

Effects of working pressure on structure and composition of TiAlN coating fabricated by co-sputtering deposition technique

Ảnh hưởng của áp suất làm việc tới cấu trúc và thành phần của màng cứng nitorit nhôm titan tạo bằng kỹ thuật đồng phún xạ

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Abstract

Keywords:

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Structure

TiN-based coatings have been used widely for protecting surface of various application fields due to their superior properties such as high hardness, low friction coefficient, and low wear rate. Indeed, adding aluminium (Al) into the TiN coatings would further increase their hardness and oxidation resistance. Generally, TiAlN coatings are synthesized using alloy targets of specific percentages of Titan (Ti) and Al. However, for control of Ti/Al ratio in the coating composition, there exists another technique, namely co-sputtering, which could be used. This technique involves using a Ti and an Al target mounted separately on two guns of the sputtering system for the deposition process. In our work, TiAlN thin coatings were fabricated on silicon (Si) wafers using a magnetron co-sputtering technique under different pressures. Chemical composition of the coatings was studied by the Energy Dispersive Spectroscopy (EDS), whereas morphology of the coating was observed by Field Emission Scanning Electron Microscope (FESEM). The experimental results showed that TiAlN coating was well formed on Si wafers and the deposition pressure strongly affected composition and morphology as well as the Ti/Al ratio of the coating.

Tóm tắt

Từ khóa:

Áp suất lắng đọng;
Cấu trúc; Đồng
phún xạ; Màng
cứng; TiAlN;

Lớp phủ gốc titan nitorit đang được sử dụng rộng rãi để bảo vệ bề mặt trong các lĩnh vực ứng dụng khác nhau bởi những ưu điểm như độ cứng cao, ma sát và mài mòn thấp. Việc bổ sung nhôm vào lớp phủ TiN giúp nâng cao hơn nữa độ cứng và khả năng chống oxy hóa. Thông thường, lớp phủ TiAlN được tổng hợp bằng cách sử dụng các bia hợp kim có tỷ lệ phần trăm titan và nhôm cố định. Tuy nhiên, để kiểm soát tỷ lệ Ti/Al trong thành phần lớp phủ, kỹ thuật đồng phún xạ được sử dụng. Kỹ thuật này sử dụng bia Ti và bia Al được gắn riêng trên hai súng của hệ thống phún xạ trong quá trình lắng đọng. Trong nội dung nghiên cứu này, lớp phủ mỏng TiAlN được chế tạo trên các tấm nền Si bằng cách sử dụng kỹ thuật đồng phún xạ từ trường với các điều kiện áp suất khác nhau. Thành phần hóa học của lớp phủ được nghiên cứu bằng EDS, hình thái học của lớp phủ được phân tích bởi FESEM. Kết quả thí nghiệm cho thấy lớp phủ TiAlN được tạo thành trên lớp nền Si và áp suất lắng đọng ảnh hưởng đến thành phần, hình thái cũng như tỷ lệ Ti/Al của lớp phủ.

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1. INTRODUCTION

In recent decades, TiN-based hard coatings have been attracting attention as a new coating material for mechanical products. These thin films have many advantages such as high hardness, high thermal resistance, good conductivity resistant, low friction coefficient, and low wear rate [1]. Therefore, TiN-based coatings have been applied in many applications such as microelectronics [2], medical fields [3], and semiconductors [4]. Al was added into the TiN coatings for increasing their hardness and oxidation resistance. Developed in the late 1980's, TiAlN coatings were as an alternative solution to TiN coatings for cutting and forming tools [5], [6]. A super hard nanocomposite TiAlN material not only exhibits superior oxidation resistance to that of TiN (800 and 550VC, respectively) [7] and better cutting behavior but also enables the use of higher cutting speeds [8]. TiAlN demonstrated good stable friction and wear mode, which was attributed to a stable aluminium oxide layer formed at the working surface [9]. TiAlN film is normally created by one of the 3 sputtering methods below.

1. Using one alloy target of Ti and Al with the fix composition [1], [10]. The advantage of the first method is the similarity between the chemical composition of the coating and of the target. However, it required one target for each composition element.

2. Using one target of Ti and apply thin sheets of Al on the top of it [11]. While this method makes it easy to experiment new chemical compositions, it leads to a difference between the relative percentage of elements in the coating and those from the composition of the exposed area on the target, and one between sputtering speeds of each element.

3. Using separate targets: Ti target and Al target or namely co-sputtering technique [12], [13]. This method shares the same advantage with the second method, while its disadvantage lies in the sensitivity control of the deposition conditions.

In our present work, we studied on fabricating the TiAlN coatings using the third method and the effects of deposition pressure on the structure, composition and Ti/Al ratio obtained through co-sputtering on Si substrates.

2. EXPERIMENTAL PROCEDURE

The experimental investigation was carried out by using co-sputtering technique. Ti target (99.999% pure) and Al target (99.999% pure) with 2.5 inch in diameter and 0.25 inch in thickness were used to deposit TiAlN coating on p-Si wafer samples (99.999% pure). The samples were ultrasonically cleaned in target organ liquid then in distilled water for 15 minutes. A physical vapor deposition (PVD) sputtering system - UNIVEX 400 was used to make the deposits. A turbo-molecular pump was used to achieve a base pressure lower than 5.0×10^{-6} mBar before introducing the gas mixtures [14]. Prior to deposition, the insert was etched by Ar (argon) ion bombardment with flow rate of 10sccm for 10 minutes to clean the targets. Co-sputtering processing used DC gun for Ti target and pDC gun for Al target. Coatings were developing with substrates temperature at 250°C [14]. the power of guns for Ti, Al targets were 150W and 100W, respectively, because the sputter yield of Al is lower than that of Ti. the flow rate of N₂ and Ar were 10sccm (N₂/Ar ratio equals 1 [11], [14]). In order to study the effects of deposition pressure on composition and micro-structure of the TiAlN, the pressure was set at 3.5×10^{-3} , 4.5×10^{-3} , and 5.5×10^{-3} mBar, which correspond to S1, S2, and S3, respectively. The experimental details are showed in Table 1.

Table 1. Co-sputtering parameters used for the TiAlN coatings on Si substrates

Sample	Gun's power for Ti target (W)	Gun's power for Al target (W)	Flow rate of Ar (sccm)	Flow rate of N ₂ (sccm)	Target - Sample distance (mm)	Substrate temperature (°C)	Deposition pressure (mBar)	Growth time (minute)
S1	150	100	10	10	100	250	3.5×10^{-3}	90
S2	150	100	10	10	100	250	4.5×10^{-3}	90
S3	150	100	10	10	100	250	5.5×10^{-3}	90

The chemical composition was obtained by Oxford Instruments 50 mm² X-Max equipment (EDS). The thickness and morphology were analyzed by JEOL JSM-7600 equipment (FESEM).

3. RESULTS AND DISCUSSION

The EDS results and thickness of the coated samples are summarized in Table 2. At first, Ti, Al, and N are mainly found in the coating composition, indicating that TiAlN was well formed on the Si substrates. In addition, it is seen that the N component always accounts for more than 55% of the alloy. Secondly, the thickness of TiAlN is positively correlated with the deposition pressure, as it is increased from S1 to S3. When the deposition pressure is raised, the ion density in the plasma increases, which in turn increases the ion current, followed by an increase in the amount of material sputtered from the target. This explains why both the deposition rates of Ti and Al is proportional to the pressure [15]. Figure 1 shows thickness of the fabricated TiAlN coatings as the function of deposition pressure. The result responds to the previous publications with the same field [15], [16].

Thirdly, it is clearly observed that Ti/Al ratio is inversely proportional to deposition pressure, as showed in Fig.1.

Table 2. Characteristics of samples of different pressures

Sample	Deposition pressure (mBar)	Thickness (nm)	Ti (at. %)	Al (at. %)	N (at. %)	Ti/Al (at. ratio)
S1	3.5×10^{-3}	379	16.78	14.02	69.20	1.20
S2	4.5×10^{-3}	486	21.52	22.57	55.91	0.95
S3	5.5×10^{-3}	518	13.79	17.48	68.74	0.79

Furthermore, it could be seen that, the ratio of Ti/Al of S2 being close to 1 met the requirements for depositing Ti₅₀Al₅₀N which was used as commercial standard for industrial coating [6]. In brief, when pressure increases, the Ti/Al ratio tends to decrease.

Fig. 2 shows the SEM images of (a) S1, (b) S2, and (c) S3, respectively. On the whole, all of the images indicated that grains are dense, relatively uniform in size and color in each deposition condition which evidences well-established processing. From the figure, it can be seen that grain sizes tend to increase with deposition pressure. The grains of S1 (Fig. 2a) are smallest compared to those of S2 (Fig. 2b) and S3 (Fig. 2c). Further, S1 shows complex-shapes and unclear boundaries among grains. Whereas the grain boundaries on S2 and S3 surfaces can be observed clearly with the sizes on the order of about 25nm. In fact, that the resultant grain sizes are smaller than 30 nm is consistent with published studies [11], [17], [18].

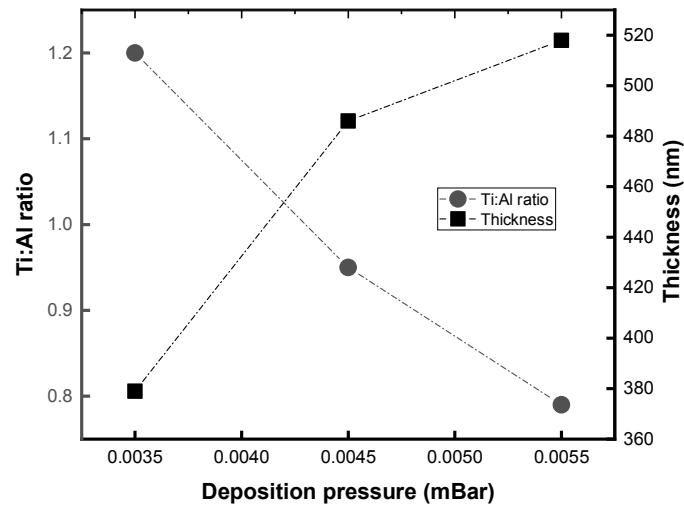


Fig. 1. The Ti/Al ratio and thickness of the coating as the function of deposition pressure

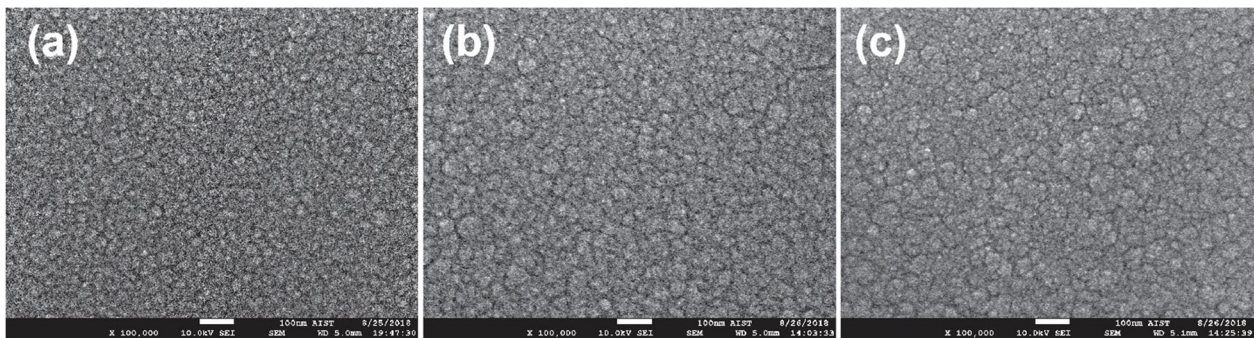


Fig. 2. Electron scanning microscopy images of the surface of the samples, with a magnification of 100,000 times for (a) S1, (b) S2, and (c) S3

Fig. 3 shows the cross-sectional SEM graph of TiAlN coated on Si. It is observed that the TiAlN coatings have the columnar structure along with the thickness of the TiAlN is increased from S1 to S3. The coating is particularly dense, uniform, homogeneous and compact. However, in the case of S1, grain boundaries seemed to be weak and easy to break and the structure is close to the grains (Fig. 3a), whereas in the cases of S2 and S3, the columnar structure is clearly observed (Fig. 3b and Fig. 3c). It is reasonable in comparison with the SEM pictures showed in above.

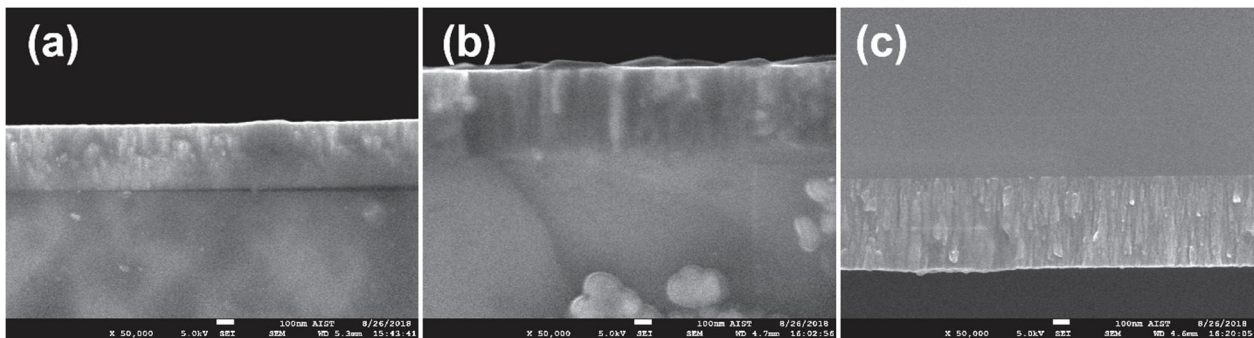


Fig. 3. Electron scanning microscopy images of the cross sections of the samples, with a magnification of 50,000 times for (a) S1, (b) S2, and (c) S3

4. CONCLUSIONS

In this work, TiAlN coatings were fabricated on Si substrates using magnetron co-sputtering technique at different deposition pressures. From experimental results, the following conclusions are drawn:

- TiAlN coating was well formed on Si wafer by the magnetron co-sputtering technique in which Ti and Al targets were used separately;
- The deposition pressure strongly influenced the thickness and the Ti/Al ratio of the coating. While the thickness was decreased with an increase of the pressure, the Ti/Al ratio showed the inverse trend;
- Grain size of the TiAlN tended to be positively correlated with the deposition pressure. When the deposition pressure was raised from 3.5×10^{-3} to 5.5×10^{-3} mbar, the grain size was increased, and the columnar structure was clearly observed for coatings deposited with higher pressures.

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