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Preferred growth of epitaxial TiN thin film on silicon substrate by pulsed laser deposition

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Epitaxial TiN thin films on silicon substrates were prepared by pulsed excimer laser (KrF, 34 ns) ablation of a hot-pressed TiN target in nitrogen gas atmosphere. X-ray diffraction (XRD) showed that the preferred orientations of TiN thin films did not change with substrate temperatures, nitrogen gas pressure and film thickness; however, they did change with the orientations of substrates. The epitaxial orientation relationships between high-quality epitaxial TiN thin films and silicon substrates [2 4 2] TiN‖ [2 4 2] Si, (1 1 1) TiN‖(1 1 1) Si and [3 1 1] TiN‖ [3 1 1] Si, (1 0 0) TiN‖(1 0 0) Si. The full-width at half-maximum (FWHM) of the rocking curve of XRD and the minimum channelling yield of Rutherford backscattered spectroscopy (RBS) of the epitaxial TiN thin film were estimated to be 0.3° and 7.3%, respectively, indicating excellent crystalline quality of the grown film. X-ray photoelectron spectroscopy confirmed that the binding energies of Ti 2*p* 3/2 and *N* 1*s* core levels in epitaxial thin film were 455.2 and 397.1 eV, respectively, corresponding to those of TiN bulk. By calibrating the RBS spectra, the chemical composition of TiN thin films was found to be titanium-rich. The typical surface roughness of TiN thin film observed by scanning probe microscopy was about 1.5 nm. © *1998 Chapman & Hall*

1. Introduction

TiN thin films have found many applications in mechanical and electronic industries owing to its unusual properties of high hardness, high melting point, and good electric conductivity. A TiN layer can be prepared by direct surface modification over a titanium plate by a laser beam [1, 2] and deposition of a thin film on a substrate by magnetron sputtering [3, 4], chemical evaporation deposition [5, 6], and pulsed-laser deposition [7–10], etc. There have been many reports of the dependence of preferred orientation of TiN thin film on the deposition parameters. Oh and Je [6] proposed that the TiN preferred orientation is determined by competition between two thermodynamic parameters: surface energy and strain energy. They concluded that the surface energy is dominant in the early stage of thin-film growth, in which the plane with the lowest surface energy (2 0 0) grows faster than other planes, resulting in the (2 0 0) preferred orientation. Then, with increasing film thickness, the orientation is developed into (1 1 1) when the strain energy begins to be dominant. Finally, they also assume that the state of strain energy corresponds to in-plane compression, which is often observed in sputter deposited films subjected to energetic particle bombardment. More recently, Greene *et al.* [3] demonstrated that the preferred orientation of TiN thin film can be controlled without introducing large in-plane compressive stress and/or changes in the strain energy as a function of layer thickness.

Reports on the epitaxial growth of TiN thin films by pulsed-laser deposition (PLD) [8–10] presented the characteristics of epitaxial TiN thin films. They demonstrated a domain match epitaxial (DME) mechanism for the growth of epitaxial thin film over a large mismatch substrate. The evolution of preferred orientation of a film prepared by PLD has not been reported as far as we know. The unique feature of non-equilibrium processing of pulsed-laser deposition definitely distinguishes it from other evaporation methods. The energy of the species ejected from the target by laser pulses ranges from 10 eV to more than 100 eV, which is much larger than that in other evaporation methods. The high kinetic energy which is dominant in the evolution of the orientation of the thin film will cause a different evolution mechanism of orientation of the TiN film. The dependence of preferred orientation on deposition parameters has rarely been reported [10].

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This report demonstrates the evolution of the orientation of TiN thin films on silicon substrates. The effects of deposition parameters (nitrogen pressure, substrate temperature, T_s) on the properties of TiN thin films are investigated. High-quality epitaxial TiN thin films were prepared on silicon substrates with two kinds of orientations (1 0 0) and (1 1 1) by a pulsed excimer laser (KrF, 248 nm, 34 ns, 20 Hz) ablation of a hot-pressed TiN target in the ambient of highly pure nitrogen gas. The structure of TiN films was investigated by X-ray diffraction (XRD). Rutherford backscattered spectroscopy (RBS) was used to analyse the crystallinity and chemical composition of the thin film. The chemical binding energies of Ti $2p$ 3/2 and N 1s core levels were analysed by X-ray photoelectron spectroscopy (XPS) to confirm the formation of TiN compound. The surface morphology and roughness of thin films were observed by scanning probe microscopy (SPM).

2. Experimental procedure

The experiments were carried out in a high-vacuum system of up to 2.0×10^{-7} torr (1 torr = 133.322 Pa) using a KrF excimer laser (248 nm wavelength, 34 ns pulse duration, 20 Hz repetition rate). TiN thin films were deposited on two kinds of substrates, Si(1 1 1) and Si(1 0 0), from a hot-pressed titanium nitride target which was placed parallel to the substrate at a separation distance of 50 mm. The substrate was etched for 10 min in 4.8% HF solution and cleaned ultrasonically for 5 min in acetone, 5 min in deionized water, and 5 min in alcohol. Prior to deposition of the TiN thin film, the substrate was heated at a high temperature of 750 °C for 10 min at a base vacuum pressure of 2.0×10^{-6} torr, which was evacuated by turbomolecular pump. Then high-purity nitrogen gas (with a purity of 99.999%) was introduced into the vacuum chamber to the required experimental pressure. The ambient pressure ranged from 5.0×10^{-2}–5.0×10^{-6} torr. In fact, no nitrogen gas was introduced into the chamber at 5.0×10^{-6} torr. The base pressure rose from 2.0×10^{-6} torr to 5.0×10^{-6} torr when the laser beam, focused by a lens with a focal length of 700 mm, irradiated the target. TiN thin films were deposited at different substrate temperatures ranging from 350 °–720 °C with a typical deposition rate of 0.01 nm per laser pulse at optimal energy density of 2–4 J cm^{-2}. The thin films were golden yellow in colour at all substrate temperatures and ambient gas pressure.

XRD θ–2θ scans, rocking curve (ω-scans) and φ-scans measurements were performed on a Philips MXP18AHF MRD high-resolution X-ray diffractometer with a point-focus Cu$K_{\alpha 1}$ radiation, four-reflection Ge(2 2 0) crystal monochromator, and a rotation sample stage. The crystallinity and atomic ratio of N/Ti of titanium nitride thin films were determined by RBS analysis using $^4He^+$ ions accelerated at 2 MeV.

ESPAC-850 XPS system using the unmonochromatized MgK_α radiation ($h\nu$ = 1253.6 eV) was used to collect the binding energy spectra of Ti $2p$ and N 1s core levels. The base pressure in the analyser and the preparation chambers was 10^{-9} torr. Prior to data acquisition, the surface of the sample was very slightly etched by Ar^+ (2 kV, 30 mA) in order to remove the natural protective titanium dioxide coating. The etching rate of Ar^+ was 0.2 nm min^{-1}. In order to compare TiN film with standard titanium nitride bulk compound, the spectra of the hot-pressed TiN sample were also collected.

The morphology and surface roughness of the thin films were observed by SPM (Di Digital Dimension 3000). Prior to the observations, the samples were cleaned with acetone in an ultrasonic bath.

3. Results and discussion

The dependence of orientation and crystallinity of TiN thin films on the deposition parameters was observed by XRD. Fig. 1a contains (1 1 1) and (2 0 0) reflection peaks of the hot-pressed TiN target. The lattice constant of TiN bulk derived from the pattern is 0.42416 nm. It is consistent with the data reported by other workers [3,8].

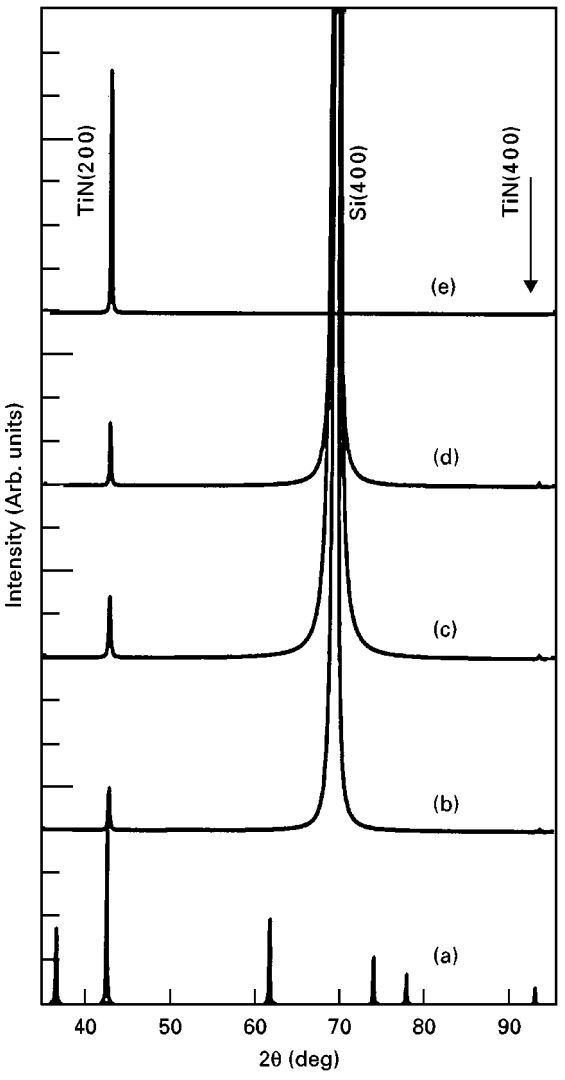

Figure 1 The XRD patterns of (a) the hot-pressed TiN target, and TiN thin films deposited at (b) 430 °C, (c) 520 °C, (d) 620 °C, (e) 720 °C, respectively.

Fig. 1b–e are θ–2θ diffraction patterns of TiN thin films deposited on Si(1 0 0) substrates at different substrate temperatures, T_s (430, 520, 620, 720 °C) with the same laser energy densities of 2.4 J cm^{-2} and nitrogen gas pressure of 2.0×10^{-6} torr. TiN thin film was amorphous when the substrate temperature was lower than 430 °C. When the substrate temperature was higher than 430 °C, the orientation of the thin films was always oriented along the preferred [2 0 0] direction. The reflection peak of the TiN(1 1 1) plane could not be detected owing to the limited precision of the diffractometer. The intensities of the TiN(2 0 0) peak increased steadily with increase in substrate temperatures.

The rocking curve of XRD is a powerful technique to determine the out-of-plane epitaxy quality of thin films. Fig. 2 shows the variation of the FWHM of diffraction peak of (2 0 0) TiN plane for the samples used for Fig. 1. This indicates that the alignment of the film with respect to the substrate normal improves steadily with increasing temperature. The crystallinity of the TiN thin films became more perfect as the deposition temperature increased. Similar results were also obtained for TiN(1 1 1) thin films on Si(1 1 1) substrates. The preferred orientation of TiN thin films on Si(1 1 1) substrates were in the [1 1 1] direction and did not change with variation of the deposition parameters.

Fig. 3 shows the lattice constants of TiN thin films deduced from Fig. 1. The lattice constant of the amorphous TiN thin film was larger than 0.42416 nm, while the lattice constants of the crystalline TiN thin films were less than those of bulk TiN target, and increased slightly with substrate temperatures. So far, the reason for the variation of lattice constants of the thin films is not clear.

The dependence of crystallinity of TiN thin films on the vacuum pressure is shown in Fig. 4. Two series of samples deposited on Si(1 0 0) at 620 and 720 °C with a laser energy density of 3.6 J cm^{-2} were used. The introduction of nitrogen gas significantly degraded the crystallinity of the TiN thin film at the T_s of 620 °C, while the effects of nitrogen gas on the crystallinity of TiN thin films were not so significant at T_s = 720 °C. The pressure of the ambient gas significantly affected the reaction kinetics during the time of flight of the particles. As the chamber pressure increased, the mean free path of the particles decreased significantly, and then the number of collisions with laser-induced plasma plume increased, and the kinetic energy of particles reaching the surface of the substrate decreased. This induced degradation of the crystallinity of the thin film. The high substrate temperature could provide a higher kinetic energy for adatoms on the surface of the substrate to compensate for loss of energy during collisions and the mobility of adatoms could be enhanced. Therefore, the crystallinity of the TiN thin film will not be affected by the ambient pressure at high substrate temperatures. The sample deposited at T_s of 720 °C, and the laser energy density of 3.6 J cm^{-2} at a pressure of 5.0×10^{-4} torr had the narrowest rocking curve. The value of the FWHM was estimated to be less than 0.5° which indicates the perfect out-of-plane epitaxy of TiN thin film over the surface of the silicon substrate.

The crystallinity of TiN thin films with different thicknesses was investigated (as shown in Fig. 5). The samples were fabricated on Si(1 0 0) substrates at 620 °C with a laser energy density of 3.6 J cm^{-2} and a pressure of 5.0×10^{-6} torr. The variation of values of

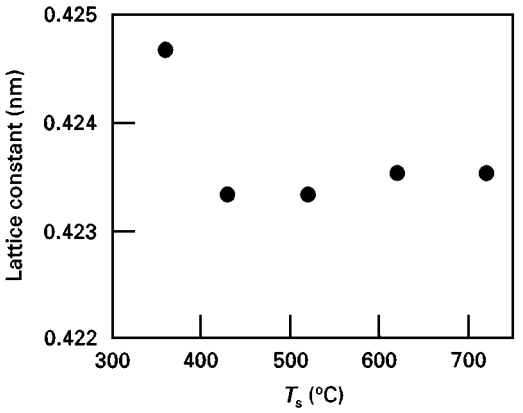

Figure 3 The dependence of lattice constants of TiN thin films on substrate temperatures.

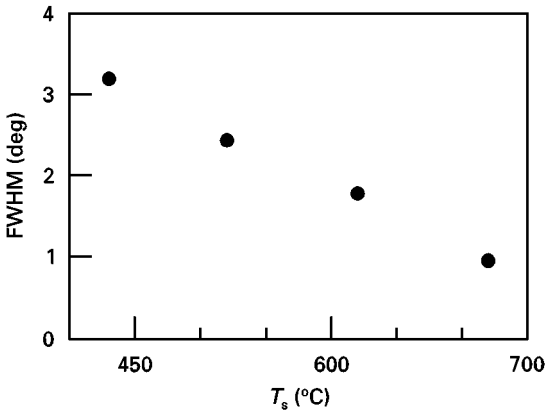

Figure 2 The dependence of FWHM of rocking curve of the (2 0 0) TiN plane on substrate temperatures, T_s.

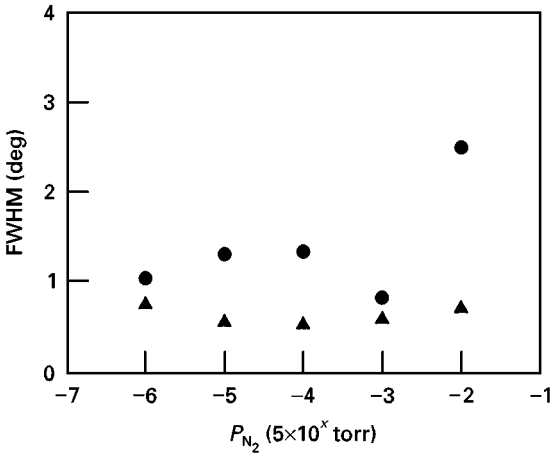

Figure 4 The relationship between the values of FWHM of rocking curve and nitrogen gas pressure at different substrate temperatures, T_s: (●) 620 °C; (▲) 720 °C.

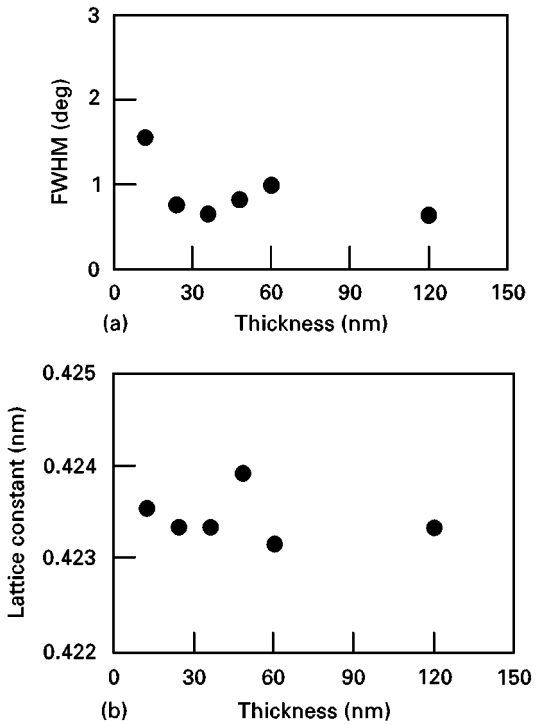

Figure 5 The dependene of FWHM values of (a) rocking curves and (b) lattice constants of TiN thin films on their thickness.

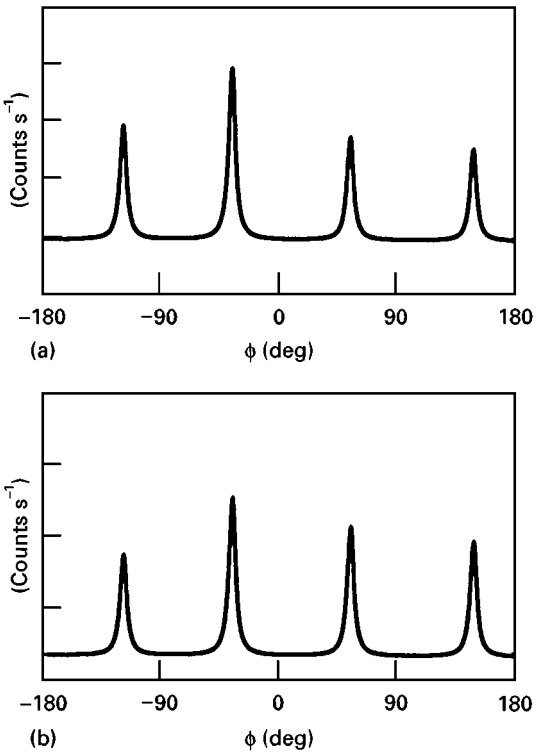

Figure 6 The ϕ-scans patterns of (a) TiN{3 1 1} diffraction and (b) Si{3 1 1} diffraction of the TiN(1 0 0) thin film on Si(1 0 0) substrate deposited at $T_s = 720\,^{\circ}C$, with a laser energy density of $3.6\,J\,cm^{-2}$ and a pressure of 5×10^{-4} torr.

FWHM of the rocking curves versus the thickness of thin films, indicates that the residual strain in the thin films was changed as a function of thin-films thickness. The lattice constants of the thin films were less than 0.4241 nm and almost independent of film thickness. A similar phenomenon was observed in TiN thin films deposited on Si(1 1 1) substrates. XRD patterns show that the preferred orientations of the thin films were always parallel to the normal directions of the silicon substrates and did not change with the thickness of the thin films. For film with a thickness of 12 nm on the Si(1 1 1) substrate, the film oriented in the surface normal of the silicon substrate was in the [1 1 1] direction, not in the [2 0 0] direction. The diffraction of the (2 0 0) plane did not appear in TiN(1 1 1) samples. Even if the deposition parameters changed, the preferred orientation of thin film on Si(1 1 1) was always in the [1 1 1] direction.

The azimuthal orientation relationship between TiN thin films and silicon substrates was determined by XRD ϕ-scans. Two azimuthal ϕ-scans were made for the respective TiN{3 1 1} and Si{3 1 1} diffractions, while the sample TiN(1 0 0)/Si(1 0 0) was rotated at a constant speed around the Si [1 0 0] axis normal to the substrate plane. For a TiN(1 1 1) thin film on a Si(1 1 1) substrate, two diffractions of TiN{2 4 2} and Si{2 4 2} were made, while the thin film of sample TiN(1 1 1) was rotated at a constant speed around the Si[1 1 1] axis normal to the substrate plane. Two samples, TiN(1 0 0)/Si(1 0 0) thin film and TiN(1 1 1)/Si(1 1 1) thin film, were deposited at the same T_s of 720°C, with a laser energy density of $3.6\,J\,cm^{-2}$ and a pressure of 5.0×10^{-4} torr and were then characterized by XRD ϕ-scans. The measured TiN{3 1 1}, Si{3 1 1} and TiN{2 4 2}, Si{2 4 2} diffractions are shown in Figs 6a, b and 7a, b, respectively. Four TiN{3 1 1} diffraction peaks, each 90° from the other, are located at the same azimuthal angular position of the Si{3 1 1} diffraction peaks. Three TiN{2 4 2} diffraction peaks, each 120° from the other, are located at the same azimuthal angular position of the Si{2 4 2} diffraction peaks. The intensities of the peaks are consistent with the diffraction intensities of the silicon substrates. The rocking curve of the TiN (2 0 0) plane of the sample TiN(1 0 0)/Si(1 0 0) shown in Fig. 8 gives the minimum value of FWHM of 0.3°. These patterns indicate that the in-plane alignment of the *a* and *b* axis of the TiN thin films were in excellent correspondence with those of the silicon substrates. There were no detectable in-plane misorientations. The orientation relationship between TiN films and silicon substrates are

$$[2\,4\,2]\mathrm{TiN} \| [2\,4\,2]\mathrm{Si},\ (1\,1\,1)\ \mathrm{TiN} \| (1\,1\,1)\ \mathrm{Si}$$

(for TiN(1 1 1) thin film)

$$[3\,1\,1]\mathrm{TiN} \| [3\,1\,1]\mathrm{Si},\ (1\,0\,0)\ \mathrm{TiN} \| (1\,0\,0)\ \mathrm{Si}$$

(for TiN(1 0 0) thin film)

The perfection of the epitaxial thin films was also confirmed by RBS measurement. Fig. 9 shows RBS spectra (random and aligned) for one of the above specimens, TiN(1 0 0)/Si(1 0 0). The minimum yield, χ_{min} (the ratio of random to aligned channelling yield at a channel number just behind surface peak of the titanium aligned spectrum) was found to be 7.3%, indicating an excellent crystallinity of the TiN thin

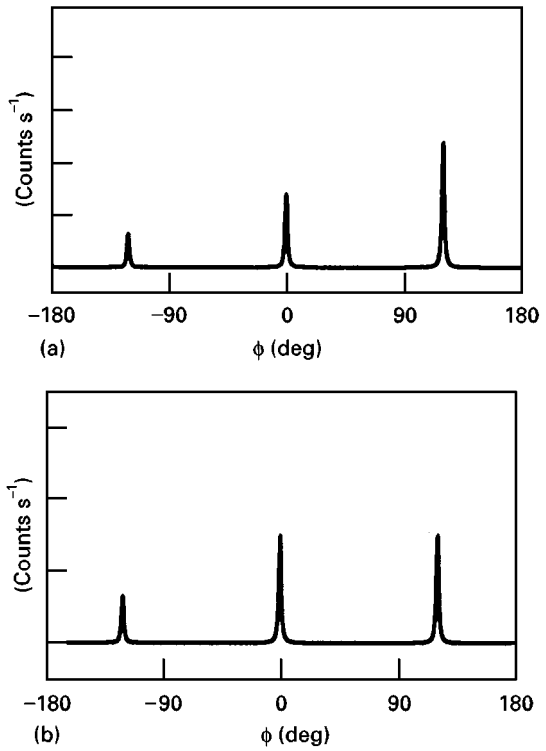

Figure 7 The ϕ-scans patterns of (a) TiN{2 4 2} diffraction and (b) Si{2 4 2} diffraction of the TiN(1 1 1) thin film on the Si(1 1 1) substrate deposited at T_s = 720°C, with a laser energy density of 3.6 J cm^{-2} and a pressure of 5×10^{-4} torr.

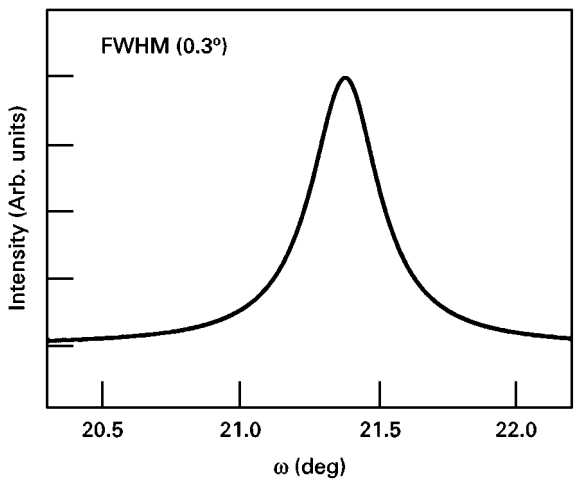

Figure 8 The rocking curve of the (2 0 0) plane of the TiN thin film sample used in Fig. 6.

film on the Si(1 0 0) substrate. This value is significantly better than that of previously published values for TiN thin films grown on silicon [9]. However, the ratio increases slightly towards the TiN/Si interface, indicating deterioration of crystallinity near the interface. The enhanced scattering near the TiN/Si interface is indicative of a high density of defects (disorder in atomic planes) due to the large lattice mismatch. This fact suggests that epitaxy near the surface is superior compared to that at the interface. The disorder near the interface affects the somewhat larger yield of the silicon-aligned spectrum. By fitting the calculated and observed spectra in Fig. 9, the composition of the thin film was determined to be 0.8 of the atomic ratio of N/Ti. RBS spectra of other samples indicated that all of the thin films ablated from the hot-pressed target were titanium-rich.

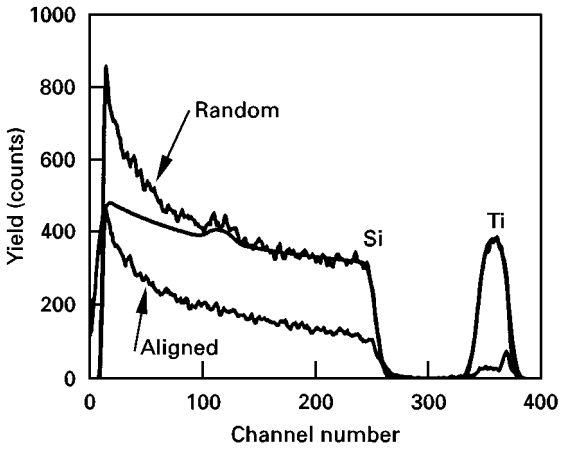

Figure 9 The RBS spectra (random and aligned) of the TiN film sample used in Fig. 6.

As stated above, the TiN thin film was amorphous when the substrate temperature was lower than 430°C. The TiN thin film was always grown with a preferred orientation parallel to the normal direction of the silicon substrate, when the temperature of substrate was higher than 430°C. The preferred orientation of the thin film did not change with deposition parameters. It was determined only by the orientation of substrate. The difference in lattice parameters between the TiN thin film (a = 0.4242 nm) and the silicon substrate (a = 0.5431 nm) is very large, with a lattice mismatch up to 24.6%. Narayan and co-workers [8, 9] suggested a domain match epitaxial (DME) mechanism for the growth of an epitaxial thin film over a large mismatch substrate. In the plane of (2 0 0), four unit cells of TiN match with three unit cells of silicon with less than 4.0% misfit. Even with this method, the residual strain still exists in the thin film and the interface of the TiN thin film and the silicon substrate [10]. When the thickness of thin film increases, the residual strain energy will increase. It is thought that the high kinetic energy of the species ablated from target by the laser may play an important role in overcoming the residual strain. Therefore, the thin film can be epitaxially grown on the surface template of silicon and the arrangement of atoms on the surface can be consistent with the template. The preferred orientation of TiN film on a silicon substrate is determined only by the orientation of the substrate, and does not change with the deposition parameters. However, the substrate temperatures, T_s, nitrogen gas pressure and film thickness can strongly affect the crystallinity of the thin film.

The formation of titanium nitride can be confirmed by the depth profile of chemical binding energies of Ti 2p 3/2 and N 1s core levels in X-ray photoelectron spectroscopy (XPS) (as shown in Fig. 10). The chemical binding energies of Ti 2p 3/2 and N 1s were located at the same positions of 455.1 and 397.1 eV,

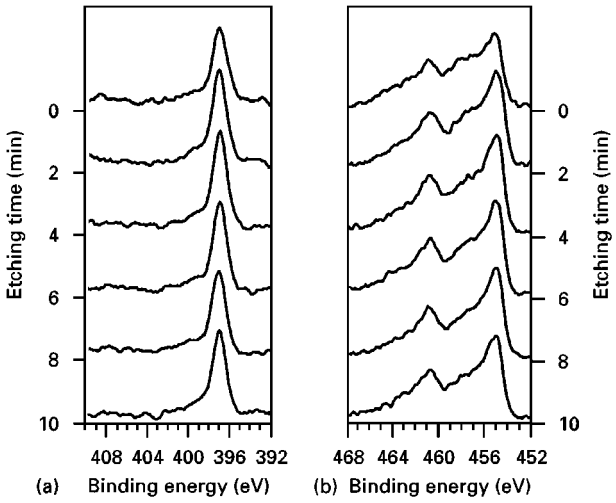

Figure 10 The XPS depth profile of (a) N 1*s* and (b) Ti 2*p* core levels of TiN thin film deposited at $T_s = 720\,^{\circ}C$, with a laser energy density of $3.6\,J\,cm^{-2}$ and a pressure of 5×10^{-4} torr.

respectively, along with the depth direction, which corresponds to the data of TiN reported in the literature. The shape and peak positions of each spectrum in Fig. 10 do not change along the depth direction. The uniform features show that no oxygen was introduced into the TiN thin film.

The surface morphology of thin films deposited at different deposition parameters was observed by SPM. Some particles and droplets with a size of 0.1 μm were embedded in the surface of thin films, which might have caused defects in the thin films and degraded their crystallinity. The surface roughness of samples was less than 5 nm, typically 1.5 nm.

4. Conclusion

The effect of deposition parameters on the properties of TiN thin films, which were deposited on silicon substrates by pulsed excimer laser under a range of substrate temperatures between 350 and 720 °C and also a range of nitrogen gas pressures was investigated. It has been shown that above the deposition temperature of 430 °C, the TiN thin films were crystallized with preferred orientations which were always parallel to the normal directions of the silicon substrates, were not changed by deposition parameters, and were determined only by the orientation of the substrates, due to the contribution of high kinetic energy of the species ablated from the target by the laser. The preferred orientations of the crystalline TiN thin films on Si(1 0 0) and Si(1 1 1) substrates were in the [1 0 0] and [1 1 1] directions, respectively. The out-of-plane epitaxial quality of the TiN thin films, determined by the values of FWHM of the rocking curves of the films, decreased with the decrease of nitrogen gas pressure and the increase of the substrate temperature. In the meanwhile, the change of deposition parameters resulted in the variation of the lattice constants of crystalline thin films in the range from 0.426–0.423 nm which were less than the lattice constant of bulk TiN target.

High-quality epitaxial TiN thin films with the minimum value of the FWHM of 0.3° of XRD rocking curves and the minimum channelling yield of 7.3% of RBS spectra were obtained. The epitaxial orientation relationship between TiN thin films and silicon substrates were [2 4 2] TiN‖ [2 4 2] Si, (1 1 1) TiN‖(1 1 1) Si and [3 1 1] TiN‖ [3 1 1] Si, (1 0 0) TiN‖(1 0 0) Si.

By fitting the RBS spectra of TiN thin films, the chemical composition of TiN thin films on silicon substrates were titanium-rich. The binding energies of Ti 2*p* 3/2 and N 1*s* core levels detected by XPS were 455.2 and 397.1 eV, respectively, indicating the formation of TiN compound. Some particles and droplets were observed by SPM to embed in the surface of the thin films. The typical surface roughness of the film was about 1.5 nm. Thus, the pulsed-laser deposition technique demonstrated here presents great potential for the formation of preferred oriented epitaxial TiN thin films.

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