

## 論文の内容の要旨

### **TiN Thin Film Growth at the Nanometer-Scale: Toward an understanding of the initial stage of non-epitaxial growth**

(TiN 薄膜のナノスケールでの成長機構：非エピタキシャル成長の初期過程の解明を目指して)

李 图强 (Tuqiang Li)

#### **Abstract**

The initial stage of non-epitaxial, heterogeneous growth of TiN thin films onto Si (111) was studied by using transition electronic microscopy. Based on the experimental findings on TiN initial growth and the previous experimental studies on metals growth. A model was proposed to understand the non-epitaxial, heterogeneous growth.

This dissertation includes nine chapters. In chapter 1, the classical theories were reviewed firstly, followed by description of the necessity of understanding non-epitaxial growth, introduction of the previous investigation on non-epitaxial growth of metals and the research background of TiN thin films, purposes and experimental approaches of this research. In chapter 2, the experimental setup and analysis was described in details. Deposition condition optimization was described in chapter 3, and the plasma properties during reactive sputtering under various conditions were given firstly, followed by listing deposition conditions for studying the initial growth mechanism. In chapter 4, the evidential results of formation of continuous, amorphous layers and thickness-dependent crystal nucleation were given. In chapter 5, effects of substrate heating and biasing on nanostructural evolution of non-epitaxially grown TiN nano-films were investigated. In chapter 6, texture formation during reactive magnetron sputtering of TiN on Si (111) was described in details. The interface properties during sputter-deposition of  $\text{TiN}_x$  onto Si (111) were investigated in chapter 7. Based on the experimental results, distinguishing features of non-epitaxial, heterogeneous growth were summarized.

#### **Chapter 1**

Thin films are of interest from many different points of views. Classical initial growth models for thin film growth have not distinguished between epitaxial growth and non-epitaxial growth. For non-epitaxial growth, besides the nucleus density, size distribution etc, which were considered principally in classical theories, the nucleus structure and the nucleus kinetic behavior should be considered in detail due to special features of non-epitaxial growth, such as weaker film-substrate interaction compared with epitaxial growth. Previous researches on non-epitaxial growth have concentrated on metals on amorphous  $\text{SiO}_2$ . In this research we investigate the initial growth of TiN on Si (111) in details at the scales of nanometers, to understand more comprehensively the non-epitaxial growth.

#### **Chapter 2**

The Si (111) substrates were H-terminated in HF solution. TiN films were deposited by

using magnetron reactive sputtering with a titanium target in an N<sub>2</sub>/Ar atmosphere, equipped with dc and rf power sources. The total flow,  $F$ , was maintained at  $F = 20$  sccm through independently controlling the Ar and N<sub>2</sub> flows. The total pressure,  $P$ , in the sputter chamber was controlled at  $P = 0.93$  Pa.  $P_{N_2}$  was calculated from N<sub>2</sub> flow and  $P, F$ . The microstructure of the films was investigated with XRD, and with plan-view and cross-sectional HRTEM. The thickness of the film (40nm – 200 nm) deposited under defined time was measured with a stylus profilometer to determine the deposition rate. The thickness of initial films was calculated from the deposition rate and time. The film composition was determined with in situ Auger Electron Spectroscopy (AES) and ex situ X-ray photoelectron spectroscopy (XPS).

### Chapter 3

The cathode discharge voltage,  $V_T$ , depends on  $P_{N_2}$  when the discharge power was kept constant at 69 W dc.  $V_T$  increased about 40 V when  $P_{N_2}$  increased from 0 to 0.47 Pa. This might be due to the less secondary electron emission on the “poisoned Ti” (TiN) surface. The floating substrate potentials,  $V_F$ , which induced from the different impinging fluxes of positive ions and electrons, increased from -23 V to -29 V when  $P_{N_2}$  changed from 0 to 0.47 Pa. The ion flux (Ar<sup>+</sup>, N<sub>2</sub><sup>+</sup>...) impinging onto the substrate or film surface, calculated from the saturated ion current, was in the order of  $10^{18}$  cm<sup>-2</sup>s<sup>-1</sup>.

The deposition conditions needed to obtain stoichiometric TiN films with good crystallinity were determined by using various N<sub>2</sub> partial pressures of the sputtering gases for both dc and rf sputtering. Both films, deposited under dc and rf power, show the same trend: for an increase in N<sub>2</sub> partial pressure from 0.015 Pa to 0.47 Pa, the preferred orientation of the film changed from TiN (111) to TiN (200). The deposition conditions needed to clarify the initial growth mechanism of TiN were an N<sub>2</sub> partial pressure of 0.047 Pa and 0.47 Pa for dc sputtering and 0.015 Pa for rf sputtering. The other parameters used to clarify the initial growth mechanism were substrate temperature,  $T_s$ , and substrate bias voltage,  $V_b$ . The deposition conditions are shown in detail in Table 1.

### Chapter 4

The initial growth stage of titanium nitride (TiN) deposited by reactive magnetron dc sputtering onto (111)-oriented Si substrates was investigated by using high-resolution transmission electron microscopy (HRTEM). During the initial growth stage, a continuous, amorphous layer was observed when the deposited film was less than 1 nm thick, as shown in Fig. 1(a) and (d). Crystal nucleation occurred from the amorphous layer when the film grew to about 2 nm thick [Fig. 1(b) and (e)]. No preferred orientation was found for the initial crystal nuclei.

The growth of the crystal grains depended on the N<sub>2</sub> partial pressure,  $P_{N_2}$ . When the films were deposited under Condition I, as the deposition time increased from 10 s ( $l_c = 2$  nm) to 30 s ( $l_c = 6$  nm), the average lateral grain size increased from 3.0 to 4.2 nm. On the other hand,

however, when the films were deposited under Condition II, as the deposition time increased from 32 s ( $l_c = 2$  nm) to 60 s ( $l_c = 4$  nm), the average grain size increased from 3.7 to 4.8 nm. Moreover, for  $P_{N_2} = 0.47$  Pa, all the planar grains with large lateral dimension were found to be (200) oriented. This large lateral size under Condition II was presumably caused by grain lateral growth and coalescence. The grains with anisotropic planar shapes have a larger top area than side area, and tend to restructure into (200)-oriented grains to minimize the surface energy under energetic bombardment of the incident atoms/ions. In Fig. 2, several grains [(e)-(h)] with a coalesced shape and large lateral size are showed, and lattice imaging shows that these grains were (200) oriented, four grains [(a)-(d)] formed during 30-s deposition under Condition I were showed as comparison.

## Chapter 5

The effects of substrate heating and substrate biasing on the initial stage of non-epitaxial heterogeneous growth of TiN on Si (111) was studied. Although TiN films deposited at room temperature ( $RT$ ) undergo a transition from continuous, amorphous films to polycrystalline films with three-dimensional grains when the film thickness increased from  $\sim 1$  to 2 nm, crystallization occurred at a substrate temperature,  $T_s = 570$  K, even for film thickness less than 1 nm [shown in Fig. 3(a)]. During the successive grain growth process, when  $l_c$  increased from  $l_c = 0.8$  to 1.6 nm the lateral grain size increased from 2.2 to 3.0 nm, and the lateral grain size was almost the same as the grain height. (shown in Fig. 4) This indicates three-dimensional grain growth and is identical to the XHRTEM results shown in Fig. 3. At  $l_c = 4.8$  nm, the lateral grain growth rate decreased due to the formation of a continuous film, which caused grains to mainly grow vertically. Compared with the grains deposited at  $T_s = 570$  K, the grains grown at  $T_s = RT$  were smaller and had lower lateral growth rate, which indicates the formation of a continuous film earlier in the film-growth process. The evolutionary selection growth, therefore occurs later at  $T_s = 570$  K than that at  $T_s = RT$ , due to that the grains become continuous later than that at  $T_s = RT$ .

At a substrate bias voltage,  $V_b = -70$  V, the grains were laterally larger and were planar as shown clearly in Fig. 5. At the film thickness 50 nm, the film deposited at  $V_b = -70$  V showed thermodynamically favored (200) preferred orientation, whereas the film deposited at  $T_s = 570$  K showed (111) preferred orientation with a weak (200) peak (shown in Fig. 6).

## Chapter 6

The initial texture formation mechanism of TiN films were investigated by using transmission electron microscopy (TEM) and X-ray diffraction (XRD). Two power sources for the sputtering, dc and rf, were compared. As has been shown in Chapter 4 that at the initial growth stage, randomly oriented nucleation occurred from continuous amorphous layers when the film thickness was about 3 nm. The nuclei grew and formed a polycrystalline layer when the film thickness was about 6 nm as shown in Fig. 7(a). As the film grew further, its

orientation changed depending on the deposition conditions. For dc sputtering, the appearance of (111) or (200)-preferred orientations depended on the  $N_2$  partial pressure, and the intensity of the preferred orientation increased with increasing film thickness. This can be seen in Fig. 7(b) and Fig. 8(a). In Fig. 7(b), the grains on the bottom of the film were still randomly oriented, whereas those on the top of the film were dominantly oriented in the (111) direction. For rf sputtering, however, when the film thickness was small, the film showed (200) orientation, independent of the  $N_2$  partial pressure, and further growth caused the film to orient to the (111) orientation when the  $N_2$  partial pressure was low (about 0.015 Pa) [as shown in Fig. 8(b)]. The results indicated that preferred orientation of TiN films is controlled by a competition between kinetic and thermodynamic effects.

## Chapter 7

Fig. 9 shows the XHRTEM images of  $TiN_x$  films deposited at various  $P_{N_2}$ . Fig. 9 (a) and (b) show the films deposited at  $P_{N_2} = 0$  and 0.015 Pa. No interlayer can be found between the deposits and the Si substrate for these two conditions. A small intermixing, with thickness less than 0.5 nm, can be found for film deposited at  $P_{N_2} = 0.047$  Pa (Condition I). For film deposited at  $P_{N_2} 0.47$  Pa (Condition II), however, a distinct interlayer with thickness 1.5-1.8 nm was formed. The contrast of the interlayer was much brighter than that of the  $TiN_x$  layer, and closer to that of Si. This indicates that the interlayer was composed of little Ti, because the relatively heavy Ti atoms efficiently scatter electrons, and would therefore darken the contrast of the layer if it contained high concentrations of Ti.

In order to investigate in details the compositions of the interlayer, ex situ XPS depth profiling was made. Fig. 10 shows the depth profiles for 20-nm thick  $TiN_x$  layers deposited under Conditions I and II. Ti and N compositions maintained a stoichiometric ratio in the films for both conditions I and II. However, for Condition II, N became rich at the TiN/Si interface. Considering that TiN film had a stoichiometric composition, the excess N at the TiN/Si interface could have been caused by the N from the amorphous interlayer. The compositions of the interlayer were mainly  $SiN_x$ .

## Chapter 8

Based on the above experimental findings for initial growth of TiN films onto Si and the previous studies for initial growth of metals, distinguishing features of non-epitaxial heterogeneous growth has been revealed, and the difference from the traditional models for epitaxial thin film growth was clarified. For non-epitaxial growth, the deposit structure is affected by the interface and surface properties, and may lead to an amorphous phase in the initial stage. Two stages (condensation and crystallization) should be considered for the initial amorphous phase of non-epitaxial growth. If the critical size of condensation nucleation is smaller than that of crystallization nucleation, amorphous to crystal transition may be observed, such as in the case of TiN/Si. If the critical size of condensation nucleation is near

to that of crystallization nucleation, amorphous to crystal transition may not be detected, such as Au/SiO<sub>2</sub>. The orientation of the initial grains is mainly determined by the grain surface energy. Restructuring may occur when there is a grain shape-change to meet the free energy minimization. An overall growth model that accounts for the mechanisms above is proposed.

## **Chapter 9 Conclusions**

- Finding of evidence of crystal nucleation from amorphous continuous initial layer
- Larger lateral grain size at high  $P_{N_2}$  or substrate-biasing, and inducing restructuring into (200) orientation
- Increasing  $T_s$  promotes initial aggregation and delays evolution selection growth
- Films grown with rf power have different orientation evolution pass-way due to different plasma effect on initial films
- Growth under the conditions with high flux ratio of  $N_2^+$  causes distinct SiN<sub>x</sub> interlayer
- An overall non-epitaxial initial growth model was proposed.