Characterization of Deposited and Nitrogen-implanted Titanium Films*

J. J. Wang and T. Yamamura
Department of Metallurgy, Tohoku University, Aramaki-Aza-Aoba 02, Aoba-ku, Sendai 980-8579, Japan

S. Yamamoto and M. Yoshikawa
Quantum Beam Science Directorate, Japan Atomic Energy Agency-Takasaki, 1233 Watanuki, Takasaki 370-1292, Japan

Y. Fujino
Center for International Exchange, Tohoku University, 41 Kawasaki, Aoba-ku, Sendai 980-8576, Japan

Y. Kasukabe†
Center for International Exchange and Department of Metallurgy, Tohoku University, 41 Kawasaki, Aoba-ku, Sendai 980-8576, Japan

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Deposited Ti films and TiN films formed by nitrogen-implantation were investigated by transmission electron microscope (TEM) observation and electron energy loss spectroscopy (EELS). Titanium films in the thickness of 100 nm were deposited by an electron beam heating method onto thermally cleaned NaCl(001) surfaces held at room temperature under ultra-high vacuum. In the deposited Ti films, there coexist mainly (03·5)-oriented hcp-Ti and (110)-oriented TiH_x crystallites: the hydrogen atoms are originally contained in NaCl substrates. The (03·5)-oriented hcp-Ti grows inheriting the fourfold symmetry of the square atomic arrangement of TiH_x grown in the early deposition stage. On the other hand, the (110)-oriented TiH_x nucleates and grows naturally inheriting the rectangle atomic arrangement of the (03·5)-oriented hcp-Ti to form the band-like region. The deposited Ti films were implanted by N^+ ions with 62 keV in the 400 kV analytical high resolution TEM combined with ion accelerators. In the N-implanted Ti film, the (001)-oriented TiN_y and (110)-oriented TiN_y crystallites are formed outside and inside the band-like regions, respectively. The (110)-oriented TiN_y is formed by nitriding the (110)-oriented TiH_x in the as-deposited Ti film, whereas the (001)-oriented TiN_y is epitaxially formed by the transformation of the (03·5)-oriented hcp-Ti to (001)-oriented fcc-Ti, partially inheriting the atomic arrangement of the square and/or the octahedron of the hcp-Ti, accompanied by the occupation of O-sites of the fcc-Ti substrate by N atoms. In these transformations, the inheritances of the local atomic arrangement of Ti sublattices play a prominent role in the epitaxial fcc-hcp and hcp-fcc formations of the Ti sublattices. The epitaxial formation mechanisms of deposited Ti films and N-implanted Ti films are discussed. [DOI: 10.1380/ejssnt.2005.476]

Keywords: deposited Ti films; ion-implantation; TiN_y; fcc-hcp transformation; in-situ TEM

I. INTRODUCTION

Titanium nitrides, TiN, formed by various techniques such as ion implantation, ion beam assisted deposition, magnetron sputtering, physical vapor deposition (PVD) and chemical vapor deposition (CVD), belong to the group of refractory compounds and have covalent property as well as metallic and ionic properties, which make it fascinating for both fundamental research and technological applications such as hard coatings and as diffusion barriers in microcircuits [1–13]. The great hardness is typical of compounds with strong covalent bonds [2, 4], while the metallic properties result in good electrical conductivity [6–13]. The interesting physical properties are related to the crystallographic (preferred oriented) and electronic structures. It has been revealed that the properties of epitaxially-grown TiN films are superior to those of polycrystalline ones. Thus, much interest has been focused on the epitaxial films [8, 10–13].

Recently, it was reported that NaCl-type (110)- and (001)-oriented TiN_y crystallites were 'epitaxially' grown by the N-implantation into CaF_2-type (110)-oriented TiH_x and (03·5)-oriented hcp-Ti in the deposited Ti films held at room temperature (RT), respectively [14–16]; here, the term 'epitaxially' is used to denote the situation of partially inheriting the atomic arrangements of unimplanted TiH_x and hcp-Ti. However, the detailed 'epitaxial' nitriding processes of Ti films with the domains of TiH_x and hcp-Ti during N-implantation, as well as the epitaxial growth processes of (110)-oriented TiH_x and (03·5)-oriented hcp-Ti in deposited Ti films, have not yet been sufficiently understood.

The purpose of this work is firstly to characterize the deposited Ti films and N-implanted Ti films, and secondly to investigate the changes in the crystallographic and electronic structures of TiN_y formed by N-implantation into deposited Ti films, using in-situ transmission electron microscope (TEM) equipped with the instrument for electron energy loss spectroscopy (EELS), and then to discuss the epitaxial growth mechanism of deposited Ti and TiN films, taking account of crystallographic and electronic structure changes with the aid of discrete variational Xo (DV-Xo) molecular orbital calculations. Most of the experimental works to clarify the crystallographic and electronic structures were carried out using samples prepared in a separate vacuum system and transferred to the analysis chamber through air, and then cleaned using a combination of Ar^+ ion bombardment and heating cycles. These processes are known to change the surface

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†Corresponding author: kasukabe@insc.tohoku.ac.jp
FIG. 1: ED pattern (a), BF image (b) and DF images (c) and (d) taken from a 100-nm-thick Ti film grown on the NaCl substrate held at RT. (c) and (d) were taken with the 002* reflection of TiH$_x$ and the 111 reflection of hcp-Ti, respectively. Note that the band-like contrast region indicated by an arrow in (b)-(d) was elongated in the $<110>$ direction of the substrate.

composition and structure, and to influence the electronic structure [9]. Therefore, for the investigation of the crystallographic and electronic structures of TiN films, $in situ$ observations during the formation of TiN films by N-implantation are performed in the TEM combined with ion accelerators.

In order to investigate the electronic structures of hcp-Ti and TiN$_y$, the self-consistent charge DV-X$\alpha$ molecular orbital (MO) calculations were also performed. The calculation method has been given elsewhere [17]. In brief, the Hartree-Fock-Slater (HFS) equations for a cluster model were self-consistently solved with the localized exchange-correlation potential ($X\alpha$ potential). The adjustable (exchange correlation) parameter $\alpha$ was fixed at 0.7. Numerical Ti 1s-4p and N 1s-2p atomic orbitals, which were obtained as solutions of the atomic HFS equations, were utilized as basis sets.

II. EXPERIMENTAL

Detailed descriptions of the preparation method for deposited Ti films were presented in earlier papers [14, 18]. The ultimate pressure of the working chamber evacuated by means of an ion pump and a Ti sublimation pump was less than $4 \times 10^{-9}$ Torr before deposition, and the pressure during deposition was $6 \times 10^{-8} - 1 \times 10^{-7}$ Torr. Titanium films of 100 nm in thickness were deposited on thermally cleaned NaCl(001) surfaces held at RT by an electron beam heating method, with a deposition rate of 10 nm/min. Nitrogen ions (N$_+^2$) with 62 keV were implanted into the deposited-Ti films at an angle of 30° to the surface normal. The implantation of N$_+^2$ was performed in the 400 kV analytical and high resolution TEM combined with ion accelerators at JAERI-Takasaki [19]. The pressure in the TEM specimen chamber was below $1 \times 10^{-7}$ Torr. According to the results of Monte Carlo simulation using the SRIM2003 code, the mean projected range and the full width at half maximum of the depth profile of N$_+^2$ with 62 keV were 55 nm and 66 nm, respectively. Thus, most of the implanted ions were to be retained inside the Ti films. The N concentrations in Ti films were estimated from the implantation dose measured by an electric current of a Faraday cage. The maximum dose in this experiment was $4.56 \times 10^{17}$ ions/cm$^2$, which corresponded to the N/Ti ratio of 0.81. This N/Ti ratio is not equal to the value of $y$ in TiN$_y$, because both hcp-Ti and TiN$_y$ crystallites are present in N-implanted Ti films and it is conceivable that the concentration of N in hcp-crystallites is less than that in TiN$_y$ crystallites. Therefore, in the present experiment, N/Ti ratios indicate the average concentration of implanted N atoms with respect to Ti atoms in the films.
III. RESULTS AND DISCUSSION

A. Deposited Ti thin films

Figures 1(a) and 1(b) show, respectively, a typical electron diffraction (ED) pattern and a bright field (BF) image taken from the Ti film deposited on a NaCl substrate at RT. An analysis of Fig. 1(a) indicates that both hcp-Ti (lattice constants: \(a = 0.296 \text{ nm}, c = 0.471 \text{ nm}\)) and CaF\(_2\)-type TiH\(_x\) \((x \approx 1.5\) [20]; lattice constant: \(a = 0.441 \text{ nm}\)) exist in this film. The reflections indicated by the four-index system and the three-index system with asterisks are obtained from the hcp-Ti and TiH\(_x\) crystallites, respectively. The growth of both hcp-Ti and TiH\(_x\) agrees with the results of previous papers [14–16]: Ti films deposited on NaCl substrates spontaneously absorbed hydrogen (H) atoms from the interior of the NaCl, and then TiH\(_x\) grew partially in addition to hcp-Ti. The orientation relationships between the hcp-Ti and the NaCl substrate are \((03\cdot5)\text{Ti} // (001)\text{NaCl} \text{ and } [\overline{2}1\overline{0}]\text{Ti} // [\overline{1}0\overline{0}]\text{NaCl}\) for \((03\cdot5)\)-oriented hcp-Ti, and \((\overline{2}1\overline{0})\text{Ti} // (001)\text{NaCl}\) and \([00\cdot1]\text{Ti} // [100]\text{NaCl}\) for \((\overline{2}1\overline{0})\cdot0\)-oriented hcp-Ti. The \((03\cdot5)\)-oriented hcp-Ti gives rise to the \(1\overline{1}0\cdot1\) reflection, for example in Fig. 1(a), whereas the \(00\cdot2\) and \(0\overline{1}\overline{1}\cdot1\) reflections in Fig. 1(a) stem from the \((\overline{2}1\overline{0})\cdot0\)-oriented hcp-Ti. On the other hand, the orientation relationship between the TiH\(_x\) and the NaCl substrate is \((110)\text{TiH}\(_x\) // (001)\text{NaCl} \text{ and } [001]\text{TiH}\(_x\) // [\overline{1}0\overline{0}]\text{NaCl}\) hereafter called \((110)\)-oriented TiH\(_x\). TiH\(_x\) gives rise to reflections labeled 002* and \(\overline{T}T1^*\), for example, in Fig. 1(a). The Ti film has band-like contrast regions elongated in the \(<110>\) direction of the NaCl substrate and TiH\(_x\), as indicated by a large arrow in Fig. 1(b). Figure 1(c) is a dark field (DF) image taken by using the 002* reflection of TiH\(_x\), while Fig. 1(d) is a DF image taken by using \(1\overline{1}0\cdot1\) reflection of hcp-Ti. Comparison of Fig. 1(b) with Fig. 1(c) reveals that the elongated bright band-like contrast region of TiH\(_x\) indicated by a large arrow in Fig. 1(c) corresponds to the band-like contrast region in Fig. 1(b). As seen in Fig. 1(d), \((03\cdot5)\)-oriented hcp-Ti crystallites preferentially exist as small dotted ones outside the band-like contrast region indicated by a large arrow. It was found from a DF image taken by using the reflection of \((\overline{2}1\overline{0})\cdot0\)-oriented hcp-Ti that a small number of \((\overline{2}1\overline{0})\cdot0\)-oriented hcp-Ti crystallites also grew outside the band-like contrast region. These results manifest that the \((110)\)-oriented TiH\(_x\) grows mainly in the band-like contrast region, whereas the \((03\cdot5)\)- and \((\overline{2}1\overline{0})\cdot0\)-oriented hcp-Ti grow only outside the band-like contrast region.

Judging from the ED intensity of Fig. 1(a), the growth of \((03\cdot5)\)-oriented hcp-Ti is preferred to that of \((110)\)-oriented TiH\(_x\) and \((\overline{2}1\overline{0})\cdot0\)-oriented hcp-Ti in the deposited Ti films on NaCl(001) surfaces. Therefore, in order to characterize deposited Ti films, we firstly survey the epitaxial growth mechanism of \((03\cdot5)\)-oriented hcp-Ti in the early deposition stage. It was found that as-deposited 'hot' Ti films in 2 nm thickness spontaneously absorb hydrogen from the substrates and become solid solutions (\(\beta\)-Ti (bcc-structure)) during the cooling of the films [21]. Annealing processes during and after deposition lead the solid solution to the formation of a hydride phase, TiH\(_x\) (fcc-Ti sublattice). The schematic representation of the above phase transformation from \(\beta\)-Ti to TiH\(_x\) is shown in Fig. 2. In Fig. 2(a), solid circles represent \(\beta\)-Ti atoms, and the direction of NC is the \(<100>\) direction of the NaCl substrate. The bcc-structure is also described using face-centered-tetragonal structure surrounded by dotted lines. (b) TiH\(_x\). Ti sublattice of TiH\(_x\) is fcc. The fcc-Ti sublattice is also described using a body-centered prismatic (bcp) cell formed of atoms from A to I surrounded by bold lines. (c) hcp-Ti. The unit cell of hcp-Ti transformed from fcc-Ti, indicated by A to I atoms with bold lines.
for example) of bcc-structure by hydrogen atom during the annealing processes, and the expansion and contraction in the [001] and [110] directions of the bcc-structure, respectively, result in the formation of the (001)-oriented TiH$_x$ (fcc-Ti sublattice, which is shown in Fig. 2(b)). This (001)-oriented fcc-Ti is also described as a body-centered prismatic (bcp) cell formed of atoms from A to I surrounded by bold lines in Fig. 2(b). This bcp cell corresponds to the unit cell of (03 5)-oriented hcp-Ti transformed from fcc-Ti, indicated by atoms from A to I with bold lines, as shown in Fig. 2(c). In order to obtain the hcp-Ti by the fcc-hcp transformation, the atoms on the (111)-plane including A, B, C, D atoms in Fig. 2(b) have to be shifted. The direction of shift is the AC $<11\overline{2}>$ direction. After the shift, the A atom, for example, has to be at the center of gravity of the ABD triangle. In the so-obtained (03 5)-oriented hcp-Ti of Fig. 2(c), a square formed by atoms of E, F, J and K is the (03 4)-plane. It is noteworthy that a dihedral angle of the (03 4) plane and the (03 5) plane which is parallel to the substrate, is about 6.2° and that therefore the former is also nearly parallel to the substrate. Moreover, this (03 4) plane in Fig. 2(c) corresponds to the square {001} planes defined by atoms E, F, J and K in Figs. 2(a) and 2(b). In other words, the fourfold symmetry of the square EFJK is preserved in the series of this transformation from Fig. 2(a) to Fig. 2(c). Therefore, it seems reasonable to conclude that the inheritance of fourfold symmetry, such as the square EFJK shown in Figs. 2(a)-2(c), plays a prominent role in the epitaxy of the (03 5)-oriented hcp-Ti.

As is apparent from Fig. 1, there mainly coexist the (110)-oriented TiH$_x$ and (03 5)-oriented hcp-Ti in the 100 nm thick Ti films, and not the (001)-oriented TiH$_x$. This means that the nucleation and growth of hcp-Ti occurs in the deposited Ti films for a thickness more than 2 nm, and that the (001)-oriented TiH$_x$ is transformed to (03 5)-oriented hcp-Ti in a further growth stage. Then, as-deposited 'hot' Ti films above 2 nm thickness absorb hydrogen from the (001)-oriented TiH$_x$ grown in the early deposition stage, because of the lack of supply of hydrogen from the substrate. Hydrogen-released TiH$_x$ becomes instable, and then transforms to hydrogen-solved hcp-Ti: the maximum solubility of hydrogen in hcp-Ti is 7.9%. Thus, the (001)-oriented TiH$_x$ disappears in the 100 nm thick Ti films. On the other hand, it was found that the band-like region of (110)-oriented TiH$_x$ appeared in the BF image of the film above 20 nm in thickness [22]. In the 100 nm thick Ti films, the (110)-oriented TiH$_x$ exist in the band region, in addition to the (03 5)-oriented hcp-Ti, as shown in Fig. 1(b). Therefore, it seems reasonable to suppose that the atomic arrangements of the (03 5)-oriented hcp-Ti participate in the epitaxial orientation of the (110)-oriented TiH$_x$. In other words, the growth of the (110)-oriented TiH$_x$ crystallites can be explained by considering the atomic arrangement of the (03 5)-oriented hcp-Ti. Figure 3 shows the detailed atomic arrangement of the (03 5)-oriented hcp-Ti. The electron beam enters in the [0 1 1]-direction, which is perpendicular to the (03 5) plane and to the substrate surface. In this orientation of hcp-Ti, the (03 8) and (03 4) planes are nearly parallel and perpendicular to the substrate surface, respectively. In fact, the (03 8) and (03 4) planes make angles of 13° and 102° with the (03 5) plane, respectively. The (03 8) plane makes an angle of 89° with the (03 4) plane, and the rectangle atomic arrangement CEKN in the (03 8) plane is similar to those in the (110) and (001) planes of the (110)-oriented TiH$_x$, respectively.
FIG. 4: ED pattern (a) and BF image (b) were taken from a N-implanted Ti film with N/Ti=0.81. DF images (c) and (d) were taken with the 002 and 020 reflections of TiN<sub>y</sub>, respectively. Note that the band-like contrast region indicated by an arrow in (b)-(d).

In-situ TEM observations of nitriding processes of Ti films, as can be seen from the comparison of Fig. 1 with Fig. 4, have revealed that the (110)-oriented TiN<sub>y</sub> is formed by nitriding the (110)-oriented TiH<sub>x</sub> in the band-like contrast region of the as-deposited Ti film. Therefore, the N-implantation makes TiH<sub>x</sub> crystallites instable and induces the transformation to other stable crystallites, TiN<sub>y</sub>, not to hcp-Ti. In other words, the H-released TiH<sub>x</sub> becomes instable and absorbs implanted N atoms to maintain the fcc-Ti sublattice in N-implanted Ti films. The release of H induced by N-implantation has been confirmed by the result of elastic recoil detection analysis in Fig. 7 of the previous paper [18]. The occupation of O-sites of the H-released fcc-Ti sublattice by implanted N atoms leads to stabilization of the instable fcc-Ti sublattice, without transformation of the sublattice to hcp-Ti. This process results in the formation of stable (110)-oriented TiN<sub>y</sub> from (110)-oriented TiH<sub>x</sub> without changing the orientation of the fcc-Ti sublattice.

Comparing of Fig. 1 with Fig. 4, it has been revealed that the (001)-oriented TiN<sub>y</sub> is mainly formed epitaxially by the transformation of the (03 · 5)-oriented hcp-Ti to (001)-oriented fcc-Ti, partially inheriting the atomic arrangement of the square and/or the octahedron of the hcp-Ti, accompanied by the occupation of O-sites of the fcc-Ti sublattice by N atoms. Schematic representation of the nitriding process of hcp-Ti is shown in Figs. 2(b) and...
FIG. 5: Variation of energy loss spectra for nitriding of TiH$_x$ grown in the deposited Ti film. N/Ti ratios are (a) 0, (b) 0.08, (c) 0.27, (d) 0.42 and (e) 0.65, respectively.

FIG. 6: Variation of energy loss spectra for nitriding of hcp-Ti grown in the deposited Ti film. N/Ti ratios are (a) 0, (b) 0.08, (c) 0.27, (d) 0.42 and (e) 0.65, respectively.

The square EFJK of hcp-Ti in Fig. 2(c) leads to the square EFJK of fcc-Ti in Fig. 2(b) during the above epitaxial hcp-fcc transformation. In order to obtain a fcc-Ti structure of Fig. 2(c), Ti atoms in the (00·1) plane including A, B, C and D atoms have to be shifted in the same way that the C atom is shifted to the center of gravity of the triangle BDC. In this transformation, the inheritance of the square EFJK in Fig. 2(c) plays a prominent role in the epitaxial formation of the fcc-Ti sublattice. This hcp-fcc epitaxial transformation process is the reverse process of the fcc-hcp epitaxial transformation in the growth of (03·5)-oriented hcp-Ti from the (001)-oriented TiH$_x$, as mentioned in Section III.A. More detailed study of this hcp-fcc epitaxial transformation mechanism has been reported in our previous paper [23].

Figures 5(a) and 6(a) show the electron energy loss spectrum obtained from the area of TiH$_x$ as shown by a large arrow in Fig. 1(b), and from the area where hcp-Ti grew outside the band-like contrast region, respectively. On the other hand, Figs. 5(b)-5(e) and 6(b)-6(e) show electron energy loss spectra obtained from the nitriding area of TiH$_x$, and from the nitriding area of hcp-Ti, respectively. Each EELS spectrum in Figs. 5 and 6 was obtained by focusing the electron beam of TEM on the corresponding area during N-implantation. Analysis of EELS spectra elucidated that the energy loss peak of ∼20 eV, indicated by a solid triangle in Fig. 5(a), was ascribed to excitation of plasma oscillation (plasmon) for TiH$_x$. The peak due to excitation of plasmon is also in agreement with that of TiH$_x$, which was reported by Thomas [24]. Further, the energy loss peak of ∼17.5 eV, indicated by a solid triangle in Fig. 6(a), is due to that of plasmon for hcp-Ti. The energy loss of ∼17.5 eV for hcp-Ti was found to agree well with that reported by Robins et al. [25] and the theoretical value of ∼17.6 eV, which is the energy loss due to excitation of plasmon, calculated assuming all 3d and 4s electrons to be free. The loss peak (∼47 eV) denoted by the line of Ti 3p-3d corresponds to the Ti 3p-3d resonant photoemission [26], in which the electron is excited from the Ti 3p state to an empty Ti 3d state and then relaxes back to the Ti 3p state, and another electron from Ti 3d states is ejected. It should be noted that the Ti 3p-3d peaks are almost invariant with the N/Ti ratio in this experiment, as seen in both Figs. 5 and 6. This means that the energy of core levels is almost invariant during the N-implantation. Therefore, inspection of the above energy loss due to the excitation of plasmon shown in Figs. 5 and 6 gives us the information on the bonding character between Ti and ligand (H or N) atoms and on the electron density of conduction and/or valence bands.

In the early N-implanting stage, the loss peak indicated by a solid triangle in Fig. 5(b) shifts to lower energy side than that in Fig. 5(a), while there is no shift between the loss peaks indicated by solid triangles in Figs. 6(a) and 6(b). This shift to lower energy side means that the electron density in the valence band consisting of Ti 3d-Ti 4p and H 1s bonding states decreases with increasing N dose in the early N-implanting stage, which suggests the release of H atoms from the TiH$_x$. In light of these results,
it can be concluded that the release of H atoms from
the TiH\textsubscript{2} occurs preferentially, rather than the occupation of
O-sites of the H-released fcc-Ti sublattice by N atoms, in
the early N-implanting stage. On the other hand, the loss
peaks indicated by solid triangles in both Figs. 5(b)-5(e) and
Figs. 6(b)-6(e) have been gradually shifted to higher
energy side in the subsequent N-implanting stage. The energy
loss peaks due to plasmon excitation indicated by
solid triangles gradually shifted to higher energies with
increasing dose. The loss peak (\(\sim 16.0 \text{ eV}\)) denoted by
the dotted line connected to the solid circle can be seen
at \(N/Ti \geq 0.266\). This peak is considered to be due to
excitation of N 2s electrons to the conduction band, as
discussed above. The peaks of the energy loss of 24.5 eV
in Figs. 5(e) and 6(e) were found to be similar to the
energy loss of 24.9 eV due to excitation of plasmon for
TiN, reported by Pfüger \textit{et al.} [1].

To investigate changes in the electronic structures of
as-deposited and N-implanted Ti films in detail, DV-X\textalpha
MO calculations have been performed for the Ti\textsubscript{19} cluster
and Ti\textsubscript{14}N\textsubscript{13} cluster models shown in Figs. 3(a) and 3(d)
of our previous paper [23]. The DOS curves for the Ti\textsubscript{19}
cluster are shown in Fig. 7. Curves of Ti 3d, Ti 4s, Ti
4p and Total correspond to DOS's of Ti 3d, Ti 4s, Ti 4p and
superimposition (total DOS), respectively. The line at 0.0 eV
represents \(E_f\).

FIG. 7: Local density of states (DOS) curves for Ti\textsubscript{19} cluster. Curves of Ti 3d, Ti 4s, Ti
4p and Total correspond to DOS’s of Ti 3d, Ti 4s, Ti 4p and
superimposition (total DOS), respectively. The line at 0.0 eV
represents \(E_f\).

FIG. 8: Local density of states (DOS) curves for Ti\textsubscript{14}N\textsubscript{13} cluster. Curves of Ti 3d, Ti 4s, Ti
4p, N 2s, N 2p and Total correspond to DOS’s of Ti 3d, Ti 4s, Ti
4p, N 2s, N 2p and superimposition (total DOS), respectively. It is seen from
Fig. 8 that the occupied states consist of bonding states
from -2.4 eV to -9.8 eV and the antibonding states from
\(E_f\) to -2.2 eV. The bonding states are mainly derived from
N 2p, whereas the antibonding states are mainly derived
from Ti 3d. The DOS curves for the Ti\textsubscript{14}N\textsubscript{13} cluster are
similar to those calculated by Pfüger \textit{et al.} [1].

The loss peaks due to the excitation of plasmon indicated
by a solid triangle in both Figs. 5(b)-5(e) and Figs. 6(b)-6(e)
have been gradually shifted to higher energy side in the
subsequent N-implanting stage. This means that the number
of N atoms bonding to Ti atoms increases, and
that the electron density in the valence band hybridized
by N 2p and Ti 3d-Ti 4p states increases gradually with
increasing N dose. In fact, it can be seen from Fig. 8 that
the proceeding of hybridization of the Ti 3d-Ti 4p states
in the N 2p state by N-implantation results in the increase
in the electron density of the valence band, which leads
to the shift of the plasmon peak to higher energy loss side
in the subsequent N-implanting stage. Comparing Fig. 8
with Fig. 7, it can be seen that , in the energy region
below \(E_f\), the DOS’s profiles of Ti 3d, 4s and 4p
apparently shift to the lower energy side as the results of their
hybridization with N 2p. Thus, the average energies of
occupied Ti 3d, 4s and 4p states are lowered by the hy-
bridization of the Ti 3d, 4s and 4p states with the N 2p
state. This reduction in the average energies gives rise to
the higher stability and hardness of TiN than those of Ti.
Moreover, careful inspection of the peak at about
\(-15 \sim -17 \text{ eV}\) indicates that the N 2s state is a main
component in the peak, although it hybridizes slightly
with the Ti 3d and 4s states. The excitation of electrons in
the slightly hybridized N 2s states to the conduction
band results in the energy loss (\(\sim 16.0 \text{ eV}\)) denoted by
the dotted line connected to the solid circle in Figs. 5 and 6.
IV. CONCLUSIONS

In the Ti films deposited on NaCl substrates, there co-exist mainly (03·5)-oriented hcp-Ti and (110)-oriented TiH<sub>2</sub> crystallites. The (03·5)-oriented hcp-Ti grows inheriting the fourfold symmetry of the square atomic arrangement of (001)-oriented TiH<sub>2</sub> grown in the early deposition stage. On the other hand, the (110)-oriented TiH<sub>2</sub> nucleates and grows naturally inheriting the rectangle angular arrangement in the (03·8) and the square atomic arrangement in the (03·4) plane of the (03·5)-oriented hcp Ti, which correspond to those in the (110) and (001) planes of the (110)-oriented TiH<sub>2</sub>, respectively, accompanied with the occupation of the T-sites by hydrogen atoms. The rectangle and square atomic arrangements continue straightly in the [2T·0] direction. Thus, (110)-oriented TiH<sub>2</sub> crystallites grow preferentially in the [2T·0] direction, which corresponds to the [T10] directions of TiH<sub>2</sub> crystallites and NaCl substrates. It is considered that so-formed incipient (110)-oriented TiH<sub>2</sub> crystallites in the (03·5)-oriented hcp-Ti combine with other (110)-oriented TiH<sub>2</sub> crystallites to form band-like regions elongating in the [T10] direction.

In the N-implanted Ti film, the (001)-oriented TiN<sub>y</sub> and (110)-oriented TiN<sub>y</sub> crystallites are formed outside and inside the band-like contrast regions, respectively. The (110)-oriented TiN<sub>y</sub> is formed by nitriding the (110)-oriented TiH<sub>2</sub> in the band-like contrast region of the as-deposited Ti film. The release of H atoms induced by N-implantation and the occupation of O-sites of the H-released fcc-Ti sublattice by implanted N atoms leads to stabilization of the unstable fcc-Ti sublattice, without transformation of the sublattice to hcp-Ti, which results in the formation of stable (110)-oriented TiN<sub>y</sub> from (110)-oriented TiH<sub>2</sub> without changing the orientation of the fcc-Ti sublattice. The release of hydrogen gives rise to the shift of the loss peak due to plasmon excitation to lower loss energy side, which means that the electron density in the valence band consisting of Ti 3d-Ti 4p and H 1s bonding states decreases with increasing N dose in the early N-implanting stage. On the other hand, it has been revealed that the (001)-oriented TiN<sub>y</sub> is epitaxially formed by the transformation of the (03·5)-oriented hcp-Ti to (011)-oriented fcc-Ti, partially inheriting the atomic arrangement of the square and/or the octahedron of the hcp-Ti, accompanied by the occupation of O-sites of the fcc-Ti sublattice by N atoms. The energy loss peaks due to plasmon excitation gradually shifted to higher energies with increasing dose. This means that the number of N atoms bonding to Ti atoms increases with the dose, and that the electron density in the hybridized N 2p/Ti 3d-4p valence band also increases with the dose.

Characterization of deposited Ti films and N-implanted Ti films suggests that the inheritances of the local atomic arrangement of Ti sublattices play a prominent role in the epitaxial fcc-hcp and hcp-fcc formations of the Ti sublattice.

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