In-situ Observation of Nitriding Processes of Deposited-Ti Thin Films due to Ion Implantation in an Analytical Transmission Electron Microscope

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Both hcp-Ti and CaF$_2$-type TiH$_x$ ($x \approx 1.5$), and only hcp-Ti, with preferred orientations have been deposited on NaCl (001) substrates held at room temperature (RT) and 250$^\circ$C, respectively. In order to clarify atomistic growth processes of TiN$_y$ films due to the implantation of nitrogen ions (N$_2^+$) with 62 keV into as-deposited Ti films, changes of the concentration of H and/or N atoms in Ti films, and of the crystallographic and electronic structures of the films by heating and by nitriding have been investigated by in-situ transmission electron microscope (TEM) equipped with electron energy loss spectroscopy (EELS), with the aid of molecular orbital calculations. Hydrogen atoms which constitute TiH$_x$ in the Ti films deposited at RT are released with heating, and are completely released at 350$^\circ$C. The H-released unstable fcc-Ti sublattice is then transformed into hcp-Ti. The energy loss peak due to the plasmon excitation observed by EELS for TiH$_x$ shifts to the lower energy side with the decrease in the electron density in the hybridized valence band, which means the release of H atoms from TiH$_x$ during heating. On the other hand, the TiN$_y$ is epitaxially formed by the N-implantation into the hcp-Ti, through the epitaxial transformation of the hcp-Ti tofcc-Ti sublattice, partially inheriting the atomic arrangement of the hcp-Ti, and accompanying the occupation of O-sites of the transformed fcc-Ti by N atoms. The energy loss peak due to the plasmon excitation during N-implantation into the hcp-Ti films gradually shifts to the higher energy side with the increase in dose of N, which means the increase in the electron density in the hybridized valence band. By comparing the results of EELS with those of Rutherford Backscattering Spectrometry, it is clarified that the maximum concentration of N in Ti films during the N-implantation depends on the implantation temperature. The comparison between the results of EELS and those of the molecular orbital calculations elucidates that the changes of electronic structures near the Fermi level depend on the ratio of N/Ti in the films. Furthermore, taking into account the bonding interaction of Ti sublattices with ligand N atoms, the transformation mechanisms between hcp-Ti and TiN$_y$ due to the implantation of N atoms are proposed. [DOI: 10.1380/ejssnt.2011.191]

Keywords: ion-implantation; TiH$_x$; TiN$_y$; fcc-hcp transformation; in-situ TEM

I. INTRODUCTION

Titanium nitrides, TiN, which are formed by various techniques such as ion implantation, ion beam assisted deposition, magnetron sputtering, physical vapor deposition (PVD) and chemical vapor deposition (CVD), are non-stoichiometric compounds and show covalent properties together with metallic and ionic properties. These make them fascinating for both fundamental research and technological applications [1–11]. The nitrides of Ti are technologically useful as, for instance, corrosion resistant technological applications [1–11]. It was reported through ex-situ experiments that NaCl-type TiN$_y$ films were “epitaxially” grown by N-implantation into as-deposited Ti films held at room temperature (RT) [12–14]. However, ex-situ experiments are known to change the surface composition and structure, and to influence the electronic structure [5]. Therefore, in the present experiment, for the detailed analysis of the crystallographic and electronic structures of TiN films, in-situ observations during the formation of TiN films by N-implantation into Ti films held at RT and 350$^\circ$C have been performed in the transmission electron microscope (TEM) equipped with the instrument for electron energy loss spectroscopy (EELS) and combined with ion accelerators. Atomistic growth processes of TiN$_y$ films due to the N-implantation, which are related to the changes of the concentration ratio of N/Ti, and of the crystallographic and electronic structures of the films during the

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The purpose of this work is to study the changes of the concentration of H and/or N atoms in Ti films, and of the crystallographic and electronic structures of the films by heating and by nitrifying during N-implantation into Ti films in in-situ TEM equipped with the instrument for EELS. And then the atomistic nitrifying processes of Ti thin films due to the N-implantation are discussed with the aid of self-consistent charge discrete variational (DV-Xα) molecular orbital (MO) calculations. The present calculations throw light on the hcp-fcc transformation mechanism between hcp-Ti sublattices and fcc-Ti sublattices due to the implantation of N atoms, taking into account the bonding interaction of Ti sublattices with ligand N atoms. Comparing the concentration ratio of N/Ti estimated by Rutherford Backscattering Spectrometry (RBS) with the N/Ti ratio of each energy loss peak area in EELS during N-implantation, the relationship between the N-concentration in Ti films and the implantation temperature is clarified. Furthermore, the comparison between the results of EELS experiments and those of DV-Xα MO calculations elucidates that the changes of electronic structures near the Fermi level depend on the ratio of N/Ti in the films, in other words, on the extent of hybridization of N atoms with Ti atoms.

II. EXPERIMENTAL

Titanium films of 100 nm in thickness were deposited on thermally cleaned NaCl (001) surfaces held at RT and 250°C, respectively, by an electron beam heating method in an ultra high vacuum. Detailed descriptions of the preparation method for deposited Ti films were presented in earlier papers [12–14]. The Ti films deposited at RT and 250°C, separated from NaCl substrates, were respectively heated up to 350°C at a heating rate of 2°C/min in a 400 kV TEM combined with ion accelerators at JAEA-Takasaki [15]. After the heat treatment, for the Ti films deposited at RT, N-implantations were performed at RT and 350°C, respectively. On the other hand, after the above heat treatment for the Ti films deposited at 250°C, N-implantations were also performed at RT and 350°C, respectively. The implantations of N2+ ions with 62 keV into Ti films held at 350°C and RT were performed in the TEM at an angle of 30° to the surface normal. According to the results of Monte Carlo simulation by the SRIM2003 code, the mean projected range and the full width at half maximum of the depth profile of N2+ with 62 keV were 55 nm and 66 nm, respectively. Judging from the previous RBS experiment [12], it is considered that the implanted N atoms exist through the film, although it is difficult to show the detailed depth profile of implanted nitrogen. The N concentrations in Ti films in the TEM were also estimated from the implantation dose measured by an electric current of a Faraday cage. The maximum dose in this experiment was 8.53×10^{17} atoms/cm², which corresponded to the N/Ti ratio of 1.508. The N/Ti ratios indicate the average atomic concentration of implanted N atoms with respect to Ti atoms in the films. The method of DV-Xα MO calculations for investigation of the electronic structures of hcp-Ti and TiN_y has been given elsewhere [16]

![Image](http://www.ssaj.org/ejssnt/ JVOLUME 9 (2011)
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FIG. 1: ED pattern (a), BF image (b) and DF image (c) were taken from a 100-nm-thick Ti film deposited on the NaCl substrate at 250°C. (c) was taken with the 10-1 reflection of (03-5)-oriented hcp-Ti. Arrows in (b) and (c) indicate bend contours. On the other hand, ED pattern (d), BF image (e) and DF image (f) were taken from a N-implanted Ti film with N/Ti=1.06 at RT. (f) was taken with the 200 reflection of (001)-oriented TiN_y. An arrow in (f) indicates one of a lot of small grains (2-4 nm in diameter).

III. RESULTS AND DISCUSSION

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 the NaCl substrate held at 250°C. The reflections indicated by the four-index system are obtained from hcp-Ti. Figure 1(c) is a dark field (DF) image taken from the 10-1 reflection in Fig. 1(a). It can be seen from the BF and DF images that there are comparatively large crystallites (grains with 20-40 nm in diameter), which show bend contours. An analysis of Figs. 1(a)-1(c) indicates that only hcp-Ti crystallites (lattice constants: a = 0.296 nm, c = 0.471 nm) exist in the film and that the orientation relationship between the hcp-Ti and NaCl is (03-5) Ti // (001) NaCl and [21-0] Ti // [110] NaCl, which is hereafter called (03-5)-oriented hcp-Ti.

Nitrogen ions with 62 keV were implanted at RT into the hcp-Ti film, which had the ED pattern as shown in Fig. 1(a). Figures 1(d) and 1(e) show, respectively, a typical ED pattern and a BF image taken from the N-implanted Ti film with N/Ti=1.06. The reflections indicated by the three-index system are obtained from TiN_y.
The DF image of Fig. 1(f) is taken from the 200 reflection of TiN$_y$ in Fig. 1(d). An analysis of Figs. 1(d)-1(f) indicates that only NaCl-type TiN$_y$ (lattice constant: $a = 0.423$ nm) crystallizes exist in this N-implanted Ti film. The orientation relationship between the TiN$_y$ and NaCl is (001) TiN$_y$ // (001) NaCl and [100] TiN$_y$ // [100] NaCl, which is hereafter called (001)-oriented TiN$_y$. It should be noted that reflections of hcp-Ti cannot be seen. Thus, the nitriding process accompanied by the transformation of (03-5)-oriented hcp-Ti to (001)-oriented TiN$_y$ (fcc-Ti sublattice) has been completed clearly. On the other hand, in the N-implanted Ti films with N/Ti$<1.0$, there coexist both hcp-Ti and TiN$_y$ crystallites. And the lattice expansions (strain) due to the occupation of N in the octahedral sites of hcp-Ti and fcc-Ti sublattice of TiN$_y$ in the present in-situ observation are observed, which is a reconfirmation of the lattice expansions reported in the ex-situ experiments [12-14]. Thus, the strain due to the increase in the lattice constant can be considered as one of the driving forces for the hcp-fcc transformation. Comparing Fig. 1(b) with Fig. 1(e), it can be seen that many grains with 2-4 nm in diameter are formed as the transformation of (03-5)-oriented hcp-Ti to (001)-oriented TiN$_y$ (fcc-Ti sublattice) will (03-5)-oriented hcp-Ti. Judging from the ED intensity, the growth of the (03-5)-oriented hcp-Ti is preferred to that of the (21-0)-oriented hcp-Ti. Furthermore, the orientation relationship between the hcp-Ti and NaCl substrate is (03-5) Ti // (001) NaCl and [21-0] Ti // [110] NaCl for (03-5)-oriented hcp-Ti, and (21-0) Ti // (001) NaCl and [00-1] Ti // [100] NaCl for (21-0)-oriented hcp-Ti. The (03-5)-oriented hcp-Ti brings the 11-1 and 10-1 reflections, whereas the 01-1 and 00-2 ones stem from the (21-0)-oriented hcp-Ti. Judging from the ED intensity, the growth of the (03-5)-oriented hcp-Ti is preferred to that of the (21-0)-oriented hcp-Ti. Furthermore, the orientation relationship between the hcp-Ti and NaCl substrate is (03-5) Ti // (001) NaCl and [21-0] Ti // [110] NaCl for (03-5)-oriented hcp-Ti, and (21-0) Ti // (001) NaCl and [00-1] Ti // [100] NaCl for (21-0)-oriented hcp-Ti. The 002* and 111* reflections in Fig. 2(a) stem from TiH$_x$ in Ti films. With increasing temperature of the as-deposited Ti film, reflections of 002* and 111* weaken gradually and disappear completely at 350°C, as shown in Fig. 2(b), whereas ED intensities of the 11-1 and the 01-1 reflections are slightly intensified, which indicates that the numbers of both the (03-5)- and the (21-0)-oriented hcp-Ti crystallites increase a little. These results show that H atoms which constitute TiH$_x$ are completely released at 350°C, and that all TiH$_x$ crystallites have been transformed into hcp-Ti at 350°C. The H-released unstable (110)-oriented fcc-Ti sublattices are transformed into hcp-Ti sublattices with two kinds of orientation: the (03-5)-oriented hcp-Ti exists preferentially compared with the (21-0)-oriented hcp-Ti crystallites. Analysis of the ED pattern in Fig. 2(c) elucidates that when N atoms are implanted into Ti films heated up.

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to 350°C that have the ED pattern as shown in Fig. 2(b), NaCl-type TiN_y crystallites with two kinds of orientation are formed. One is (001)-oriented TiN_y: (001) TiN_y // [001] NaCl and [100] TiN_y // [100] NaCl, and the other is (110)-oriented TiN_y: (110) TiN_y // (001) NaCl and [001] TiN_y // [110] NaCl. The (001)- and (110)-oriented TiN_y give rise to the 020 and ¯111 reflections in Fig. 2(c), respectively. In the N-implanted Ti film (N/Ti=0.954), there coexist TiN_y (lattice constant: a = 0.424 nm) and a small amount of hcp-Ti (lattice constant: a = 0.296 nm, c = 0.485 nm). The orientation relationships of hcp-Ti are the same as those in as-deposited Ti films. The formation of (001)-oriented TiN_y is preferred to that of (110)-oriented TiN_y in N-implanted Ti films. On the other hand, the implantation of nitrogen ions with 62 keV at RT into the Ti film that has the ED pattern as shown in Fig. 2(b), also gives rise to the results just like those of the above N-implantation at 350°C.

Figure 3 shows the variation of energy loss spectra with the increase in temperature of the films that were deposited at RT. Figures 3(a) and 3(b) show the electron energy loss spectra obtained from the area of hcp-Ti at RT and from that of TiH_x at RT, respectively. The loss peak (∼47 eV) denoted by the line of Ti 3p–3d corresponds to the Ti 3p–3d resonant photoemission [17], in which an electron is excited from the Ti 3p state to an empty Ti 3d state and then an electron relaxes back to the Ti 3p state, and another electron of Ti 3d states is ejected. It should be noted that the positions of Ti 3p–3d peaks are almost invariant with increasing the temperature in the present experiments, as seen in both Figs. 3(a) and 3(b). This means that the energy of core levels is almost invariant with the temperature. Therefore, inspection of the energy loss due to the excitation of plasmon shown in Figs. 3(a) and 3(b) gives us the information on the bonding character between Ti and ligand H atoms and on the electron density of conduction and/or valence bands. Analysis of EELS spectra elucidates that the energy loss peak of ∼17.0 eV, indicated by a solid triangle in Fig. 3(a), is ascribed to excitation of plasmon for hcp-Ti. This energy loss of ∼17.0 eV, is found to agree well with the theoretical value, ∼17.6 eV, of the energy loss due to excitation of plasmon, calculated with the assumption that 3d and 4s electrons are all free [18]. For TiH_x in Fig. 3(b), the energy loss peak of ∼19.5 eV, indicated by a solid triangle at RT, is due to excitation of plasmons by electrons in the valence band consisting of bonding states formed by Ti 3d–4p and H 1s orbitals, which is in agreement with the energy loss reported by Thomas [19]. The higher energy loss for TiH_x than for hcp-Ti at RT can be considered to reflect the existence of additional electrons from H atoms, which results in an increase in the electron density of the hybridized band of Ti 3d–4p and H 1s orbitals. The energy of the loss peaks indicated by solid triangles for TiH_x in Fig. 3(b) shifts to the lower energy side with increasing film temperature, while there is no shift among the loss peaks indicated by solid triangles for hcp-Ti in Fig. 3(a). This means that the electron density in the valence band consisting of Ti 3d–4p and H 1s bonding states decreases with the release of H atoms from the TiH_x due to the increase in film temperature. Thus, it is considered that the excitation of electrons of Ti 3d–4p and H 1s bonding states to the anti-bonding states has been induced by heating the TiH_x up to 100-150°C, and that the increase in the number of phonons by heating mainly contributes to make the excitation of electrons of the bonding states to the anti-bonding states easy.

Figure 4 shows the variation of the area ratio, N/Ti, of energy loss peaks by N 1s (K) and Ti 2p (L_2,3) electrons in EELS spectra with respect to the atomic concentra-
FIG. 5: Variation of N/Ti ratios for the Ti films deposited and N-implanted at RT, evaluated from RBS with respect to the dose of N and the ratio of N/Ti estimated by the dose of N. The vertical axis is the atomic concentration ratio of N/Ti estimated from RBS spectrum, taking account of the nuclear elastic scattering cross section for N reported by Kashy et al. [20] and Rutherford scattering cross section for Ti.

FIG. 6: (a) Variation of EELS spectra with the dose of N. Solid triangles indicate the energy loss peaks due to plasmon excitation. (b) Variation of energy loss peaks due to excitation of Ti 2p (L_{2,3}) electrons in EELS spectra during N-implantation.

The ratios of N/Ti estimated by the dose of N directly reflect the ratios of components of N/Ti in Ti films during N-implantation before the saturation stage. This is because before the saturation stage, the ratios of N/Ti evaluated from RBS vary with those estimated by the dose of N along with the ideal straight line, which suggests that there is no escape of N before the saturation stage during N-implantation. As a result, it can be considered that with the knowledge of N/Ti ratios of each peak area in EELS, the constitution of Ti films during N implantation before the saturation can be in-situ obtained.

Furthermore, in the saturation stage, the ratios of N/Ti in Fig. 4 are separated into two tendencies characterized by dotted and broken saturation lines depending on different implantation temperatures. The value of broken saturation line of N-implantation at 350°C is smaller than that at RT indicated by the dotted line. This means that the number of N atoms bonding to Ti atoms decreases with increasing the N-implantation temperature in the saturation stage from RT to 350°C. Thus, it is considered that the frequency for the excitation of electrons from bonding states consisting of Ti 3d–4p and N 2p to the anti-bonding states is higher at 350°C than at RT during N-implantation in the saturation stage. Besides, the increase in the number of phonons by increasing the temperature also contributes to the excitation of electrons from the bonding states to the anti-bonding states easier.

As a result, the excited lighter atoms, N atoms, become unstable and escape from the Ti film. Thus, there are lesser N atoms reserved in the film at the higher implantation temperature.

Figure 6(a) shows the variation of energy loss spectra with N-implantation into hcp-Ti at RT. It can be seen from Fig. 6(a) that the energy loss peaks due to plasmon excitation indicated by solid triangles gradually shift to the higher energy side with increasing dose of N. This means that the number of N atoms bonding to Ti atoms increases, and that the electron density in the valence
been performed for the Ti of the epitaxial transformation of Ti thin films due to the energy loss of 24.5 eV for N/Ti=0.962 in Fig. 6(a) is similar to the energy loss of 24.9 eV due to excitation of plasmon for TiN, reported by Pfüger et al. [1].

Figure 6(b) shows the variation of energy loss peaks due to excitation of Ti 2p (L2,3) electrons in EELS spectra during N-implantation. The two energy loss peaks due to excitation of Ti 2p (L2,3) electrons can not be distinctly seen in EELS spectra as usual. The reason is that in the present experiments the high probability of multiple scattering of incident electrons leads to low resolution in EELS spectra especially in high energy loss region, since the thickness of Ti films is 100 nm, which is thick for elastic scattering of electrons. However, from the Fig. 6(b), it can be seen that with the increase in the ratio of N/Ti, the two peaks due to excitation of Ti 2p (L2,3) electrons become broaden, which finally leads to the smearing of the distinction of the two peaks. The reason for this change will be discussed by using the local density of states (DOS) calculations later.

In order to elucidate the atomistic nitriding processes of the epitaxial transformation of Ti thin films due to N-implantation in detail, DV-Xa MO calculations have been performed for the TiN cluster and TiN cluster models shown in Fig. 7(a), and the TiN cluster model in Fig. 7(b), respectively. The TiN cluster model, which does not include a nitrogen atom indicated by an open circle G in Fig. 7(a), corresponds to a part of the hcp-Ti structure. The Ti-Ti distances are taken to be 0.29238 nm, corresponding to those of the ideal bulk crystal structure of TiN. The values of calculated Mulliken bond overlap population (OP) of each bond between Ti atoms for TiN cluster models in Fig. 7(a) have been inspected in detail, and are shown in Table I.

| Cluster model | A-B, A-C | A-D, A-E | A-I, A-H | C-B, D-E | C-I, D-H |
|---------------|----------|----------|----------|----------|----------|
| TiN           | 0.231    | 0.231    | 0.319    | 0.319    | 0.319    |
| TiN           | 0.135    | 0.254    | 0.200    | 0.348    |

The OP values refer to the strength of covalent bonds. Table I shows relatively large differences between the OP value of A-B, A-C, A-D, A-E atoms and that of A-I, A-H atoms, and between the OP value of C-B, D-E atoms and that of C-I, D-H atoms for TiN, compared with those for TiN. This indicates that bonds between Ti atoms of the octahedron occupied by N atoms, as the octahedra ABCDEFG in Fig. 7(a), weaken, whereas bonds between Ti atoms of the octahedron not occupied by N atoms, as the octahedra ACDEHIJ, are not changed, or rather strengthen a little. The weakening of Ti–Ti bonds caused by the occupation of the O-sites by N atoms promotes expansion of the spacing between (001)-planes, which results in the TEM-observed lattice expansion in the c-axis of hcp-Ti by N-implantation. On the other hand, the OP value of Ti–N bonds as A-G and F-G bonds in Fig. 7(a) is 0.277, and becomes relatively larger compared with the OP value of Ti–Ti bonds (0.135) in the octahedra ABCDEFG for TiN. Thus, it can be considered that the strengthening of the A-G and F-G bonds promotes the shear in the FL (010) direction on the (001)-plane including B, E, F atoms for the TiN model. In order to obtain an fcc sublattice by the hcp-fcc transformation, the atoms on the (001)-plane including B, E, F atoms for TiN have to be shifted. The direction of shift is the FL (010) direction. After the shift, the F atom, for example, has to be at the center of gravity of the BEF triangle. The projected line of line FA to the (001)-plane including B, E, F atoms for TiN is on the line FL. The square formed by C, D, H and I atoms and the octahedra formed by A, C, D, H, I and J atoms in Fig. 7(a) are preserved during this hcp-fcc transformation. The inheritance of square atomic arrangement formed by C, D, H and I atoms and the octahedra is responsible for the epitaxial growth of (001)-oriented TiN. Thus, the shift of the F atom to the center of gravity of the triangle BEF promoted by the forming of the strong A–G and F–G bonds and the weakening of the C–B and D–E bonds for TiN, and the inheritance of square atomic arrangement formed by C, D, H and I atoms, can be considered to be the origin for the hcp-fcc transformation of Ti sublattices and epitaxial growth of TiN.

The calculated local DOS curves for the hcp-TiN and TiN cluster models are shown in Figs. 8(a) and (b), respectively. The lines at 0 eV represent the Fermi level, $E_F$. 

![FIG. 7: Schematic illustrations of (a) TiN and (b) TiN cluster models and (b) TiN cluster model. Solid circles and open circles represent Ti and N atoms, respectively.](http://www.sssj.org/ejssnt/)

TABLE I: Overlap population of each bond between Ti atoms for the TiN and TiN cluster models shown in Fig. 7(a).
FIG. 8: The calculated density of states (DOS) curves for (a) the hcp-Ti$_{19}$ and (b) the Ti$_{14}$N$_{13}$ cluster models, respectively. The line at 0 eV represents the Fermi level, $E_f$.

By comparing the DOS between cluster models of hcp-Ti$_{19}$ and Ti$_{14}$N$_{13}$, it can be seen that the peak indicated by the 3d-max (maximum density of states) is broadened, which comes from newly forming the hybridized states by Ti 3d and N 2p states. Taking account of the selection rule of dipole transition, the excitation from Ti 2p to Ti 3d is preferred. The unoccupied DOS (mainly 3d character) for Ti 2p (L$_{2,3}$) electrons to be excited become expanded. Therefore, the two energy loss peaks due to excitation of Ti 2p (L$_{2,3}$) electrons become smearing with each other even if the core levels of Ti 2p (L$_{2,3}$) are invariant. It can be considered that this broadening of unoccupied 3d DOS near the Fermi level gives rise to the metallic property of TiN$_y$, regardless of forming the strong Ti–N covalent bonds. The further investigation concerning the changing in energy loss peaks due to Ti 2p (L$_{2,3}$) during N-implantation is in progress.

IV. CONCLUSIONS

In order to clarify atomistic growth processes of TiN$_y$ films due to N-implantation into as-deposited Ti films, changes of the concentration ratio of N/Ti, the crystallographic and electronic structures of Ti films by heating and by nitridding during N-implantation were investigated by in-situ observations of TEM and EELS, with the aid of DV-Xo calculations. Hcp-Ti and CaF$_2$-type TiH$_x$ (x $\approx$ 1.5), with preferred orientations had been grown in Ti films deposited on NaCl (001) substrates held at RT. On the other hand, only hcp-Ti with preferred orientation had been grown in Ti films deposited on NaCl (001) substrates held at 250°C. After the separation from NaCl substrates, the Ti films were heated up to 350°C in the TEM connected to ion accelerators. Hydrogen atoms which constituted TiH$_x$ were released from the as-deposited Ti films with heating, and were completely released at 350°C. The H-released unstable fcc-Ti sublattice was transformed into hcp-Ti. Thus, before N-implantation, only hcp-Ti was observed in the Ti films, despite the differences in Ti-deposition temperatures. The energy loss peak due to the plasmon excitation by EELS for TiH$_x$ shifted to the lower energy side resulting from the release of H atoms in TiH$_x$ during heating. The TiN$_y$ was epitaxially formed by the N-implantation into the hcp-Ti films, through the transformation of the hcp-Ti to fcc-Ti sublattice, partially inheriting the atomic arrangement of the hcp-Ti and accompanying the occupation of O-sites of the fcc-Ti by N atoms. The energy loss peak during N-implantation into hcp-Ti films gradually shifted to the higher energy side with the increase in dose, due to the increase in the electron density in the hybridised valence band. The bonding interaction of Ti sublattices with N atoms gave rise to the formation of stronger covalent bonds, and to the weakening of Ti–Ti bonds. Thus, it is considered that the shear in the ⟨011⟩ direction of hcp-Ti promoted by the formation of the strong Ti-N bonds and the weakening of the Ti-Ti bonds is the origin for the hcp-fcc transformation of Ti sublattices. Therefore, it is concluded that the shift of the atoms on the closed-packed plane induced by the change of bonding interaction of Ti sublattices with ligand N atoms plays an important role in the transformation of hcp-Ti sublattices to fcc-Ti sublattices due to the occupation by N atoms. By comparing the EELS experiments with RBS experiments, it was clarified that the concentration of N in Ti films before the saturation stage and the maximum concentration in the saturation stage depended on the implantation dose and the implantation temperature, respectively. The value of the maximum concentration in the saturation stage at 350°C was smaller than that at RT. This indicates that the number of N atoms bonding to Ti atoms decreases with increasing the temperature of Ti films during N-implantation. Then, it is considered that the frequency for the excitation of electrons from Ti 3d–4p and N 2p bonding states to the anti-bonding states is higher at 350°C than at RT in the saturation stage, taking account of the increase in the number of phonons. Furthermore, The two energy loss peaks due to excitation of Ti 2p (L$_{2,3}$) electrons in EELS spectra became smeared with each other during N-implantation. This means that the unoccupied DOS (mainly 3d character) for Ti 2p (L$_{2,3}$) electrons to be excited become expanded, as can be suggested by MO calculations, which leads to the metallic property of TiN$_y$. In other words, it is considered that both metallic and covalent properties of TiN$_y$ originate from the hybridization interaction of Ti 3d with N 2p orbitals.

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