



Article Surface Conductivity and Preferred Orientation of TiN Film for Ti Bipolar Plate

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Abstract: The properties of thin films are often influenced by the crystal's preferred orientation. In the present study, we report the strong dependence of surface conductivity on the preferred orientation of TiN film that acts as the coating material for Ti bipolar plate. The preferred orientation of TiN film is successfully controlled along the (111) or (200) planes by adjusting the N₂ flow rate or Ti substrate temperature during the deposition process via DC (direct current) reactive magnetron sputtering. Small N₂ flow rate of 3 to 6 sccm or low substrate temperature (e.g., 25 °C) facilitates the growth of TiN films along the (111). The (111) preferred orientated TiN films show much lower interfacial contact resistance (ICR) than the (200) preferred orientated films. A considerably low ICR value of 1.9 m Ω ·cm² at 140 N/cm² is achieved at the N₂ flow of 4 sccm and the substrate temperature of 25 °C.

Keywords: bipolar plate; TiN film; preferred orientation; surface conductivity; local density of states

1. Introduction

Recently, the proton exchange membrane fuel cell (PEMFC) has been widely considered as one of the most promising power sources for vehicles, stationary power generators and other portable applications due to its advantages of highly efficient energy conversion, low operating temperature, zero emission, and rapid start-up [1,2]. Bipolar plate (BPP) is one of the crucial components accounting largely for the total weight and cost of the PEMFC stack and playing a key role in collecting current, separating reaction gas, connecting monomer modules, and removing residual water [3,4]. Graphite has been developed as the first-generation bipolar plate owing to the excellent electrical conductivity and corrosion resistance. Nevertheless, the high brittleness of graphite leads to poor machining properties and high cost [5,6]. Metallic bipolar plates are attracting wide attention because of their superior mechanical properties and manufacturability, which is conducive to their cost-effective mass production [7-10]. Among these metal materials, Ti, with a low density of 4.50 g/cm³, superior mechanical properties, and high electric conductivity of 2.34×10^{6} S/m, can greatly improve the power density of PEMFC stack [11]. However, in the harsh acidic working environment of PEMFC, the passive oxide film formed on the Ti surface will increase the interfacial contact resistance (ICR) value between BPP and gas diffusion layer (GDL), which seriously deteriorates the cell performance [12–14]. Therefore, it is highly necessary to improve the Ti corrosion resistance using coating materials with high electronic conductivity.



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The protective coating materials mainly include noble metals such as Au [15], metal nitrides, including TiN [11,16] and TiZrN [17], carbon-based materials such as TiC [18], NbC [13], ZrCN [19], and some composites such as carbon/PTFE/TiN composites [20], Ni-P/TiN/PTFE composites [21], N/Ta-co-doped TiO₂ [22], etc. Among them, TiN is a widely used coating material owing to its low cost, high hardness, and good corrosion resistance. The excellent electrical conductivity of 4.55×10^6 S/m and slight difference of 0.63% in thermal expansion coefficient with Ti substrate could be the advantages needed for TiN to be utilized as the coating material for metallic Ti BPP.

The properties of TiN thin films are largely dependent on the crystal orientation. Considerable efforts have been devoted to improving the hardness [23–25], infrared emissivity [26], anti-impact performance [27], and optical transmission [28] of TiN films through the adjustment of crystal orientation. However, controversial results have been reported on the impact of crystal orientation on the resistivity of TiN. The resistivity of TiN film was reported to decrease as the preferred orientation changes from (111) to (200) in some research [29,30], while the (111) preferred orientated TiN films were found to exhibit lower resistivity in other studies [26,31]. Therefore, it is of great significance to unveil the impact of preferred orientation on the surface conductivity of TiN films, especially in the scenario of acting as the coating material for Ti BPPs.

In the present study, the TiN films were deposited on Ti substrates via DC reactive magnetron sputtering. The ICR values of TiN films show strong dependence on the preferred orientation, which can be tuned by adjusting the N₂ flow rate and substrate temperature. By controlling the growth of TiN film along the (111) plane, a low ICR of 1.9 m Ω ·cm² at 140 N/cm² is successfully achieved. The origination of surface conductivity dependence on preferred orientation are investigated by Density Functional Theory (DFT)calculation, and the influence of surface roughness and N and O concentrations on surface conductivity is also discussed.

2. Materials and Methods

2.1. Deposition of TiN Films

The TiN films were deposited on Ti substrates by DC reactive magnetron sputtering method (CJC450) using a Ti target in the mixture of Ar and N₂. To remove impurities and oil from the surface, the Ti substrates prior to deposition were ultrasonically cleaned in deionized water, acetone, and ethanol for 30 min, respectively. The Ti substrates were fixed on the substrate holder with a distance of 5 cm from the target. Before deposition, the chamber was evacuated to below 0.0008 Pa. Subsequently, the surfaces of Ti substrates were bombarded by Ar⁺ ion for 10 min with high voltage of 2500 V and Ar pressure of 2 Pa. TiN was deposited by sputtering reaction between Ti target and N₂ for 20 min with DC power of 300 W, working pressure of 0.62 Pa, a substrate bias voltage of 70 V and a constant Ar flow rate at 90 sccm. Two parameters were investigated including N₂ flow rate varying from 3 to 12 sccm and substrate temperature from 25 to 150 °C.

2.2. Characterization of TiN Films

The phase structures of the films were analyzed by X-ray diffraction (XRD) using Oxford Xcalibur E diffractometer (Liaoning, China) with Cu K α radiation source (λ = 1.5418 Å). The surface and cross-section morphologies were observed by Hitachi (REGULUS8230, Tokyo, Japan) scanning electron microscope (SEM). The surface roughness (R_a) was measured by Surface Roughmeter with a scanning length of 4 mm (Dongyang Instruments, TR210, Beijing, China). The Ti/N ratio of the surface were determined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha+, Waltham, MA, USA).

2.3. Measurement of Interfacial Contact Resistance

The ICR values were measured in a sandwich structure using DC Low Resistance Tester (Changzhou Tonghui Electronics Co., Ltd., TH2512, Changzhou, China) under different compaction forces of 20 to 160 N/cm² according to the method reported in our previous study [16].

2.4. Electrochemical Measurement

The corrosion properties were evaluated by potentiodynamic polarization carried on an electrochemical workstation (DongHua Instruments Inc., DH7000, Jiangsu, China) in a 0.05 M $H_2SO_4 + 2$ ppm HF solution at 80 °C, where air was pumped to simulate the cathode working environment of PEMFC. A conventional three-electrode system was used in the test with a platinum sheet, a saturated Hg/Hg₂SO₄ electrode, the coated or uncoated sample as the counter electrode, reference electrode and working electrode, respectively. During the electrochemical measurement, all the samples were stabilized at an open circuit potential (OCP) for 60 min followed by potentiodynamic polarization tests at a scanning rate of 0.3 mV·s⁻¹.

2.5. Computational Method

The density functional theory (DFT) calculations were performed with Vienna Abinitio Simulation Package (VASP) 5.4 using PBE as exchange-correlation functional. The wave functions were expanded in plane waves with a kinetic energy cutoff of 400 eV, and the interaction between the ions and electrons was described by projector augmented wave (PAW) potentials. The periodically repeated simulation cells of TiN (200) included slabs of 6 substrate layers and 11 layers for TiN (111), with the vacuum between the slabs of 15 Å. The unit cell was (1 × 1) repetition. Monkhorst–Pack grid sampling of the Brillouin zone (BZ) was used with $7 \times 7 \times 1$ k-points for DOS calculation. Specifically, atomic positions were relaxed until forces on each atom were less than 0.5 meV/atom.

3. Results and Discussion

3.1. Characterization of TiN Films

Figure 1a shows the XRD patterns of TiN films prepared at different N₂ flow rates when the Ti substrate temperature was fixed at 25 °C. Besides the reflection peaks of Ti substrate (PDF#44-1294), the (111) and/or (200) crystal planes of FCC TiN (PDF#38-1420) can be observed in the series of coated samples. The TiN films show strong preferred orientation along the (111) plane when N₂ flow is ≤ 6 sccm and along (200) plane when N₂ flow is ≥ 8 sccm. Furthermore, the (200) reflection is fully suppressed at the low N₂ flow of 3 sccm and the (111) reflection disappears at the high N₂ flow of 10 and 12 sccm. Additionally, the peaks of the (111) and (200) shift to higher diffraction angles at higher N₂ flow rate, which could be explained by the formation of severely nitrogen-deficient film (Table S1) [27,32,33], as evidenced by XPS measurement (Figure S1). Note that, as the N₂ flow increases, the full width at half maximum (FWHM) of the (111) and (200) reflections become smaller (Table S2) suggesting the declining crystallinity, which may lead to high resistivity [34].

The composition of TiN films is estimated by XPS measurement (Table S1). With the increase of N₂ flow rate, the N concentration in TiN films grows slightly and reaches the maximum of 40.61 mol%, which decreases slightly to \leq 36.72 mol% as the N₂ flow rate further increases \geq 8 sccm. However, higher N₂ flows leading to the more frequent collisions could reduce the energy used for the dissociation of nitrogen molecules [29]. Thus, the N atom concentration near the substrate may decrease when high N₂ flow rises up to \geq 8 sccm, resulting in lower N content in the TiN film.



Figure 1. (a) XRD patterns of TiN films prepared at different N_2 flow rates and the substrate temperature of 25 °C, and (b) the texture coefficients of individual reflections of the (111) and (200) planes.

The degree of the preferred orientation is also determined using the texture coefficient (T_c) according to Equation (1) [35],

$$T_{\rm c}({\rm hkl}) = \frac{I_m({\rm hkl})/I_0({\rm hkl})}{\sum_1^n [I_m({\rm hkl})/I_0({\rm hkl})]}$$
(1)

where I_m (hkl) and I_0 (hkl) represent the measured relative intensity of the (hkl) plane and the same plane in a standard reference sample, and n is the total number of reflection peaks from the coated sample. The relationship between the T_c values of the (111) and (200) planes and the N₂ flow rate is exhibited in Figure 1b. The preferred orientation of the film growth changes from (111) to (200) plane with the increase of N₂ flow rate. Impressively, TiN film becomes fully (111) orientated at the N₂ flow of 3 sccm and converts to full (200) orientation at the N₂ flow of 10 and 12 sccm.

The TiN films are tightly bound to Ti substrates as shown in the inset of Figures 2a and S2. The thickness of TiN films lies between $0.80 \sim 1.23 \,\mu\text{m}$. Thus, the deposition rate is calculated based on the thickness and deposition time, which slows down as the N₂ flow rate rises (Figure 2a). The surface morphologies of TiN films also show strong dependence on the N₂ flow rates (Figure 2b). At the low N₂ flow rates of 3 to 6 sccm, the TiN films with the (111) plane preferred orientation are composed of regular and sharp polyhedral particles evenly distributing on the surface. At the moderate N₂ flow rate of 8 sccm, the polyhedron structure disappears when the preferred orientation of TiN film transfers from the (111) to the (200) plane. At the higher N₂ flow rates of 10 and 12 sccm, the surfaces of TiN films are fully covered by spheres when TiN films grow completely along the (200) plane.



Figure 2. (a) The deposition rates and (b) SEM images of TiN films prepared at different N_2 flow rates with the substrate temperature fixed at 25 °C.

The change of preferred orientation of TiN film could be attributed to the competition between surface energy and strain energy. For FCC TiN crystals, the (111) plane shows the lowest strain energy due to the anisotropy in Young's modulus, while the (200) plane shows the lowest surface energy [36,37]. At higher deposition rates, many nuclei in a state of high energy are condensed at the same time, leading to a relatively large internal stress in the film. Accordingly, TiN preferably grows along the direction of the (111) plane to relieve strain energy and minimize the overall energy of the films at low N₂ flow rates. On the contrary, the surface energy dominates the competition with strain energy at low deposition rates and hence, the (200) plane with the lowest surface energy becomes preferred at high N₂ flow rates.

The preferred orientation of TiN film is also influenced by substrate temperature. Figure 3 shows the XRD patterns of TiN films prepared at different substrate temperatures with the N₂ flow fixed at 4 sccm. The (111) plane is dominant at the substrate temperature of 25 °C, while the (200) plane becomes dominant as the substrate temperature rises up to 150 °C. Moreover, the surface morphology changes from sharp polyhedral particles for the film prepared at the substrate temperature of 25 °C to spheres for the film prepared at the substrate temperature of 25 °C to spheres for the film prepared at the substrate temperature of 25 °C to spheres for the film prepared at the substrate temperature of 25 °C. The surface of TiN films becomes more compact and smoother when the substrate temperature is increased up to 150 °C. The thickness of TiN film slightly decreases from 1.20 µm for the film prepared at the substrate temperature of 25 °C to 1.06 µm for the film prepared at the substrate temperature of 25 °C to 1.06 µm for the film prepared at the substrate temperature of 25 °C to 3.06 µm for the film prepared at the substrate temperature of 25 °C to 3.06 µm for the film prepared at the substrate temperature of 25 °C to 3.06 µm for the film prepared at the substrate temperature of 25 °C to 3.06 µm for the film prepared at the substrate temperature of 25 °C to 3.06 µm for the film prepared at the substrate temperature of 25 °C to 3.06 µm for the film prepared at the substrate temperature of 3.00 °C.



Figure 3. (a) XRD patterns of TiN films prepared at different substrate temperatures with N_2 flow fixed at 4 sccm, and (b) the texture coefficients of individual reflections of the (111) and (200) plane, and (c) SEM images of TiN films prepared at different substrate temperatures.

3.2. ICR Test

Figure 4a,b show the ICR values of TiN films at different compaction forces, and Figure 4c,d summarize the interfacial contact resistance (ICR) at 140 N/cm² as a function of the N₂ flow rate and substrate temperature. The ICR values decrease rapidly with the increase of the testing compaction pressure due to the increase of actual contact area. In Figure 4c, TiN films show small ICR values of $1.9 \sim 2.3 \text{ m}\Omega \cdot \text{cm}^2$ at N₂ flow $\leq 6 \text{ sccm}$, which jumps to $8.0 \sim 25.1 \text{ m}\Omega \cdot \text{cm}^2$ at the N₂ flow $\geq 8 \text{ sccm}$. In Figure 4d, the ICR value increases from 1.9 m $\Omega \cdot \text{cm}^2$ at the substrate temperature of 25 °C to 7.5 m $\Omega \cdot \text{cm}^2$ at the substrate temperature of 150 °C. The smallest ICR of 1.9 m $\Omega \cdot \text{cm}^2$ is achieved at the N₂ flow of 4 sccm and substrate temperature of 25 °C, which surpasses remarkably the DOE 2020 target of 10 m $\Omega \cdot \text{cm}^2$. Compared to the (111) preferred orientation, the (200) preferred orientation contributes significantly to the higher ICR values $\geq 8 \text{ m}\Omega \cdot \text{cm}^2$. The distinctly different ICR values between TiN films regarding different N₂ flow rates and substrate temperatures can be majorly attributed to the different preferred orientation, as illustrated in Figure 4c,d.



Figure 4. ICR values of TiN films prepared at different (**a**) N_2 flow rates and (**b**) substrate temperatures at different compaction forces, and ICR values at 140 N/cm² as the function of (**c**) N_2 flow rate and (**d**) substrate temperature.

To further understand how different preferred orientation influences the surface electronic conductivity of TiN, the local density of states (LDOS) of the (111) and (200) surface facets using the optimized surface structures are calculated, as shown in Figure 5. Due to the continuous energy band, both the (111) and (200) surface facets are favorable for electron conduction (Figure 5a,b), in which the main contribution of conduction band comes from Ti atoms rather than N atoms (Figure 5c,d). However, for the unoccupied states above the Fermi level (0 eV), the (111) surface facet shows a much stronger peak area than the (200) surface facet (Figure 5a,b), indicating the presence of more free electrons in the (111) plane. Consequently, higher surface conductivity and low ICR values are achieved in TiN films with the (111) preferred orientation.

The influence of surface roughness (R_a) on surface conductivity was also investigated. As shown in Figure 6a, small R_a values of 0.19~0.23 µm are observed at the low N_2 flow rate of 3 to 6 sccm, while TiN films show also small ICR values of 1.9~2.3 m Ω ·cm². At the high N_2 flow rate of 8 to 12 sccm, the R_a value rises up from 0.32 to 0.41 µm, while TiN films show also high ICR values of 8.0~25.1 m Ω ·cm². On the other hand, the R_a value decreases from 0.19 to 0.15 µm when the substrate temperature increases from 25 to 150 °C (Figure 6b), due to the formation of more compact and smoother surfaces at higher temperatures (Figure 3c). However, the smaller R_a values at the higher temperatures of 100 and 150 °C do not contribute to the smaller ICR values (Figure 4b), indicating that surface roughness is not the major factor determining surface conductivity.



Figure 5. LDOS of (**a**) TiN (111) surfaces and (**b**) N-terminated TiN (200) surfaces; inset showing top views of N-terminated TiN (111) and TiN (200) surfaces (the gray and blue spheres represent Ti and N atoms, respectively), and representative contribution of Ti and N atoms on (**c**) (111) and (**d**) (200) planes.



Figure 6. Surface roughness as the function of (a) N_2 flow rate and (b) substrate temperature.

In addition, the N and O concentrations in TiN would influence surface conductivity. As reported in [32,38], higher N and lower O concentrations contribute to higher electrical conductivity. For the TiN films prepared at 25 °C, it is also observed that at N₂ flow \leq 6 sccm, TiN films shows slightly higher N and lower O concentrations, and lower ICR values than the films prepared at N₂ flow \geq 8 sccm (Table S1). Compared to the other TiN films with the (111) preferred orientation (Figure 4c), the TiN film prepared at N₂ flow of 3 sccm shows the lower N concentration of 38.24 mol% and higher O concentration of 15.06 mol% (Table S1) and hence, a relatively higher ICR value of 2.3 mΩ·cm² is measured for this film, although it is fully (111) orientated (Figure 1).

3.3. Electrochemical Analysis

The corrosion resistance of TiN films is evaluated by potentiodynamic polarization measurements in the acid solution (0.05 M H₂SO₄ + 2 ppm HF) bubbling with air at 80 °C (shown in Figure 7). The corrosion current densities (I_{corr}) of all coated or uncoated samples are deduced from the above-mentioned polarization curves by Tafel extrapolation method [39]. The TiN film prepared at N₂ flow of 4 sccm and substrate temperature of 25 °C exhibits a low I_{corr} of 0.91 μ A/cm², which meets the DOE 2020 target of 1 μ A/cm² on corrosion resistance requirement for BPP. I_{corr} is further reduced to 0.63 μ A/cm² in the TiN film prepared at the substrate temperature of 150 °C, possibly owing to the improvement in surface compactness (shown in Figure 3c).



Figure 7. Potentiodynamic polarization curves of bare Ti and TiN films prepared at different substrate temperatures with N₂ flow fixed at 4 sccm.

4. Conclusions

In summary, we demonstrate the strong dependence of surface conductivity on preferred orientation of TiN film, which is successfully controlled along the (111) or (200) planes by adjusting the N₂ flow rate or Ti substrate temperature during the preparation process. The results indicate that the (111) preferred orientated TiN films show much lower ICR values than the (200) preferred orientated films. The TiN film prepared at the N₂ flow of 4 sccm and the substrate temperature of 25 °C exhibits a low ICR value of 1.9 m $\Omega \cdot \text{cm}^2$ at 140 N/cm² and a low I_{corr} of 0.91 μ A/cm² (0.05 M H₂SO₄ + 2 ppm HF solution at 80 °C), which surpass both of the DOE 2020 targets on surface conductivity and corrosion resistance for bipolar plates.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/coatings12040454/s1, Figure S1: (a) XPS survey spectra and (b) deconvoluted XPS spectra of Ti 2p of TiN films prepared at different N₂ flow rates with the substrate temperature fixed at 25 °C.; Figure S2: SEM cross-section images of TiN-Ti prepared at different N₂ flow rates with the substrate temperature fixed at 25 °C; Figure S3: SEM cross-section images of TiN films prepared at different substrate temperatures with N₂ flow fixed at 4 sccm. Table S1: The compositions and ICR values of TiN films, derived from the XPS survey spectra in Figure S1; Table S2: The full width at half maximum of (111) and (200) peaks derived from the XRD patterns of TiN films in Figure 1a.

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