

Preferred orientation of TiN thin films produced by Ion Beam Assist Deposition

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ABSTRACT

The crystal structure properties of TiN thin films deposited on SKD61 steel and Si(100) substrates by Ion Beam Assisted Deposition have been studied to clarify the thin film growth mechanism by using XRD, XPS, RBS, SEM, and AFM. The preferred orientation of TiN thin films changes from (111) to (100) as increasing the assisted energy. This tendency is independent of the substrate structure. The TiN thin film grow with (100) direction having surface free energy minimum as the assisted energy increases.

1. INTRODUCTION

The ion beam assisted deposition (IBAD) has been widely applied to thin film formations as a very useful technique since it has been proved to have advantages such as the thin film formation at low temperature, strong adhesion between the thin film and the substrate, and the easy control of the composition.⁽¹⁻⁸⁾ Especially, the TiN thin films prepared by IBAD have been confirmed to possess distinctive properties,⁽⁷⁻¹⁴⁾ such as high hardness and reproducibility, very good resistance to wear and corrosion, chemical stability, and an attractive golden color. The TiN thin film is one of the materials of which the preferred orientation has been extensively studied to clarify the reason why the thin films grow with preferred orientation. Bradley et al.⁽¹⁵⁾ proposed a model based on the sputtering effects to explain the preferentially oriented crystal growth on low energy IBAD. Kiuchi⁽¹⁶⁾ et al. proposed a channelling model of a variation of preferentially oriented TiN crystal growth in the dynamic mixing process. Recently, Pelleg et al.⁽¹⁷⁾ proposed a model which took account of the correlation between the surface energy and the strain energy of the film to explain the mechanism resulting in a preferred orientation. The basic mechanism of the crystal growth under IBAD, however, has not yet been well understood. Therefore, we studied crystal structure of TiN thin films to find out the correlation between the preferred orientation and the assisted ion energy with the aim of clarifying the mechanism of the film growth by IBAD.

For the present work, an Ultra-High Vacuum (UHV) IBAD apparatus has been set up. The TiN thin films have been investigated by using XRD, XPS, RBS, SEM, and AFM. The results show that the preferred orientation has been changed from (111) to (100) as the assisted ion energy increases, which may be closely related to the grain growth of TiN thin film.

2. EXPERIMENT

The TiN thin films were deposited on SKD61 steel and Si(001) at room temperature. The Si(100)

substrates were cleaned by ultrasonic cleaning and chemical etching in a dilute HF solution to remove the oxide layers before loading into the growing chamber. The deposition chamber was evacuated up to 5×10^{10} torr by using a turbo pump, an ion pump and a titanium sublimation pump. The N_2 gas flowed into the growing chamber up to $5 \times 10^7 \sim 2 \times 10^6$ torr during deposition.

Generally, Ar gas is introduced into the chamber for discharge, and this makes the film growth mechanism more complicated.⁽¹⁸⁾ In this work, the N_2^+ ion beam has been used as assisted ion beam to simplify the film growth mechanism. The primary energy of N_2^+ ion beam produced by the cold cathode type ion gun(VG-AG500) was changed from 0.7keV to 3keV. The current density was varied from $5 \mu A/cm^2$ to $25 \mu A/cm^2$, and the evaporation rate of Ti by e-beam bombardments was kept constant at $0.2 \text{ \AA}/sec$.

The thickness of the TiN thin film was monitored with quartz oscillator. The real thickness of the TiN film deposited on the substrate, however, cannot be directly accessed from this thickness monitoring because N_2^+ ions sputter the surface. Therefore, the thickness of the thin films was estimated by using RBS experiments. 2MeV He^+ source was used for the RBS analysis with the backscattering angle of 170° and the total accumulated charge of $10 \mu C$.

The structure of the deposited TiN films was analyzed by X-ray diffractometry(XRD). For XRD analysis a ScinTag DMS-200 diffractometer was used. XPS experiments were performed with VG-ESCALAB 210. The surface morphology has been observed by SEM(Topcon-ABT 150F) and AFM(Digital Instruments nanoscope-3).

3. RESULT and DISCUSSION

Fig. 1(a) shows the grazing-angle X-ray diffraction(GXRD) patterns of TiN thin films with the thickness of about 50nm on the SKD61 steel substrate at various current density of the assisted N_2^+ ion beam. The TiN(111) and TiN(100) structures coexist at the low current density($0.6 \mu A/cm^2$). However the TiN(111) peak disappears as the current density increases, and only the TiN(100) structure remains at high current density. As can be seen in Fig. 1(b), the preferred orientation has been changed from (111) to (100) as the primary energy of assisted ion beam increases.

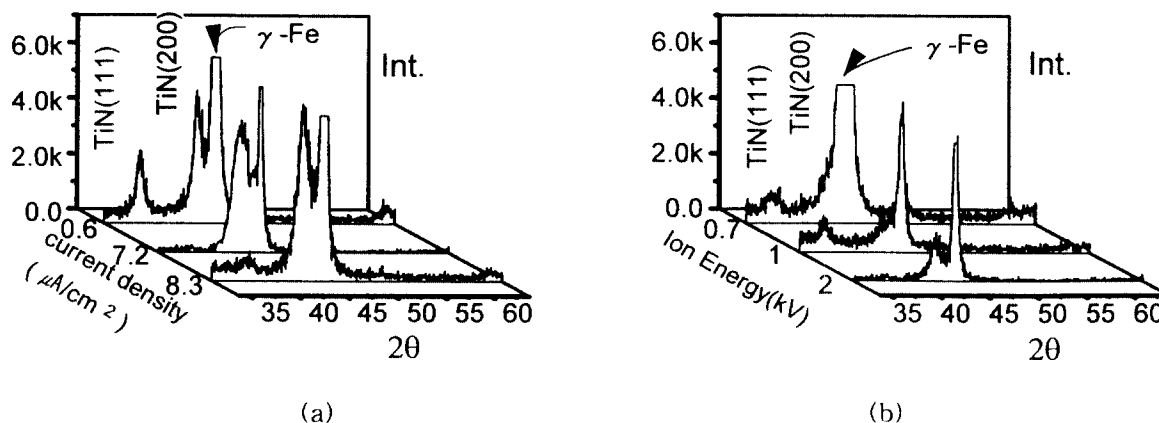


Fig. 1 GXRD patterns of TiN thin films(50nm) on SKD61 steel as a function of (a) the current density and (b) the primary energy of assisted N_2^+ ion beam.

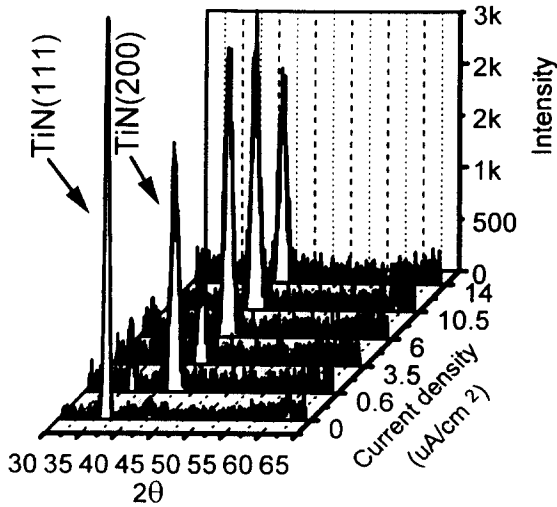


Fig. 2 XRD patterns of TiN thin films(100nm) on Si(100) as a function of current density of assisted N_2^+ ion beam.

Fig. 2 shows the XRD patterns of TiN thin films with the thickness of about 100nm on Si(100) as increasing the current density. Here, the energy of N_2^+ ion beam is fixed at 2keV. As can be seen in fig. 2, the preferred orientation is dependent on the current density of assisted N_2^+ ion beam. In the case of no assisted ion beam, the TiN thin film shows the (111) peak along with tiny peaks of (200) and (110). (111), (200) peaks coexist at low current density and finally (100) direction becomes the preferred orientation at high current density.

These change in the preferred orientation can be explained in terms of the assisted energy, which is defined as the ratio of the total assisted ion energy to the number of arrival atoms of TiN. The results are tabulated in Tables I and II for SKD61 steel and Si(100) substrates, respectively. These results clearly indicate that the crystal orientation is independent of substrates, and that the assisted energy systematically changes the preferred orientation of TiN thin films.

As can be seen in Table I, the crystal structure of TiN(111) and TiN(100) coexists at low assisted energy, but only TiN(100) remains at the assisted energy higher than 200eV. Similar result can be obtained from Table II for Si(100) substrate. Here, the primary ion energy of N_2^+ ion beam was 2keV and only the current density was changed. TiN(111) and TiN(200) peaks coexist at low assisted energy and only the (200) peak remains at high assisted energy. The change of the preferred orientation from (111) to (100) may be attributed the composition change of thin films due to the assisted ion energy.

To investigate further, we studied the surface composition by using XPS and RBS, and the results are shown in Fig. 3 and 4, respectively.

TABLE. I

Assisted energy and Crystal structure of TiN thin films on SKD61 steel

Energy (kV)	Current density ($\mu A/cm^2$)	Assisted energy (eV/atom)	Crystal structure
0.7	2.5	26	(111),(100)
1	4.7	69	(111),(100)
2	7.2	209	(100)
2	0.6	18	(111),(100)
2	7.2	209	(100)
2	8.3	239	(100)

TABLE. II

Assisted energy and Crystal structure of TiN thin films on Si(100)

Energy (kV)	Current density ($\mu A/cm^2$)	Assisted energy (eV/atom)	Crystal structure
0	0	0	(111)
2	0.6	18	(111),(100)
2	3.5	105	(111),(100)
2	6	179	(100)
2	10.5	314	(100)
2	14	418	(100)

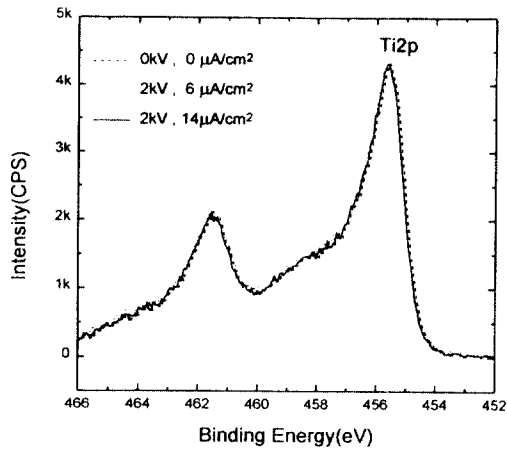


Fig. 3 Ti2p XPS spectra from TiN thin films(100nm) on Si(100) at various current density.

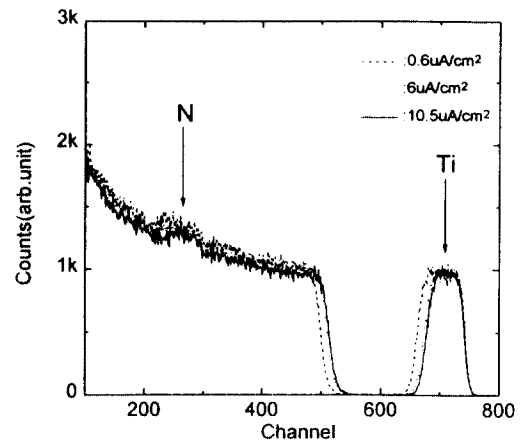


Fig. 4 RBS spectra of TiN thin films(100nm) on Si(100) at various current density.

These results indicate that the composition of TiN thin film does not depend on the assisted ion energy. It means that the change of the preferred orientation is not due to the composition change of thin films. These results are consistent with a model based on the surface energy and the strain energy suggested by Pelleg et. al.⁽¹⁷⁾

The total free energy of the system(W_{hkl}) is described as the sum of the surface energy (S_{hkl}) and the strain energy(U_{hkl}) of the TiN film:

$$W_{hkl} = S_{hkl} + U_{hkl} ,$$

where $S_{111} > S_{110} > S_{100}$ and $U_{100} > U_{110} > U_{111}$. Here, W_{hkl} should be minimal at thermodynamic equilibrium. In the case of TiN system, the lowest surface energy plane is (100), and the lowest strain energy plane is (111). Therefore, a preferred (100) orientation can be considered as one for which the surface energy is dominant over the strain energy. On the other hand, the (111) orientation should be preferred when the strain energy is dominant. Therefore, we can conclude that TiN thin film grows with the (111) preferred orientation at no or low assisted energy while the (100) orientation is preferred at high assisted energy.

To observe the surface morphology of the TiN thin films at no assisted or with the assisted energy, we obtained the SEM and AFM images.

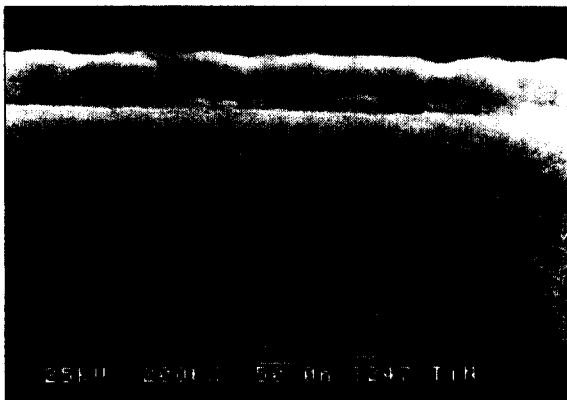


Fig. 5 Cross-sectional SEM image of the TiN thin film(50nm) on Si(100)

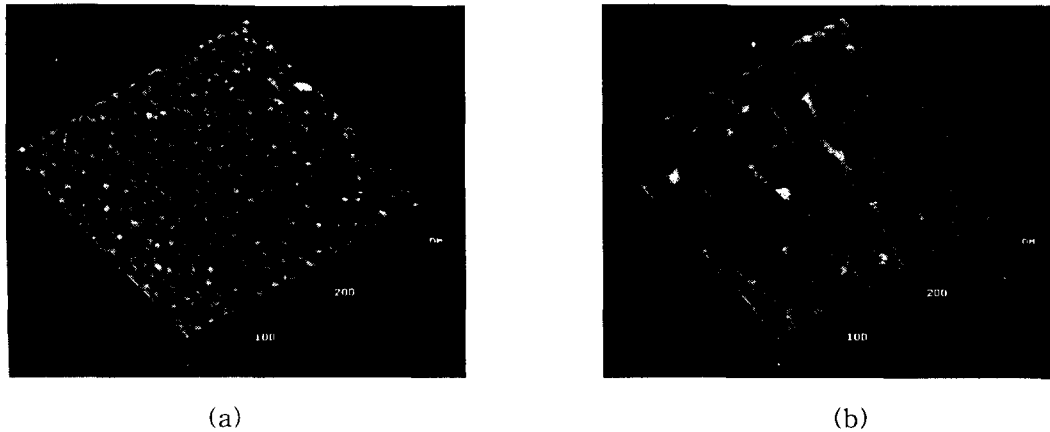


Fig. 6 AFM surface morphologies of TiN thin films on Si(100) (a) no assisted, (b) assisted N_2^+ ion beam

Fig. 5 shows the cross-sectional SEM image obtained from 50nm TiN thin film on Si(100) with the assisted energy of 2keV. The interface is relatively flat and the grain size is about 50nm~100nm. Fig. 6(a) and (b) show the AFM images obtained from TiN thin films on Si(100) with no assisted and with assisted ion beam, respectively. In the case of no assisted ion beam, the grain size is relatively small. On the other hand, in the case of assisted ion beam, one can observe much larger grains grow with (100) preferred orientation. These results indicate that the preferred orientation may be closely related with the grain growth.

CONCLUSIONS

The crystal structure of TiN thin films on SKD61 steel and Si(100) substrates has been studied to clarify the film growth mechanism of IBAD by using XRD, XPS, RBS, SEM and AFM. The results are as follows;

- (1) The assisted ion energy plays an important role in the change of the preferred orientation. The preferred orientation of TiN thin films changes from (111) to (100) as increasing the assisted energy, which is independent of substrate structure.
- (2) The TiN thin film grows with the (111) preferred orientation having the lowest strain energy at no or low assisted energy, but grows with (100) preferred orientation having the lowest surface energy at above 200eV of assisted energy.
- (3) The grain size of TiN thin films is dependent of the assisted energy. the grain size of TiN thin film having (100) preferred orientation is larger than that having (111) preferred orientation.

From these results, we can conclude that the TiN thin film by IBAD grows with the direction of surface free energy minimum, which may be closely related with grain growth of TiN thin film by IBAD.

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