conventional magnetron sputtering at similar or even lower target voltages. Consequently, the target surface exhibits an inverse volt-ampere relationship in the glow-arc transition region.

2.2 Effect of Discharge Characteristics on Deposited Particle Distribution

The thickness variation and fitting curves of samples along the target-to-substrate distance are shown in [Figure 3: see original paper]. All four film groups exhibit decreasing thickness with increasing target-to-substrate distance. For the two films deposited in the glow discharge region (Samples No.1 and No.2), thickness at any given distance increases with peak current density i. The fitting curve slopes indicate consistent thickness increase rates across all target-to-substrate positions. In the glow discharge region, deposited particles rely primarily on collisional sputtering. As i increases, the number of Ar$^+$ ions bombarding the target surface increases, leading to more deposited particles, but the emission mechanism and ionization rate remain essentially unchanged, resulting in consistent thickness variation patterns.

In contrast, for films deposited in the glow-arc transition region (Samples No.3 and No.4), a transition occurs at 200 mm target-to-substrate distance. At distances less than 200 mm, Sample No.4 shows lower thickness than Sample No.3, but beyond 200 mm, Sample No.4 becomes thicker. This indicates that at $i =$ 0.250 A/cm^2 (Sample No.4), more deposited particles reach distant positions from the target. Calculating the thickness reduction rate between 100 and 300 mm reveals that as i increases from 0.083 to 0.250 A/cm^2, the thickness reduction rate decreases from 97.4% to 89.5%. This demonstrates that in the glow-arc transition region, the collision kinetic energy of Ar$^+$ and Joule heating can induce thermal emission of deposited particles, while the exponentially increased number of target atoms and electrons in the cathode sheath region dramatically enhances collisional ionization. During deposition, highly ionized particles can migrate to positions far from the target under the influence of substrate negative bias. Therefore, the hybrid collision-heating emission mechanism improves both the ionization rate and distribution uniformity of deposited particles.

2.3 Effect of Discharge Characteristics on Film Microstructure

The XRD patterns of the four film groups are shown in [Figure 4: see original paper]. Samples No.1 and No.2 exhibit low diffraction peak intensities, indicating nanocrystalline structures with small grain sizes. Samples No.3 and No.4 show significantly enhanced diffraction peak intensities, suggesting increased grain size and nucleation density. The average grain size was calculated using the Scherrer formula applied to the (100), (002), and (101) crystal planes, yielding values of 12, 13, 18, and 18 nm, respectively. Additionally, discharge characteristics influence preferred orientation. Samples No.1 and No.2 show preferred orientation along the (002) plane, while Samples No.3 and No.4 exhibit dual preferred orientations of (002) and (101).

During film growth, crystal structure, grain size, and preferred orientation are primarily affected by the energy and density of deposited particles. In the glow discharge region, limited by low sputtering yield and low energy transfer coefficients, deposited particles have low energy (<5 eV) and density, resulting in low surface activity and diffusion energy on the substrate. This favors the formation of nanocrystalline structures with small grain sizes. The relatively low deposition rate also provides sufficient time for atomic diffusion, promoting preferred growth along the (002) plane with the lowest free energy. In the glow-arc transition region, thermal emission increases particle energy and density. Consequently, highly active particles enhance nucleation density and grain size while facilitating preferred growth along close-packed planes with the lowest free energy. The higher deposition rate simultaneously inhibits further grain growth, limiting grain size to below 20 nm. Thus, films deposited in the glow-arc transition region exhibit nanopolycrystalline structures with grain sizes under 20 nm. Titanium has an hcp structure at room temperature with a lattice constant ratio $c/a < 1.633$. When $c/a < 1.633$, the (101) plane replaces the (002) plane as the close-packed plane with the lowest free energy. Therefore, as i increases, films gradually develop dual preferred orientations of (002) and (101).

High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) analyses further validate these microstructural differences, as shown in [Figure 5: see original paper]. Sample No.1 consists primarily of nanocrystals 10–15 nm in size with numerous disordered atomic arrangements at grain boundaries, and the diffraction pattern shows faint halo rings characteristic of nanocrystalline structures. Sample No.2 also exhibits 10–15 nm nanocrystals, but the disordered structures at grain boundaries begin to disappear. Samples No.3 and No.4 show grain sizes increasing to 15–20 nm with essentially no disordered structures at grain boundaries. The SAED patterns transition from halo rings to intense multiple diffraction spots, confirming the nanopolycrystalline nature of films deposited in the glow-arc transition region, consistent with XRD results.

2.4 Effect of Discharge Characteristics on Film Growth Structure

Surface and cross-sectional SEM images of the four film groups are shown in [Figure 6: see original paper]. All films exhibit columnar crystal growth. Sample No.1 shows irregular, non-uniform disk-like surface morphologies typical of columnar crystals, with numerous micro-pores between columns indicating poor densification. Samples No.2 and No.3 show increased and more uniform circular grain sizes, with reduced porosity between columnar structures. Sample No.4 shows no observable pores, and the cross-section reveals narrow, densely packed columns, indicating high densification. AFM measurements show surface roughness (Ra) values of 46.1, 82.3, 41.2, and 8.8 nm for Samples No.1-No.4, respectively, confirming that Sample No.4 deposited in the glow-arc transition region has high density and a smooth surface.

Film thicknesses measured from cross-sectional SEM images are 2.12, 3.72, 4.93, and 4.56 m, corresponding to deposition rates (at 200 mm target-to-substrate distance) of 35.3, 62.0, 82.2, and 76.0 nm/min, respectively. This demonstrates that the hybrid collision-heating emission mechanism achieves higher deposition rates than pure collisional sputtering at equivalent target voltages. These results confirm that in the glow discharge region, collisionally sputtered particles have low ionization, low energy, and low density, resulting in low surface activity and diffusion energy. This leads to isolated island growth with numerous intergranular pores and reduced deposition rates. In the glow-arc transition region, the hybrid emission mechanism produces particles with high energy, high ionization, and high density. Higher energy enhances particle activity and diffusion, promoting lateral migration to fill intergranular voids and enabling dense layer-by-layer growth. High density and ionization increase deposition rates while ion bombardment under negative bias removes protrusions and weakly bonded structures, yielding smooth, dense films.

2.5 Film-Substrate Adhesion

Critical load values, representing the load at which films first exhibit spalling, damage, or fracture, were used to evaluate adhesion strength. The critical load test results and OM images of scratch regions are shown in [Figure 7: see original paper] and [Figure 8: see original paper]. Samples No.1 and No.2 deposited in the glow discharge region show low critical loads (<8 N), while Samples No.3 and No.4 from the glow-arc transition region exhibit significantly higher critical loads, with Sample No.4 reaching 25.2 N. OM images reveal that Samples No.1 and No.2 undergo fracture and large-area delamination at low loads, whereas Samples No.3 and No.4 show no delamination throughout the scratch test, demonstrating excellent film-substrate adhesion.

This difference arises because collisionally sputtered particles in the glow discharge region are primarily low-energy neutral atoms. During growth, low-diffusion-energy atoms are susceptible to shadowing effects, forming porous structures with high residual stress that lead to early fracture and delamination. Shadowing occurs when low-diffusion-energy particles are blocked by previously deposited clusters, preventing them from filling micro-voids. In the glow-arc transition region, highly ionized and high-energy particles can overcome shadowing effects to form dense structures with reduced residual stress, resulting in strong adhesion. Although critical load is thickness-dependent, the test samples were placed at 150 mm target-to-substrate distance where film thicknesses are similar. The critical load does not follow the same trend as thickness variation, indicating minimal thickness influence on adhesion in this study.

Conclusions

(1) Increasing target current density can shift gas discharge into the glow-arc transition region, which occurs at current densities above 0.2 A/cm^2 and is characterized by an inverse current-voltage relationship.

(2) In the glow-arc transition region, the hybrid collision-heating emission mechanism produces deposited particles with high density, high ionization, and high energy.

(3) Compared with the glow discharge region, films deposited in the glow-arc transition region ($i = 0.217$ and 0.250 A/cm^2) exhibit lower thickness reduction rates along the target-to-substrate direction, nanopolycrystalline structures with 18 nm grain size, dense columnar growth structures, and excellent film-substrate adhesion.

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