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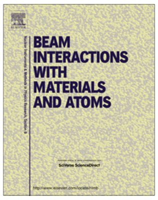

Characterization of epitaxial transformation phenomena induced by the interaction of implanted N-ions with Ti thin films

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ABSTRACT

In order to clarify correlations between implanted N-ions, and Ti sublattices and its ligand atoms (H atoms in TiH_x) in the early N-implantation stage, nitriding processes of Ti thin films during N-implantation were investigated by in situ observations of TEM and EELS, with the aid of DV-Xα calculations. Nitriding of TiH_x in the deposited Ti films by N-occupations of octahedral sites of H-released fcc-Ti sublattices leads to the formation of TiN_y without transformation of Ti sublattices. On the other hand, the shift of the atoms on the closed-packed (00·1) plane of hcp-Ti induced by the bonding interaction of Ti sublattices with implanted N atoms plays an important role in the epitaxial transformation of hcp-Ti to fcc-Ti sublattices due to the occupation by N atoms, partially inheriting the specific atomic arrangements of hcp-Ti. Moreover, it has been found from the analyses of EELS measurements that the hcp–fcc transformation occurs preferentially above a critical concentration ratio, N/Ti ~ 0.25. This means that above the N/Ti ~ 0.25, the invasion of an implanted N atom to the N-unoccupied octahedral site in the neighboring unit cell next to the N-occupied one in hcp-Ti occurs preferentially, and induces the growth of nucleus of the hcp–fcc transformation.

1. 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), are non-stoichiometric compounds and show covalent properties as well as metallic and ionic properties, which make them fascinating for both fundamental research and technological applications [1–11]. Their fascinating properties are naturally related to the crystallographic and electronic structures. Due to the covalent properties [2,9–11], the nitrides of Ti are technologically useful as, for instance, corrosion resistant coatings on cutting tools and diffusion barriers in silicon microcircuits [3–8]. It has been revealed that the interesting physical properties are related to the crystallographic (preferred oriented) and electronic structures, and that some properties of epitaxially grown TiN films are superior to those of polycrystalline ones. Thus, much interest has been focused on the epitaxial films and the atomistic interfacial structures between TiN films and substrates [4,6–11]. Recently, it was reported that NaCl-type TiN_y films were "epitaxially" grown by N-implantation into epitaxially deposited Ti films held at room temperature (RT) [12–14], as follows. As-deposited Ti films on NaCl (001) surfaces held at RT consisted mainly of (03·5)-oriented hcp-Ti (lattice constants: $a = 0.296$ nm, $c = 0.471$ nm) and (110)-oriented TiH_x ($x \cong 1.5$; lattice constant: $a = 0.441$ nm). The (110)-oriented TiH_x grew mainly in the band-like contrast region, whereas the (03·5)-oriented hcp-Ti grew only outside the band-like contrast region. (110)-oriented TiN_y crystallites by N-implantation into these deposited Ti films were grown in the band-like contrast region elongated in the $\langle 110 \rangle$ direction of the NaCl substrate, and were distinguished from the (001)-oriented TiN_y crystallites grown preferentially outside the band-like contrast region. These observations have revealed that the TiH_x area can be easily distinguished from the hcp-Ti area in in situ transmission electron microscope (TEM), which leads to acquisitions of information on nitriding processes of both hcp-Ti and TiH_x areas, respectively, by in situ electron energy loss spectroscopy (EELS). However, atomistic growth processes of TiN_y films due to ion implantation, especially correlations between implanted ions and deposited Ti films in the early N-implantation stage, have not been sufficiently studied.

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The purpose of this work is to study correlations between implanted ions, Ti sublattice and its ligand atoms (H atoms in TiH_x) in the early N-implantation stage into Ti films, and then to elucidate epitaxial growth processes of TiN_y films due to ion implantation, using in situ TEM equipped with the instrument for EELS with the aid of self-consistent charge discrete variational $X\alpha$ (DV-$X\alpha$) molecular orbital (MO) calculations. The present study throw light on the detailed relationship between the release of H atoms from as-deposited Ti films and the occupation of octahedral (O-) sites of Ti sublattices by N atoms in the early N-implantation stage.

2. Experimental

Titanium films of 100 nm in thickness were deposited on thermally cleaned NaCl (001) surfaces held at RT 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]. Nitrogen ions (N_2^+) with 62 keV were implanted into the as-deposited Ti films separated from the NaCl substrate, held at RT at an angle of 30° to the surface normal. The implantation of N_2^+ ions, and in situ TEM and EELS observations were performed without removal from the evacuated system in the 400 kV analytical and high resolution TEM connected ion accelerators at JAEA-Takasaki [15]. The Ti film surface is parallel to the NaCl (001), hcp-Ti (03·5), and TiH_x (110) surfaces. The incident direction of the electron beam in TEM is [01·1] of (03·5)-oriented hcp-Ti and the film surface normal. The N_2^+ ion beam is implanted at an angle of 30° to [01·1] of (03·5)-oriented hcp-Ti and [110] of (110)-oriented TiH_x in TEM, although these oriented Ti films are not single crystals [12–14]. 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 and 66 nm, respectively. Judging from this simulation and the previous RBS experiments [12,13], 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 were estimated from the amount of implanted N atoms measured by an electric current of a Faraday cage. In this experiment, the amount of implanted N atoms were from 1.1×10^{16} to 4.3×10^{17} atoms/cm^2, which corresponded to the average concentration ratios of N/Ti from 0.02 to 0.67. In the present experiment, N/Ti ratios are not equal to the value of y in TiN_y, but indicate the average concentration of implanted N atoms with respect to Ti atoms in the films. The method of DV-$X\alpha$ MO calculations for investigation of the electronic structures of hcp-Ti and TiN_y has been given elsewhere [14,16].

3. Results

3.1. TEM observations

Nitrogen ions were implanted into the as-deposited Ti films, which showed the electron diffraction (ED) pattern such as Fig. 1(a) of the previous paper [13]. Fig. 1(a) and (b) show, respectively, typical ED patterns taken from the N-implanted Ti films with N/Ti = 0.054 and 0.135. Reflections indicated by three-index system with and without an asterisk are obtained from CaF_2-type TiH_x and NaCl-type TiN_y, respectively: 002* and 002 reflections in Fig. 1(a) stem from TiH_x and TiN_y, respectively. On the other hand, reflections indicated by four-index system are obtained from hcp-Ti. An analysis of Fig. 1(a) indicates that hcp-Ti (lattice constants: a = 0.296 nm, c = 0.474 nm), TiN_y (lattice constant: a = 0.420 nm) and TiH_x (lattice constant: a = 0.437 nm) coexist in this film. It is worth noting that (110)-oriented TiH_x remains and coexists with (03·5)-oriented hcp-Ti and newly formed TiN_y in the film, although the lattice is slightly contracted by about 1% of that of as-deposited films. This means that H atoms are gradually dissociated from TiH_x during N-implantation. The orientation relationships between hcp-Ti, TiH_x and NaCl substrates are the same as those in as-deposited Ti films. TiN_y is grown in the two orientation; (110)TiN_y // (001)NaCl and [001] TiN_y // $[\bar{1}10]$ NaCl for (110)-oriented TiN_y, and (001)TiN_y//(001)NaCl and [100] TiN_y//[100] NaCl for (001)-oriented TiN_y. Note that the former gives rise to the 002 reflection, whereas the latter gives rise to the 200 one. It can be seen from an analysis of Fig. 1(b) that hcp-Ti (lattice constants: a = 0.297 nm, c = 0.478 nm) and TiN_y (lattice constant: a = 0.420 nm) exist in this film. It is worth noting that reflections of TiH_x cannot be seen. This elucidates that the H atoms that constitute TiH_x are completely dissociated from TiH_x crystallites, and then the transformation from TiH_x to TiN_y occurs at the beginning of N-implantation. Moreover, it should be noted that the intensity of reflections of TiN_y increases with the increase in the amount of implanted N atoms. This means that the implantation of a larger amount of N atoms leads to an increase in the TiN_y area. Therefore, the N-implantation makes TiH_x crystallites unstable and induces the transformation to other stable crystallites, TiN_y, not to hcp-Ti. In other words, it is considered that the H-released TiH_x absorbs implanted N atoms to maintain the fcc-Ti sublattice in N-implanted Ti films. The release of H induced by N-implantation had also been confirmed by the result of elastic recoil detection analysis in the previous paper [12]. 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. This process results in the formation of stable (110)-oriented TiN_y from (110)-oriented TiH_x without changing the orientation of the fcc-Ti sublattice. On the other hand, it has been confirmed that the (001)-oriented TiN_y is mainly formed by the transformation of the (03·5)-oriented hcp-Ti to (001)-oriented fcc-Ti, accompanied by the occupation of O-sites of the fcc-Ti sublattice by N atoms. This epitaxial transformation mechanism of the (001)-oriented TiN_y will be discussed in detail later.

3.2. EELS observations

The electron energy loss spectra during N-implantation obtained from the regions of TiH_x and hcp-Ti are shown in Fig. 2(a) and (b), 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. Since the Ti 3p–3d peaks are almost invariant with the increase of N/Ti ratio in this experiment, as shown in both Fig. 2(a) and (b), the energy loss due to the excitation of electrons in core levels is almost invariant during the N-implantation. The loss peak due to excitation of plasma oscillation of TiH_x is 20.0 eV, as shown in Fig. 2(a) when the ratio N/Ti is 0, which is in agreement with that reported by Thomas [18]. With the increase in N/Ti ratios, for example, from 0.00 to 0.02 and then to 0.07 in Fig. 2(a), the loss peaks shift to the lower energy loss side, near 17.5 eV, which corresponds to the plasmon loss of hcp-Ti. This value also agrees well with the theoretical value for hcp-Ti reported by Robins et al. [19]. This shift to lower energy loss side indicates the decrease in electron density in the hybridized band consisting of Ti 3d-Ti 4p and H 1s bonding states, which suggests that the release of H atoms in TiH_x proceeds with the increase in N-concentration. However, with further increase in N-concentration, the loss peaks shift to higher energy loss side, as shown by those loss peaks with N/Ti ratios from 0.16 to 0.67. It is noticeable that the energy loss reaches 21.0 eV at N/Ti = 0.67, which is smaller than the plasmon loss of TiN_y ($y \sim 1.0$) 24.5 eV reported by Pflüger et al. [1]. This means that the