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Composition and texture of TiN thin films fabricated by ECR enhanced sputtering deposition

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Abstract

TiN thin films were fabricated on Si (100) substrates using Electron Cyclotron Resonance (ECR) microwave plasma technique. The composition, texture and microstructure of the as-deposited films had been investigated by use of X-ray Photoelectron Spectroscopy, X-ray Diffraction and Scanning Electron Microscopy. TiN compound with atomic ratio N/Ti near 1.2 and (111) preferential orientation was the basic phase, and impurities such as TiO_2, Ti_2O_3 and TiC existed in the films. The cross-sectional morphology of the films was columnar. The effects of the bombardment and the pre-treatment for the substrate surface by energetic ions on the properties of the films were also analyzed.
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1. Introduction

TiN thin films have wide applications, where they are used as hard or wear resistant coatings on the cutting tools or machining devices [1–3], diffusion barriers to prevent the interaction between metals and Si in micro-electronic devices for its chemical stability and low electrical resistivity [5–10]. In addition, they are also used to save energy for the preferential reflection for infrared rays [8] and act as decorative coatings due to the golden color. The main methods for fabricating TiN films are chemical vapor deposition (CVD) [1,9–13] and physical vapor deposition (PVD) [1–8,14,15] processes. Among these processes, Electron Cyclotron Resonance (ECR) microwave plasma enhanced sputter deposition is a novel and very useful technique for fabricating good quality TiN films due to its advantageous characteristics such as high-density plasma, high ion flux near the substrates and highly reactive species [6,7,9,10]. However, in many cases, there are always oxides and other impurities presented in TiN films [2,5,6,9,10,14] prepared by these methods. Usually, the composition, content and structure of these impurities influence strongly the properties of TiN films.

In the present work, TiN thin films had been deposited on Si (100) wafers using ECR microwave plasma source at ambient temperature in different processing approaches, and X-ray Photoelectron Spectroscopy (XPS), X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were performed to investigate the composition, texture and microstructure of the TiN films.

2. Experimental details

The TiN films were fabricated by using a direct current sputtering type implantation and deposition apparatus with ECR microwave plasma source in different approaches, for direct deposition (marked with A), deposition enhanced by pulsed plasma with energy of 3 keV upon the substrates (marked with B) and deposition under the same conditions as for A after the substrates were pretreated with 3 keV nitrogen and argon ions (marked with C). The power of the microwave source was 360 W and the DC voltage on the pure titanium target was set to −380 V with current of 2.1–

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Table 1
The analysis results of the high-resolution XPS spectra of Ti2p, N1s, O1s and C1s for the TiN films

		Ti			N	O		C
		TiN(TiC)	Ti_2O_3	TiO_2	TiN	TiO_2	Ti_2O_3	TiC
A	BE (eV)	455.4	457.3	458.6	397.1	530.5	532.0	281.9
	Percentage (at.%)	31.0	7.1	5.0	31.0	10.0	10.7	5.1
	X:Ti (X=N, O)	1.20	1.51	2.02				
B	BE (eV)	455.5	457.6	458.9	397.0	529.6	531.0	281.8
	Percentage (at.%)	32.7	7.2	4.3	33.0	8.1	10.1	4.6
	X:Ti (X=N, O)	1.17	1.41	1.88				
C	BE (eV)	455.5	457.7	458.6	397.0	529.9	530.9	282.0
	Percentage (at.%)	35.2	4.7	3.5	38.6	7.1	7.4	3.4
	X:Ti (X=N, O)	1.21	1.57	2.00				

2.5 A. Commercial Si (100) wafers cleaned with an ultrasonic bath in ethanol for 30 min were used as substrates. Prior deposition the substrates were sputter-cleaned by argon ions for 40 min with negative DC substrate bias of 300 V. During depositing, the negative DC substrates bias was set to 60 V and the mixed gas pressure was kept constant at $(6.8–8.0)\times 10^{-2}$ Pa. In the process of B the repetition frequency and width of the pulses were set to 300 Hz and 5 μs, respectively.

The chemical composition and chemical state of the elements in the films were determined by XPS using AlK_α radiation ($h\nu=1486.6$ eV). In order to remove the adsorbates on the surface of the films each sample was sputtered with Ar^+ (3 keV, 20 μA/cm^2) for 2 min before the measurement. The pass energy was set to 50 eV. The data of the high-resolution spectra were averaged by the results of five scans in which the step was of 0.1 eV and calibrated with the binding energy (BE) of C1s (284.8 eV). XPSpeak4.1 software was used to extract more information of chemical state and component. Background correction was carried out using Shirley and linearity method and the fitting function was defined as 20% Lorentzian and 80% Gaussian. The microstructure was examined by XRD using CuK_α radiation ($\lambda=0.15406$ nm). The cross-sectional morphologies of the films were observed with SEM.

3. Results and discussions

3.1. XPS analysis

XPS survey spectra of the TiN films (not be shown here) indicated that there were not only Ti and N but also O and C. Usually, it is considered that the existence of O and C in the measurement is the peculiar characteristic of XPS analysis [7], which is caused by the ambient atmosphere in the analysis chamber. But it is uncertain to attribute them to adsorption entirely. This will be explained in the following. Fig. 1 shows the high-resolution XPS spectra of Ti2p, N1s, O1s and C1s for the TiN film fabricated with method B and the results of curve fitting. The similar fitting results for sample A and C were also obtained. The results of XPS quantitative analyses with relative sensitivity factor method are given in the Table 1.

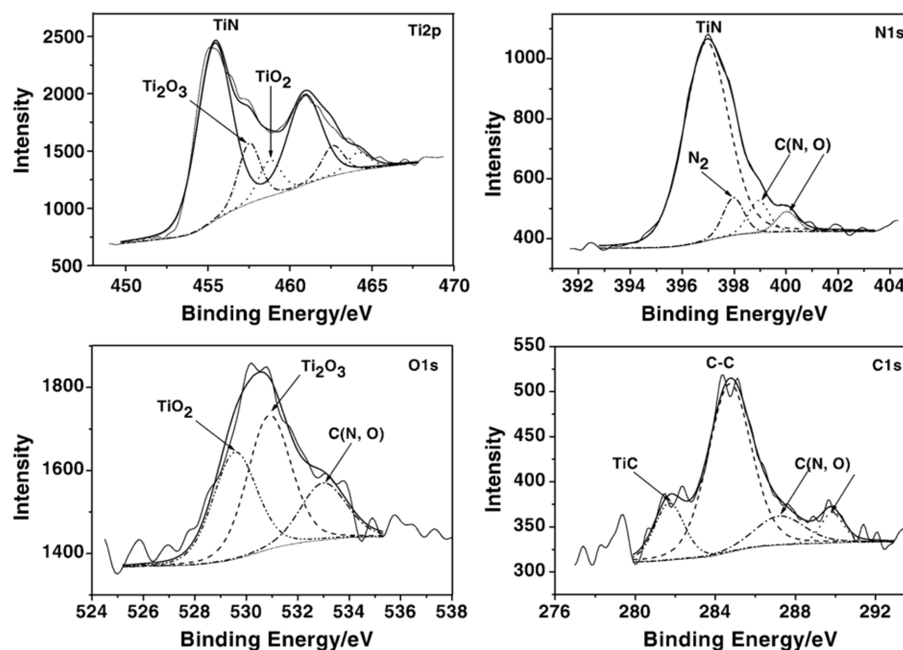

Fig. 1. The fitting analysis for the high-resolution XPS spectra of the TiN film fabricated with method B.

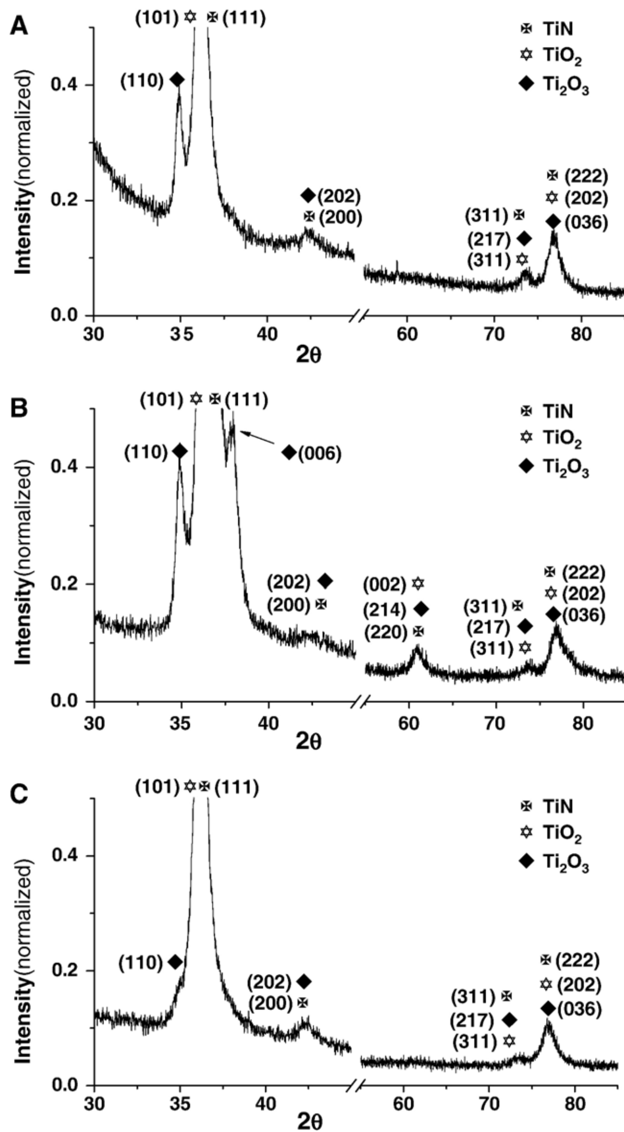

Fig. 2. X-ray diffraction patterns of the TiN films fabricated with methods A, B and C.

Deducting C, N and O belonged to the residual matter in the analyses chamber, the real atomic ratios of Ti:N:O:C are 1.00:0.72:0.48:0.12, 1.00:0.75:0.41:0.11 and 1.00:0.89:0.33:0.08, respectively. According to the XPS data [16] and the literatures [2–4,7,8], the sub-peaks of Ti2$p_{3/2}$ and N1s located from 455.4 eV to 455.5 eV and from 397.0 eV to 397.1 eV, respectively, correspond to titanium nitride, with which the atomic ratio of N:Ti was in the range of 1.17–1.21. And the sub-peaks of Ti2$p_{3/2}$ located in the range of 458.6 eV to 458.9 and of 457.3 eV to 457.7 eV belong to titanium oxides. This is supported by the sub-peaks of O1s with the binding energy (BE) of 529.6 eV to 530.5 eV and of 530.9 eV to 532.0 eV. The corresponding atomic ratios of O:Ti are in the range from 1.41 to 1.57 and from 1.88 to 2.02. So we think that these oxides should be Ti_2O_3 and TiO_2, respectively. The presence of TiC cannot be obtained from the spectra of Ti2p because the BE of Ti2$p_{3/2}$ in TiC compound is very close to that in TiN. However, it can be confirmed by the sub-peaks of C1s with BE in the range of 281.8 eV to 282.0 eV, which belongs to C1s in TiC. The other sub-peaks of N1s, O1s, and C1s correspond to residual matter such as nitrogen, graphite and organic compounds in the testing chamber, which earmarked with N_2, C–C and C(N,O), respectively.

Among these, the atomic ratio of O:Ti and N:Ti of sample B are both lower than that of sample A or C in the measurements. According to Pauling's electronegativity criterion, oxygen is more active than nitrogen and a small amount of O can play a significant role for oxide formation. So, the oxides had been formed during deposition. With the energetic ions (3 keV) bombardment the ionization of nitrogen was facilitated thus the combination of Ti with N was enhanced, and at the same time the combination of Ti and O was lowered relatively. Therefore, closer stoichiometric TiN and oxygen deficient titanium oxides were formed. During the deposition, C decomposed from organic compounds in the

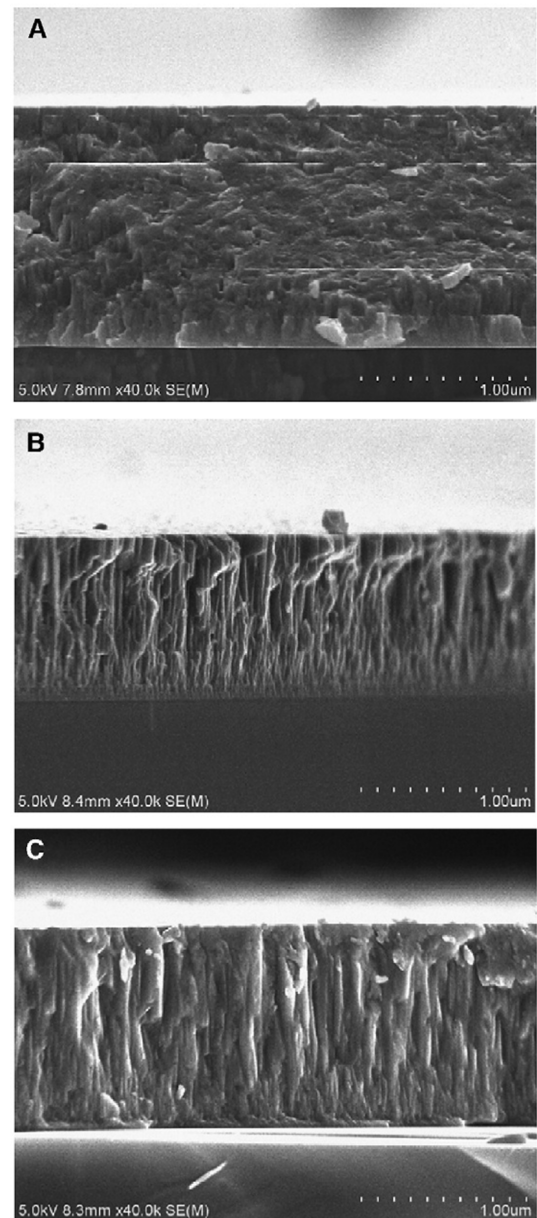

Fig. 3. SEM micrographs of cross-section of the TiN films fabricated with methods A, B and C.

deposition chamber was combined with Ti, so that a small amount of TiC was formed. In addition, the total contents of carbon and oxygen in sample C are lower than that in the others. This due to the pre-treatment with energetic ions of nitrogen and argon for the substrates that efficiently reduced carbon and oxygen, in which the latter came partially from the autoxidation layer of the surface of the silicon substrates.

3.2. Analysis of XRD and SEM

Typical X-ray diffraction patterns of these films shown in Fig. 2 indicated that the films were polycrystalline. The phases in the films were mainly consisted of TiN, TiO_2 and Ti_2O_3, which is agreement with the results of XPS analysis. Strong diffraction patterns of TiN (111), TiO_2 (101) and other weak peaks such as Ti_2O_3 (110), TiN (220), TiO_2 (202), and so on, were observed.

It is obvious that the TiN films prepared with method B had wider TiN (111) diffraction peak. And the diffraction peaks of Ti_2O_3 (006) that was somewhat stronger than Ti_2O_3 (110) peak relatively, TiN (220), TiO_2 (002) and Ti_2O_3 (214) appeared only in the pattern of sample B. The stronger Ti_2O_3 (110) diffraction peak of sample A and sample B became very weak in the pattern of sample C. This maybe caused by the bombardment of energy ions of Ar and N before deposition. The surface layer of silicon dioxide formed on the Si substrates naturally, which may provide oxygen atoms that can combine with Ti, was removed effectively due to the sputtering. In addition, the surface chemical state was changed due to ion bombardment, which also influenced the growth of the films.

The cross-sectional morphologies of the TiN films are shown in Fig. 3. It can be seen that the cross-section of the films are columnar in structure, which are often observed in the films prepared with ion beam technology. The thickness of the film deposited with method B is somewhat thinner than the others that were of about 1 μm due to the re-sputtering caused by energetic ions during the deposition.

4. Conclusions

Polycrystalline TiN films with atomic ratio of N:Ti approximately equal 1.2 and (111) dominant orientation had been deposited on Si(100) substrates. TiN compound was the basic composition besides some phases formed due to impurities, such as TiC, TiO_2 with dominated orientation of (101) and Ti_2O_3 with dominated orientation of (110) or (110) and (006) presented in the films. The cross-section was columnar in structure. The composition content and microstructure varied for the different fabrication methods. The bombardment of energetic ions enhanced the combination of Ti with N because the facilitation effect of the ionization of nitrogen, synchronously lowered the reaction between O and Ti. In addition, it caused the growth of Ti_2O_3 (006) orientation. The pre-treatment of the substrates with energetic ions further reduced the content of oxygen and carbon in the films and changed the chemical state of the substrate surface, therefore, affected the growth of the films.

Acknowledgments

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