Bias voltage influence on surface morphology of titanium nitride synthesized by dynamic nitrogen and titanium plasma immersion ion implantation and deposition

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Abstract

Titanium nitride films were prepared on silicon wafers employing dual titanium and nitrogen plasmas in an immersion configuration. The vacuum arc source provided the titanium plasma and the nitrogen plasma was sustained by hot filament glow discharge. A 30 μs implantation duration and 270 μs titanium arc duration were used in our plasma immersion ion implantation and deposition (PIII–D) process. The impact of the implantation voltages (8, 16 and 23 kV) on the film surface morphology was investigated using atomic force microscopy (AFM). The 8 kV sample shows a surface featuring small islands. The surface of the 16 kV sample is smoother. The cones are more abundant but they are smaller and uniformly distributed on the surface. On the surface of the 23 kV sample, the islands exhibit a directional ripple structure. The implantation voltage unequivocally alters the fabrication dynamics of the coatings, and the difference is believed to be due to the variation in the energy imparted to the substrate at different depths by the incident ions. Films with the optimal surface morphology thus require a suitable voltage process window in the PIII–D technique. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ion bombardment assisted deposition (IBAD) has attracted increasing interests due to its capability to fabricate strongly adhering coatings by ion mixing the films and substrates [1–3]. It has been demonstrated that the surface topography is affected by the ion energy, ion current density, deposited particle flux to incident ion flux ratio, ion species, ion irradiation, and other factors. Most of the previous studies have concentrated on the high-energy ion-beam-scanning mixing effects [1–4] and low-energy large-scale film deposition techniques, such as ion plating, glow discharge sputtering, and plasma-enhanced chemical-vapor deposition in which ion irradiation is concurrent with film growth. Recently, the technique of plasma immersion ion implantation and deposition (PIII–D) has gained publicity, but the influence of high-energy ion irradiation on the morphology of the coatings during PIII–D has seldom been investigated. During PIII–D, the ion mixing effects are substantially different from those in the other aforementioned processes. PIII–D combines pulsed plasma deposition and pulsed high-energy ion irradiation. Consequently, the film is not deposited continuously and neither is ion irradiation. In fact in PIII–D, ion irradiation only occupies a small fraction of the processing time. For example, in our experiments reported earlier [5,6] a cathodic arc with a pulse duration of 200 μs and pulsing frequency of 100 Hz was used while the implantation pulse duration was only 30 μs with the same pulsing frequency as the cathodic arc. Hence, the effective deposition time ratio is 2% and the ion-mixing ratio is 0.3%. The plasma ion assisted film growth process is thus different from that in conventional ones. In this work, we fabricate Ti–N films on silicon using PIII–D and investigate the influence of the irradiation energy on the surface morphology of the films. Ti–O films are also synthe-
sized to compare the effects of the film materials and processing parameters. There is much interest in Ti–N and Ti–O films because Ti–N possesses excellent mechanical and chemical properties such as high hardness, low wear coefficient, and chemical stability [7], whereas Ti–O films have good biocompatibility, high refractive index, and dielectric constant [8,9].

2. Experimental

The samples were cut from commercial silicon wafers in 1 cm² pieces. Before PIII–D, the samples were sputter-cleaned using argon high frequency, low-voltage plasma ion bombardment [10]. The pretreatment conditions were: pulsing frequency = 5 kHz, pulse duration = 25 μs, and bias voltage = −2 kV. Afterwards, nitrogen was bled into the vacuum chamber and a nitrogen plasma was triggered by hot filament glow discharge at a pressure of 0.5 mTorr. A titanium plasma was simultaneously produced using a cathodic arc plasma source [11]. In our experiments, we used three different pulsing voltages, 8, 16 and 23 kV, to investigate the effects of the sample bias on the surface morphology. An implantation duration of 30 μs and repetition frequency of 200 Hz were employed, and the total dynamic mixing and deposition time was 30 min. The length and phase of the deposition and implantation processes could be adjusted easily on the fly in our experiments, and it is one of the distinct advantages of dynamic PIII–D. The actual duration and phase of the metal arc and high voltage pulses were synchronized as shown in Fig. 1. The implantation to deposition ratio was about 1–9. During the implantation phase, both nitrogen and titanium ions were simultaneously implanted and the mixing effects depend on the implantation voltage.

3. Results and discussion

Fig. 2(a–c) depict the three-dimensional atomic force microscopy (AFM) images taken from the films fabricated at the three bias voltages and significant differences can be observed. The surface of the 8 kV sample depicted in Figs. 2 and 3 reveal the existence of uniformly-distributed, large, irregular, and dome-shape features. The round top is about 300 nm in size. The boundaries between the columnar grains do not appear dense as indicated by some holes near the boundaries. At a higher voltage (16 kV), the grains become more abundant but smaller, and the surface is in general smoother. The boundaries are invisible and the grains are in close proximity. In comparison, the surface morphology of the sample treated at 23 kV shows an entirely different pattern. The grains are not uniformly distributed and aligned preferentially in one direction. The bias voltage also affects the surface roughness. As shown in Figs. 3 and 4, the 16 kV sample possesses the smallest roughness corresponding to a root-mean-square (RMS) of 0.23 nm. This value is similar for the 23 kV sample. In contrast, the surface roughness of the 8 kV sample is larger by a factor of 2. This may be due to the deeper grain boundaries as shown in Fig. 3. It should be noted that different processing parameters and variables, including gas species, plasma generation method, and gas pressure affect the surface topography. In our similar experiments in which Ti–O films are synthesized using titanium and nitrogen PIII–D, the RMS roughness is about 2.98 nm [9]. The surface morphology of the two kinds of films is evidently different, even though the bias voltages are very similar, 25 kV for Ti–O and 23 kV for Ti–N (Fig. 5).

In our process, titanium ions condense onto the substrate surface when the sample bias voltage is off while the metal arc voltage is on, and both titanium and nitrogen ions are implanted into the substrate when both voltages are on. When both the titanium arc and sample voltage pulses are off, nitrogen particles from the overlying plasma, including neutral, excited, and molecular species, adsorb onto the sample surface. Dynamic PIII–D is thus more complicated than other processes involving concurrent ion beam bombardment during film growth [2,12] or post-implantation into deposited films [13]. In comparison with low voltage IBAD, our process utilizes high-energy ion bombardment, which provides the necessary ion mixing for good film properties such as strong film adhesion, but on the other hand leads to preferential sputtering altering the surface topography of the samples. In short, our technique is a combined pulsed film growth and IBAD process.

It has been proposed that implanted ions can create a high density of nucleation sites on the surface and provide additional energy to enhance atom mobility [14]. The influence of the ion energy on the nitride...
surface morphology under nitrogen ion bombardment has been observed [2,12]. In the case in which the ratio of nitrogen to titanium is about 1, the TiN grain size changes from ~50 to 200–400 nm with an increase in the nitrogen ion energy from 1 to 40 keV [2]. The CrN grain size also changes from 100 (6 keV) to 200 nm (16
The difference can be attributed to the activation of the crystal growth under high-energy ion irradiation. Therefore, it is not totally surprising that our 8 and 16 kV samples possess larger grains compared to the films deposited directly using vacuum arc due to the enhancement in the atomic mobility [1].

It should be noted that the reduction in the grain size when the bias voltage is increased in our experiments is somewhat different from the CrN or TiN film formation process discussed in the previous paragraph. Our work indicates a relationship between the bias voltage and the grain size and that there exists a bias voltage for the largest grain size. Under high-energy ion-beam bombardment, besides the enhancement of the deposited adatom mobility, another important process, sputtering, occurs in concert. The synergistic effects arising from ion beam induced sample heating, larger ratio of N/Ti, and smaller sputtering yield may lead to that the CrN or TiN grain growth at higher bias voltage [2,12]. Owing to the pulsing nature of the process, the heating effect is not continuous. In fact, the actual duty cycle is quite low, and surface diffusion, atomic mobility, and the implantation to deposition ratio are not large. It has been proposed that the energy dissipated at different depths by the incident ions may be responsible for the change in the surface morphology. For instance, 40 keV Ne and Xe ion bombardment lead to different surface topographies [1]. In the former case involving Ne, many small spike-shape cones can be observed on the surface. The average size of the cone is slightly larger than that of columns without ion bombardment. Using Xe bombardment, the TiN film has a surface topography characterized by larger columns. This may be attributed to that the heavier Xe ions lose more energy closer to the surface and the lighter Ne ions lose their energy over a
larger depth. An analogy can be drawn between 8 kV titanium ion bombardment in our experiment and Xe ion bombardment. The same is true between our 16 kV process and Ne ion bombardment. As shown in the profile simulated using TRIM 95 in Fig. 6, a larger portion of the energy is lost to the near surface region in the 8 kV process. This implies that the collision probability between the incident ions and the atoms in the near surface region is high thereby facilitating more atomic movement. Consequently, the larger column grains form. At a bias voltage of 16 kV, the ions lose their energies over a larger depth leading to smaller and spikier cones. The density of the film around the grain boundaries may not altered significantly when diffusion and sputtering occur simultaneously in the near surface region [1]. It is more difficult for the smaller grains to coalesce into larger cones. Hence, the smaller columns grow on the surface in abundance while the expansion of the columns along the vertical and horizontal directions is not big, and a smoother surface morphology results. When the voltage is increased to 23 kV, the boundaries are more severely sputtered and ripples form on the surface. We are investigating the mechanism in more details and will report more findings in the future. Nonetheless, the phenomenon appears to be due to ion-induced instability [15,16]. All in all, our results reveal that ion irradiation can effectively alter the nucleation and growth kinetics, consequently modifying the morphology and properties of the films [1].

4. Conclusion

Dynamic PIII–D is an effective, albeit complex, process to synthesize thin films. Our results show that the bias voltage affects the surface morphology. The different surface morphologies appear to arise from the difference in the energy deposited into the substrate by the incident ions. At a lower bias voltage, more energy is dissipated in the near surface region enhancing atomic mobility to form larger grains. When the bias voltage is increased, the grains become smaller and have a spike shape. Ripples are also observed on the surface. Our results show that the surface topography of the titanium nitride thin films can be readily optimized by adjusting the processing parameters such as the bias voltage, plasma density, pulse duration, and pulsing frequency in the PIII–D experiments.

Acknowledgements

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References