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Effect of temperature on residual stress and mechanical properties of Ti films prepared by both ion implantation and ion beam assisted deposition

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ABSTRACT

Ti films with a thickness of 1.6 μm (group A) and 4.6 μm (group B) were prepared on surface of silicon crystal by metal vapor vacuum arc (MEVVA) ion implantation combined with ion beam assisted deposition (IBAD). Different anneal temperatures ranging from 100 to 500 °C were used to investigate effect of temperature on residual stress and mechanical properties of the Ti films. X-ray diffraction (XRD) was used to measure residual stress of the Ti films. The morphology, depth profile, roughness, nanohardness, and modulus of the Ti films were measured by scanning electron microscopy (SEM), scanning Auger nanoprobe (SAN), atomic force microscopy (AFM), and nanoindentation, respectively. The experimental results suggest that residual stress was sensitive to film thickness and anneal temperature. The critical temperatures of the sample groups A and B that residual stress changed from compressive to tensile were 404 and 428 °C, respectively. The mean surface roughness and grain size of the annealed Ti films increased with increasing anneal temperature. The values of nanohardness and modulus of the Ti films reached their maximum values near the surface, then, reached corresponding values with increasing depth of the indentation. The mechanism of stress relaxation of the Ti films is discussed in terms of re-crystallization and difference of coefficient of thermal expansion between Ti film and Si substrate.

1. Introduction

Ti thin films have been extensively studied for their potential applications in micro-electro-mechanical systems (MEMS), medical implants, and intelligent materials [1–9]. However, residual tensile stress in the deposited films will become one critical problem for their wide application, as it influences not only adhesion between film and substrate, but also deformation of MEMS structure, mechanics and thermodynamics of dislocation transformation, and super elasticity effect, etc. [10–12]. The residual stress of thin films has been widely studied [7,8,10–12]. For instance, Fu and Grummon investigated the effects of annealing on residual stress evolution for shape memory TiNi film, and found that stress values are sensitive to annealing process [10,11]. It is clear that long-term stability of the thin metal film is a major concern, and is related closely with the critical temperature. Because the residual stress changing from compressive to tensile is an essential factor for film stability [3,13]. Unfortunately, few investigations on the critical temperature of metal film are reported. It is necessary to study stress relaxation behavior of the metal films annealed at different temperatures, and the critical temperature of the metal film could be deduced. On the other hand, effect of temperature on mechanical properties of the metal film should also be investigated, which is also important to film stability [12–15].

The metal vapor vacuum arc (MEVVA) ion-source implanter was invented in the mid-1980s [16,17]. Ion implantation was proved to be useful to increase adhesive strength between film and substrate [18]. Yu has reported that a mixed layer between a Cu film and a Si substrate, which was created by implantation of Cu ions into the Si matrix, increased the adhesive strength [19]. Ion beam assisted deposition (IBAD) has been used to deposit semiconductor and metal films. It can provide precise control of the ion energy and current. In this work, combination of the standard commercial MEVVA ion-source implanter with an IBAD system in a joint-device was used, that is, Ti ion implantation into

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Si substrate followed by in situ deposition of Ti atoms in the same vacuum chamber. Ti films with a high adhesive strength on surface of the Si substrate were prepared.

In this paper, changes of residual stress and mechanical properties of the Ti films with increasing annealing temperature are reported, and mechanism of stress relaxation is discussed.

2. Experimental

Size of the samples was 10 mm × 10 mm prepared from a 100 mm diameter, (1 0 0) oriented, 435 μm thick silicon wafer with a resistivity of 5.5 Ω cm. The samples were divided into two groups in which they were numbered as A1, A2, A3, A4, A5, A6 (A group), and B1, B2, B3, B4, B5, B6 (B group), respectively. The samples were ultrasonically cleaned with acetone and alcohol, and then rinsed with deionized water before setting into the vacuum chamber. The vacuum chamber was pumped by a turbomolecular pump, assuring a base pressure better than 4×10^{-4} Pa. A pure Ti plate was used as Ti target. Prior to deposition, some additional processes as follows were applied. Firstly, the sample groups A and B were irradiated by argon ions with 20 keV energy and 0.02 mA/cm^2 ion density for 10 min to clean away oxide and impurity on surface of the samples. Secondly, Ti ions with 82 keV energy were implanted into the sample groups A and B by using a metal vapor vacuum arc (MEVVA) ion implanter. Finally, Ti films were deposited on surfaces of the samples by IBAD. The argon ion energy was 2750 eV. The deposition time of IBAD for the sample groups A and B, was 60 and 270 min, respectively. More details of MEVVA–IBAD device can be found somewhere [18,19].

After deposition, the samples were annealed. The anneal process was carried out in a vacuum chamber with a base pressure better than 6×10^{-4} Pa. The samples A1 and B1 were used as control samples. The samples A2 and B2 were heated to 100 °C at a rate of 4 °C/min and kept at 100 °C for 10 min, other samples were heated following the same rate. A3, B3 were heated to 200 °C and kept for 10 min, A4, B4 to 300 °C and kept for 10 min, A5, B5 to 400 °C and kept for 10 min, A6, B6 to 500 °C and kept for 10 min, respectively. The preparation parameters and thickness of all the samples are summarized in Table 1.

The residual stresses of the Ti films were measured by the conventional $\sin^2\psi$–2θ method (XRD measurement) with Cu Kα irradiation at 45 kV/30 mA [15,17]. In the present work, the peak corresponding to Ti (2 0 1) was analyzed. Scanning electron microscopy (SEM), model S450, was used to observe morphology of the samples. Scanning auger nanoprobe (SAN), model PHI 700, LVAC-PHI, Japan, was employed to measure depth profile of the Ti films. Atomic force microscopy (AFM) was used to investigate details of morphology, roughness, and grain size of the Ti films. XP Nano Indenter, MTS, was employed to measure nanohardness and modulus of the Ti films.

3. Results and discussions

3.1. Morphologies

The morphologies of the Ti films were observed by SEM. Fig. 1(a)–(d) shows SEM images of the samples A1, A4, B1 and B4, respectively. In general, the Ti films were uniform. It is found that there is apparent dissimilarity between the control Ti films (A1 and B1) and the annealed Ti films (A4 and B4). Surface of the samples A4 and B4 were much smoother than those of the samples A1 and B1. It indicates that heat effect of the anneal process could influence morphology of the titanium films greatly.

Fig. 2 shows cross-section images of the control samples A1 and B1, respectively. They display clearly the interfaces between Ti film and Si substrate.

3.2. Scanning Auger nano-probe analysis

The depth profiles of the samples A1 and B1 were analysed by scanning Auger nanoprobe (SAN). The argon ion beam with energy of 5 keV was used in the profile measurement. The spot of scanning Ar ion beam was ≤7 nm, and pressure of the analysis chamber was $<3\times 10^{-9}$ Torr. The energy resolution of SAN was 0.1%. Fig. 3 shows depth profile of the control sample A1. It is clear in Fig. 3 that two elements, titanium and silicon were observed. The sputtering rate of the Ti/Si film sputtered by Ar ion with energy of 5 keV was 95 nm/min. The thickness of the sample A1 was 1600 nm. Instead of an abrupt decrease of titanium atomic percentage, a gradient distribution of titanium atom along the depth was obtained. Titanium atoms diffused into the silicon substrate at least 500 nm in depth. It reveals the high adhesion strength of the sample A1 between the Ti film and Si substrate. The depth profile of the control sample B1 was similar with one of the control sample A1, and was not shown here.

3.3. XRD analysis

Fig. 4 shows X-ray diffraction spectra (Cu Kα irradiation, λ = 0.1542 nm) of the samples A2, A4, A6. The XRD spectra of other samples are similar and not shown here. Ti (2 0 1) and Si (4 0 0) peaks were clearly observed in Fig. 4.

A diffracted peak used in the XRD Omega stress method is shown in Fig. 5 [15,17]. The diffracted peak is related to (2 0 1) plane of the titanium film. The 2θ is calculated and plotted as a function of $\sin^2\psi$, as shown in Fig. 6. The residual stress in the titanium films is indicated by the linear behavior of this plot. The positive slope observed in Fig. 6 corresponds to a compressive stress in the Ti film, and the negative slope means a tensile stress.

The residual stress in the MEVVA–IBAD deposited Ti films was formed during preparation process [18–19]. In this experiment, the residual stress in both the sample group A and the sample group B

Table 1
Preparation parameters of the different samples used in the work.

Sample no.	MEVVA ion energy (keV)	IBAD ion energy (eV)/deposition time (min)	Annealing temperature (°C)	Thickness (μm)
A1	82	2750/60	None	1.6
A2	82	2750/60	100	1.6
A3	82	2750/60	200	1.6
A4	82	2750/60	300	1.6
A5	82	2750/60	400	1.6
A6	82	2750/60	500	1.6
B1	82	2750/270	None	4.6
B2	82	2750/270	100	4.6
B3	82	2750/270	200	4.6
B4	82	2750/270	300	4.6
B5	82	2750/270	400	4.6
B6	82	2750/270	500	4.6