

Influence of substrate bias on microstructure and morphology of ZrN thin films deposited by arc ion plating

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Abstract: Zirconium nitride thin films were fabricated using arc ion plating under negative substrate biases to investigate the influence of substrate bias on the ZrN films. The phase, composition, and surface morphology of the ZrN films, with respect to substrate bias, were studied by XRD, EPMA, and FE-SEM, respectively. The results show that cubic ZrN and hexagonal Zr phases form in the ZrN films. The competition between surface energy and strain energy makes the preferred orientation change from (111) to (200) and then back to highly (111) preferred orientation as a function of substrate bias. With the increase of bias voltage, the crystallite size of ZrN films reduces from 30 to 15 nm. Meanwhile, the film microstructure evolves from an apparent columnar structure to a highly dense equiaxed structure, indicating that the ion bombardment enhanced by substrate bias can suppress the columnar growth in the ZrN films. Deposition rate and mole ratio of Zr to N increase with the increase of bias voltage and reach the maximum at -50 V, and then show a decline trend when bias voltage further increases.

Key words: zirconium nitride (ZrN); thin film; arc ion plating; substrate bias; microstructure

1 Introduction

More recently, zirconium nitride (ZrN) films are gaining considerable attention due to their superior mechanical properties [1], golden color [2], various applications such as diffusion barriers in the microelectronic industry [3], and protection layer used in the fission reactors [4]. However, zirconium has a higher melting point, a lower vapor pressure, and higher susceptibility of the contamination by oxygen and carbon, thus, it is more difficult to deposit ZrN films than TiN or CrN films [5]. As a result, fewer studies have been performed on ZrN than those popular transition metal nitride films. Arc ion plating is one of the most widely-used physical vapor deposition techniques, and it exhibits the unique features such as high ionizing rate, high deposition rate, high adhesion force and film densification [6]. Additionally, arc ion plating is robust and can be utilized in a relatively high gas pressure [7].

So, it is feasible to fabricate ZrN films using arc ion plating.

One of the most critical parameters involved in the deposition process is substrate bias. The negative bias applied on the substrate influences the kinetic energy and momentum of the charged particles delivered to the growing film by accelerating the particles. Therefore, the corresponding preferred orientation, grain size, and point defects of the film may vary as well. JENG and CHEN [8] investigated the effect of substrate bias and nitrogen flow ratio on the sputtered ZrN_x films. In a study by FRAGIEL et al [9], ZrN films were fabricated using reactive magnetron sputtering, and the mechanical properties and tribological behavior of the ZrN films were investigated. Domestically, YANG et al [10] studied the composition and color of ZrN films by mid-frequency reactive magnetron sputtering. NIU and SUN [11] investigated the influence of N_2 partial pressure on the color of the rf-sputtered ZrN films. To date, few literatures focus on the ZrN films fabricated

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using arc ion plating method. Additionally, it is of significance to reveal the influence of substrate bias on the composition, deposition rate, microstructure and surface morphology of the arc ion plated ZrN films.

In this work, ZrN thin films were deposited on p-(100) silicon substrates by arc ion plating technique. A negative bias ranging from 0 to -100 V was applied on the substrate. The purpose of this work was to investigate the influence of substrate bias on the composition, deposition rate, microstructure and surface morphology of the as-deposited ZrN films.

2 Experimental

The ZrN films were fabricated on p-(100) Si wafer substrates using the arc ion plating technique. One Zr target with a purity of 99.99% was used in the arc ion plating system. A rotational substrate holder was located at the center of the vacuum chamber which was well water-cooled. The distance between the Zr target and substrate holder was 350 mm. P-(100) silicon wafers ($30\text{ mm} \times 60\text{ mm} \times 0.7\text{ mm}$) were selected as substrates. The substrates were ultrasonically cleaned in acetone, ethanol and de-ionized water sequentially for 15 min. Then, they were blown dry with N_2 and adhered vertically to the holder.

The chamber was evacuated to a base pressure less than 6.0×10^{-3} Pa using a rotate pump and a cryopump, and then heated to and kept at a desired temperature by electrical heating. Prior to the deposition, the substrates were sputter-cleaned by Ar ions for 10 min with a bias of -600 V in Ar atmosphere of 2.0 Pa. The deposition took place in an atmosphere of Ar (99.99% purity) and N_2 (99.99% purity) with a working pressure of 0.5 Pa. The inlet flux rate of Ar gas was fixed at $40\text{ cm}^3/\text{min}$. The flux rate of N_2 was $80\text{ cm}^3/\text{min}$. The total chamber pressure was controlled at 0.5 Pa by a throat valve. During the deposition, the rotational velocity of the substrate holder was fixed at 25 r/min. A DC bias varying from 0 to -100 V was applied to the substrates. The deposition parameters are summarized in Table 1.

The film thickness was measured by an α -step apparatus (Surface profiler, Tencor, USA). Deposition rate was calculated from film thickness and deposition time. The composition of ZrN films was determined by an electron probe micro-area analyzer (EPMA). Structural characterizations were performed with a high resolution X-ray diffractometer (Bruker D8 DISCOVER) operating with a $\text{Cu K}\alpha$ radiation. The grain size of ZrN thin film was calculated using the Scherrer's formula [12] on the basis of the ZrN (111) peak. Lattice constant was analyzed and calculated according to the Bragg's

Table 1 Deposition parameters for ZrN films by arc ion plating

Parameter	Value
Base pressure/Pa	6.0×10^{-3}
Working pressure/Pa	0.5
Ar flux rate/ $(\text{cm}^3 \cdot \text{min}^{-1})$	40
N_2 flux rate/ $(\text{cm}^3 \cdot \text{min}^{-1})$	80
Arc current/A	80
Deposition temperature/ $^{\circ}\text{C}$	300
Deposition time/min	75 (15 min Zr interlayer, 60 min ZrN)
Substrate bias/V	0, -25 , -50 , -100

law. The surface morphology was observed using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800).

3 Results and discussion

Figure 1 shows the composition and deposition rate of ZrN films obtained in this work. The results indicate that the mole ratio of Zr to N ($n(\text{Zr})/n(\text{N})$) and deposition rate follow the same trend as a function of substrate bias voltage. They both initially increase with the increase of substrate bias and then show a declining trend; at -50 V, $n(\text{Zr})/n(\text{N})$ and deposition rate reach the maximum value, 3.75 and $2.03\text{ }\mu\text{m}/\text{h}$, respectively. Such a change in the deposition rate is related to two simultaneous effects brought by the substrate bias. One is the accelerating-deposition effect resulting from the increase of the ion quantity and velocity; the other is the re-sputtering effect due to the ion bombardment [13]. At a low substrate bias voltage, the former is dominating; while at a high bias voltage, the latter is overwhelming.

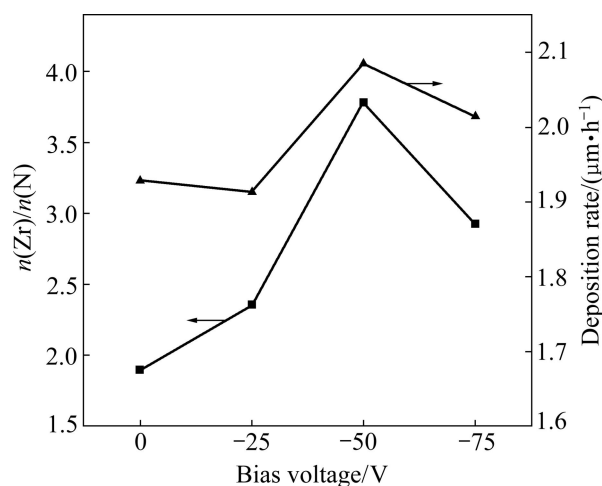


Fig. 1 Dependence of $n(\text{Zr})/n(\text{N})$ and deposition rate on substrate bias voltage

From Fig. 1, it is found that the value of $n(\text{Zr})/n(\text{N})$ is much larger than 1.0. Thus, it can be deduced that Zr ions substitute some N sites, or enter the interval space of some lattices. Zr ion, with a relative atomic mass of 92, is much heavier than N ion (atomic relative mass only 14), therefore, N ions are more feasible to be sputtered out and substituted by Zr ions, resulting in N-poor ZrN films.

Figure 2 shows XRD patterns of ZrN films deposited at different bias voltages. It can be seen that the films consist of hexagonal α -Zr and face-centered cubic ZrN phases. For the ZrN films deposited at 0 V, XRD pattern can be identified by face centered cubic ZrN phase using ICSD card #311493. Only a peak corresponding to (320) plane from α -Zr phase occurs at 32.1° . The peak at 34° corresponding to ZrN (111) plane has a dominant orientation. When the bias voltage increases to -25, -50 and -100 V, the (200), (220) and (222) peaks of ZrN phase weaken gradually and even disappear. Different from these peaks, the (111) peak of ZrN weakens initially; when the bias voltage increases to -50 and -100 V, the intensity of the peak changes to increase gradually even surpasses that of 0 V. In short, the preferred orientation at (111) plane is more and more apparent with the increase of substrate bias. In other words, substrate bias facilitates the growth of ZrN film with a preferred orientation at (111) plane. Additionally, the (111) peak of ZrN film broadens and shows a little shift to the lower values of 2θ angle. The reason for the peak shift towards the lower 2θ angle was the residual compressive stress in films resulting from energetic ion bombardment [14].

Figures 3(a) and (b) show the lattice constant and

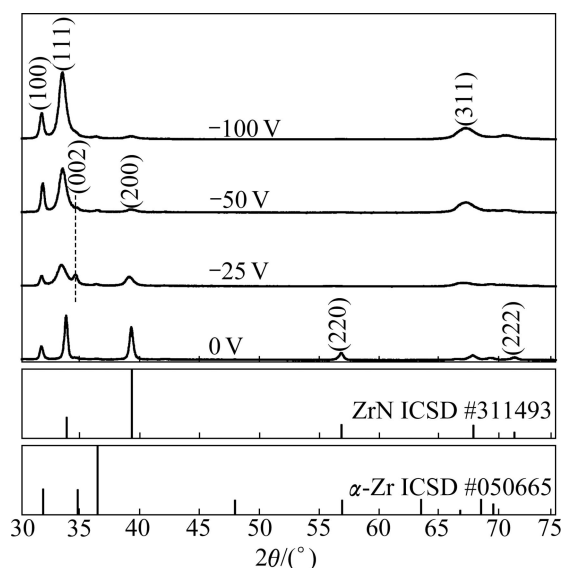


Fig. 2 XRD patterns of ZrN films deposited at different substrate bias voltages and standard patterns of ZrN and Zr phases

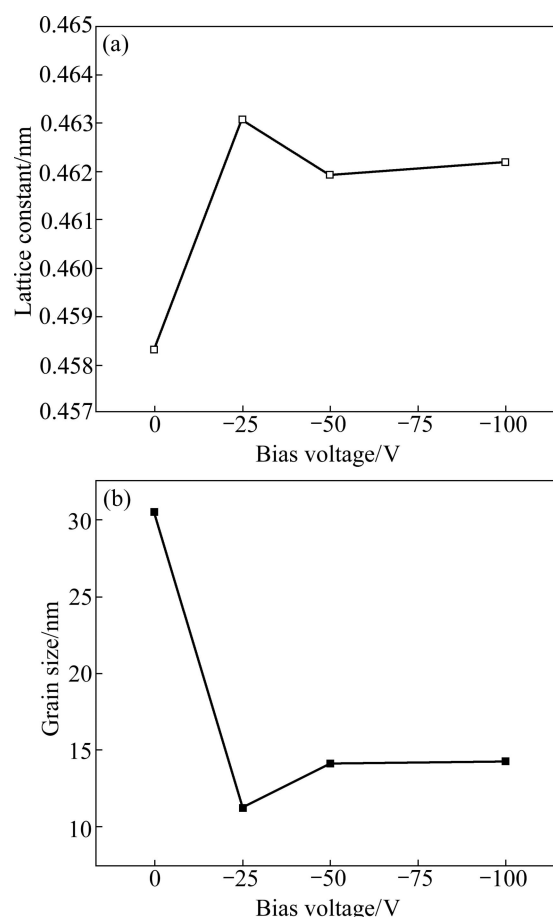


Fig. 3 Dependence of lattice constant (a) and grain size (b) on substrate bias voltage

grain size respectively, calculated from ZrN (111) peak using Bragg and Scherrer equations. It can be seen from Fig. 3(a) that applying substrate bias voltage causes a little enlargement of ZrN crystal lattice. It may be attributed to the occupancy of interstitial sites by some Zr ions. From Fig. 3(b), it can be seen that the grain size of ZrN films at 0 V is around 30 nm; while upon applying substrate bias voltages of -25, -50 and -100 V, the grain size reduces to less than 15 nm, indicating the grain refinement induced by applying a negative substrate bias voltage.

Figure 4 shows the surface and cross-sectional morphologies of ZrN films deposited at 0 and -50 V. It can be obviously observed that the grain size of the deposited ZrN films decreases with the increase of bias voltage, which is in good agreement with the aforementioned XRD results. In other words, applying a higher bias voltage can bring the grain refinement effect. From Figs. 4(b) and (d), it can also be figured out that the film microstructure evolves from an apparent columnar structure to a highly dense one with the increase of bias voltage. That is to say, increasing bias voltage can densify the deposited films. Similar results

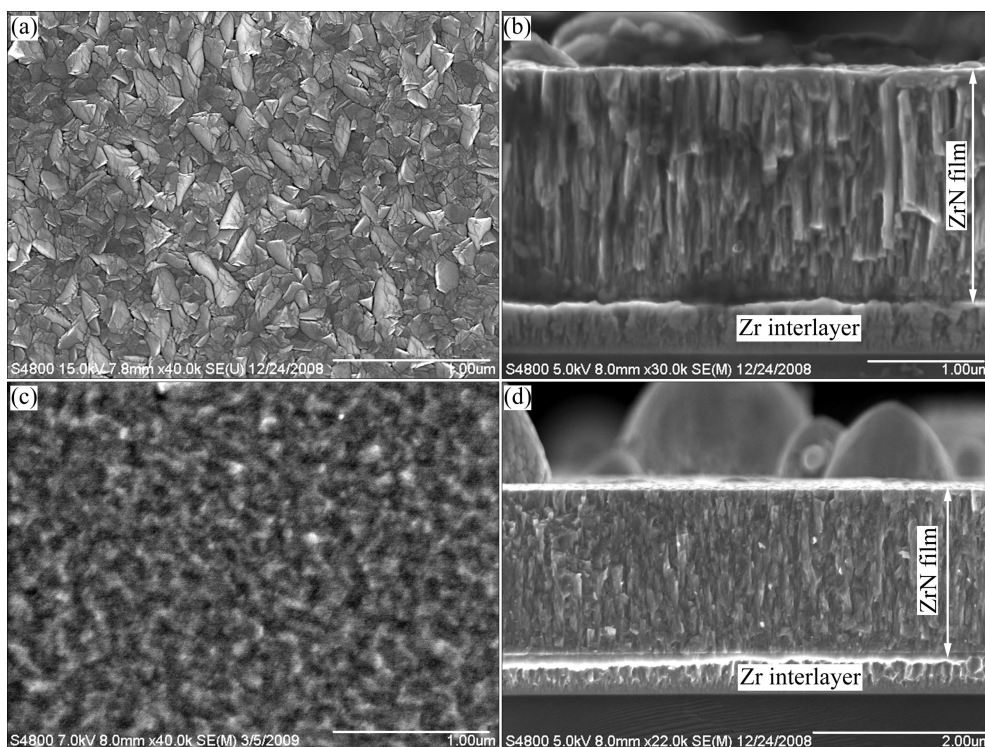


Fig. 4 Surface ((a), (c)) and cross-sectional morphologies ((b), (d)) of ZrN films deposited at different substrate bias voltages: (a), (b) 0 V; (c), (d) -50 V

were found by LI [15]. According to the numerous experimental results and simulation presented by authors in Refs. [5,7,16–20], the grain refinement effect and film densification caused by substrate bias are attributed to the ion bombardment governed by substrate bias.

4 Conclusions

1) The substrate bias voltage has a large influence on the film preferred orientation, composition, deposition rate and surface morphology.

2) The deposition rate and mole ratio of Zr to N increase with the increase of bias voltage and reach the maximum at -50 V, and then show a decline trend when bias voltage further increases.

3) Cubic ZrN and hexagonal Zr phases form in the obtained films. The substrate bias facilitates the growth of ZrN film with a preferred orientation at (111) plane.

4) With the increase of bias voltage, the crystallite size of ZrN films reduces from 30 to 15 nm, i.e., grain refinement. Meanwhile, the film microstructure evolves from an apparent columnar structure to a highly dense one.

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基片偏压对电弧离子镀 ZrN 薄膜微结构和表面形貌的影响

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摘 要: 在不同的基片偏压下利用电弧离子镀技术制备氮化锆薄膜, 以考察基片偏压对氮化锆薄膜微结构和表面形貌的影响。利用 XRD、EPMA 和 FE-SEM 等技术对不同偏压时得到 ZrN 薄膜的相结构、成分和表面形貌进行表征。结果表明, 薄膜中存在立方氮化锆和六方纯锆相; 随着基片偏压的增大, 薄膜的择优取向由(111)变为(200), 最后变为(111), 晶粒尺寸由 30 nm 减小至 15 nm。同时发现, 随着基片偏压的增大, 薄膜微结构由明显的柱状特征变为致密的等轴晶特征, 表明由偏压增强的离子轰击能有效抑制柱状晶生长; 薄膜沉积速率和锆氮摩尔比随着基片偏压的增大先增大后减小, 在-50 V 时达到最大。

关键词: 氮化锆; 薄膜; 电弧离子镀; 基片偏压; 微结构

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