

Diffusion barrier performance of nanoscale TaN_x thin-film

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Abstract: TaN_x nanoscale thin-films and Cu/TaN_x multilayer structures were deposited on P-type Si(100) substrates by DC reactive magnetron sputtering. The characteristics of TaN_x films and thermal stabilities of Cu/TaN_x/Si systems annealed at various temperatures were studied by four-point probe(FPP) sheet resistance measurement, atomic force microscopy(AFM), scanning electron microscope-energy dispersive spectrum (SEM-EDS), Alpha-Step IQ Profilers and X-ray diffraction(XRD), respectively. The results show that the surfaces of deposited TaN_x thin-films are smooth. With the increasing of N₂ partial pressure, the deposition rate and root-mean-square(RMS) decrease, while the content of N and sheet resistance of the TaN_x thin-films increase, and the diffusion barrier properties of TaN_x thin-films is improved. TaN_{1.09} can prevent interdiffusion between Cu and Si effectively after annealing up to 650 °C for 60 s. The failure of TaN_x is mainly attributed to the formation of Cu₃Si on TaN/Si interface, which results from Cu diffusion along the grain boundaries of polycrystalline TaN.

Key words: reactive magnetron sputtering; TaN_x nanoscale thin-film; Cu diffusion barrier; diffusion barrier property

1 Introduction

One of the urgent research topics for Cu interconnection in ULSI is to find a suitable barrier to prevent Cu diffusion in silicon crystal[1]. The refractory metals and its nitrides have been widely studied due to their high thermochemical stability and excellent conductivity. Ta-based thin-films, so-called Cu diffusion barrier, are believed to have the brightest application prospect. As a diffusion barrier, Ta has some advantages, such as good adhesion, being immiscible with Cu and low resistivity. But pure Ta thin-film is difficult to be amorphous, so defects (including microcracks, voids and grain boundaries etc) may act as fast diffusion paths and hence decrease the barrier performance. One way to improve the performance is to add N, C or Si into Ta thin-films during the deposition process to change the microstructure[2].

Up to now, Ta and its compounds have been investigated in different aspects. For example, the influence of fabrication methods (sputtering, CVD), microstructure, thickness and annealing ambient of thin-film on diffusion barrier performance[3–4]. However, few researches about this field have been

reported in our country. In this study, the influence of N₂ partial pressure on the surface morphology, properties of TaN_x thin-films, Cu/TaN_x multilayer structures was probed. The failure mechanism of TaN_x barrier after high temperature annealing was discussed.

2 Experimental

TaN_x nanoscale thin-films were deposited onto P-type Si(100) substrates with nominal resistivity of 33–35 Ω·cm in N₂/Ar ambient by DC reactive magnetron sputtering. The Si wafers were cleaned with RCA (the name from the Radio Corporation of American) method, then were loaded into the vacuum chamber. The base pressure of the system was pumped down to 1.0×10^{-3} Pa, and the distance between target and substrate is 6 cm. During the TaN_x layer deposition, the working pressure was maintained constant at 0.9 Pa, while N₂ flow was varied from 5, 7, 15 to 18 cm³/s, respectively, in order to obtain TaN_x thin-films with different N contents. The power of Ta target (with the purity of 99.9%, mass fraction) was kept constant at 110 W, while the sputtering time was adjusted from 1 to 3 min, in order to get 50 nm TaN_x thin-films at different N₂ partial pressures. Then without breaking the vacuum, a 400 nm-thick Cu film was

deposited onto some Ta_xN_y thin-films to obtain $\text{Cu}/\text{Ta}_x\text{N}_y/\text{Si}$ multilayer structures. The power of Cu target (with the purity of 99.99%) was 100 W and deposition time was 5 min.

For some samples, the rapid thermal annealing (RTA) was made by tungsten halide lamp at 300–950 °C in N_2 ambient with the purity of 99.99%. The ramping rate during temperature increasing process was 100 °C/s. The samples were kept at the set temperature for 60 s and then quickly dropped to room temperature. Alpha-step IQ Profiler was carried out to measure the thickness. The sheet resistance was measured by using a SDY-4D four-point probe. And NT-MDT Solver-P47 AFM was used to measure the root-mean-square (RMS) of surface before and after RTA. Quanta 200 SEM and SEM-EDS were employed to investigate the surface morphology and the component of the thin-films. D/MAX 2550 XRD was used to analyze the crystal structure of Ta_xN_y thin-films.

3 Results and discussion

3.1 Effects of N content on properties of Ta_xN_y thin-films

The effect of N_2 partial pressure on properties of as-deposited Ta_xN_y thin-films such as composition, sheet resistance, deposition rate and RMS is summarized in Table 1. In Table 1, the mean deposition rate is equal to the ratio of the thin-films thickness to the deposition time.

The composition of thin-films in Table 1 was measured by SEM-EDS. Obviously, with the increasing of N_2 partial pressure, the content of N in Ta_xN_y also increases. The result shows that N atoms in the thin films have two effects. One is reaction with Ta to form compound, and the other is action as impurity in compound. With the increasing of N_2 partial pressure during reactive sputtering, Ta_xN_y , Ta_2N , Ta_3N_5 phases will appear sequentially [5–6].

As listed in Table 1, with the N content increasing in Ta_xN_y films, the sheet resistance also increases. The sheet resistance is quite sensitive to the N content in the Ta_xN_y thin-films.

Fig. 1 shows the effect of annealing temperature on the sheet resistance of the Ta_xN_y thin-films. After 500–600 °C, 60 s RTA process, the sheet resistance of

the samples decreases obviously. This is mainly due to the grain growth and the defects reduction in the Ta_xN_y thin-films. For sample 4, the sheet resistance drops sharply after 600 °C, 60 s RTA. This is mainly due to the “volatilization” of N atoms in the thin-film. During the RTA temperature duration of 300–500 °C, the sheet resistance of samples 2–4 abnormally rises. According to the analysis result of SEM-EDS, about 8% O impurity exists in the films, so this abnormal rise of sheet resistance is most probably due to the formation of high resistance oxide from the reaction between O and metallic Ta during RTA process. The similar behavior was observed by ZHANG et al [7], and they considered that the immoderate annealing temperature would increase the dispersion and deviation degree of grain, or there existed a kind of mechanism about grain boundary increasing and transformation at high temperature, then big grain split and mean grain size decreased, so the conductivity of the films became lower.

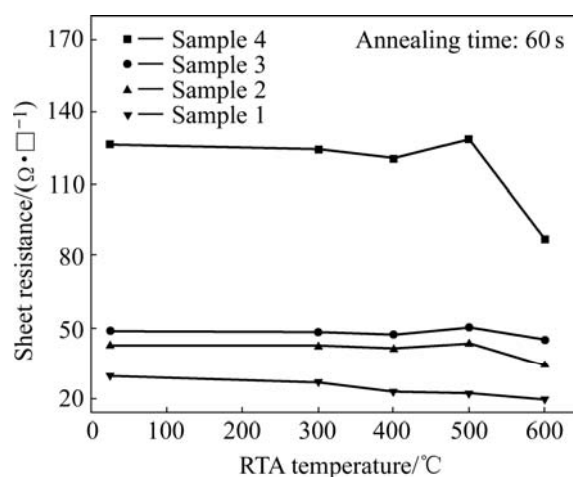


Fig. 1 Effect of RTA condition on sheet resistance

From Table 1, it is also found that the deposition rate of Ta_xN_y films declines with the increasing of N_2 partial pressure. The sputtering yield of N is lower than that of Ar, when keeping working pressure constant. The higher the N_2 partial pressure, the less the Ar gas flow. Thus the sputtering yield decreases. Furthermore, the increasing of N_2 partial pressure will cause “target poisoning” (which means the surface of Ta target becomes into nitrid) and lead to the sputtering mode

Table 1 Effect of N_2 partial pressure on properties of as-deposited Ta_xN_y thin-films

Sample No.	N_2 partial pressure/%	Composition	Sheet resistance/ ($\Omega \cdot \square^{-1}$)	Thickness/ nm	Deposition rate/ ($\text{nm} \cdot \text{min}^{-1}$)	RMS/ nm
1	3.68	$\text{Ta}_{0.36}\text{N}_{0.36}$	43.00	48	30.43	3.784
2	5.11	$\text{Ta}_{0.57}\text{N}_{0.57}$	49.14	52	27.80	1.961
3	10.60	$\text{Ta}_{1.09}\text{N}_{1.09}$	126.45	50	22.00	1.592
4	12.68	$\text{Ta}_{1.25}\text{N}_{1.25}$	210.36	48	18.25	1.268

change from metal to nitride. So the deposition rate declines.

At the same time, with the increasing of N_2 partial pressure, the experimental results support that the RMS of TaN_x films declines consistently. Lower deposition rate will be helpful to form smoother films and N could refine grains, so TaN_x films with high N content have smoother surface. Based on the consideration of application, the surface morphologies of the TaN_x thin-films will greatly influence its properties. Lower RMS will be helpful to improve the diffusion barrier performance.

3.2 Effects of N atom content on properties of Cu/ TaN_x multilayer structures

Fig.2 shows the sheet resistance change curves as a function of RTA temperature for Cu/ TaN_x /Si. Since the Cu film is much thicker and has a markedly lower bulk resistivity than TaN_x or other reaction products, the measured sheet resistance is dominated by the unreacted Cu films. For Cu/ $TaN_{0.36}$, Cu/ $TaN_{0.57}$, Cu/ $TaN_{1.09}$ and Cu/ $TaN_{1.25}$ samples, the sheet resistance slightly decreases with the RTA temperature increasing up to 550 °C. This may be due to the reduction of crystal defects and grain growth in the Cu films. However, after RTA at 600, 650, 800 and 850 °C, respectively, the sheet resistance of the samples increases abruptly. This indicates that Cu diffuses into TaN_x films and the diffusion barrier is failed. Furthermore, the temperatures, at which the sheet resistances of Cu/ $TaN_{0.36}$, Cu/ $TaN_{0.57}$, Cu/ $TaN_{1.09}$ and Cu/ $TaN_{1.25}$ increase abruptly, are improved gradually, respectively. TaN_x thin-films with higher N content could endure higher temperature RTA process. RTA process is inevitable in fabrication of semiconductor device, so TaN_x thin-films with higher N content have better diffusion barrier performance.

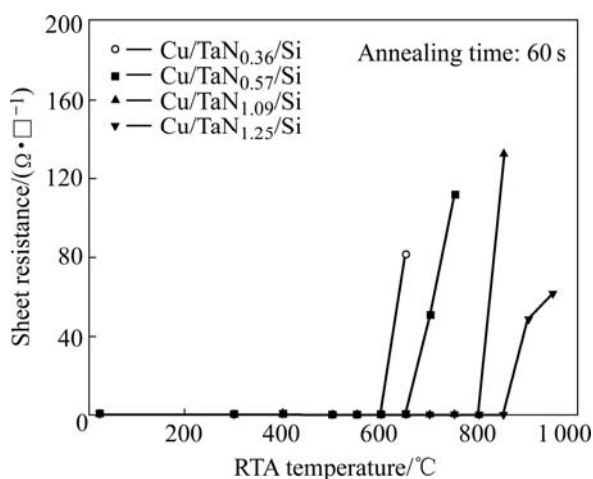


Fig.2 Curves of sheet resistance vs RTA temperature

3.3 Failure mechanism of Cu/ TaN_x /Si multilayer structures

From the above experimental results, with the increasing of N content, the diffusion barrier property of TaN_x films is improved. Generally speaking, the resistivity of Cu diffusion barrier should be less than 1 000 $\mu\Omega\cdot\text{cm}$ and the diffusion barrier's thickness should be less than 100 nm[8]. From our experiment results, in the four TaN_x samples, $TaN_{1.09}$ is the best choice as the diffusion barrier.

Fig.3 shows the XRD patterns of the Cu/ $TaN_{1.09}$ /Si samples annealed at various temperatures. For as-deposited sample, there are three Cu diffraction peaks, (111), (200) and (220), respectively. The intensity of Cu (111) is stronger than the other two and the intensity ratio of $I_{(111)}/I_{(200)}$ is 5.1. Generally speaking, when the value of ratio is greater than 3.3, the Cu(111) texture appears in the Cu thin-films[9]. So there is strong Cu(111) texture for all experimental samples. It is well known that strongly oriented Cu(111) film enhances the electromigration stability remarkably just as shown in Ref.[9]. With the RTA temperature increasing up to 750 °C, the intensity of Cu peaks increases, and the peaks become more acute and tend to move to higher diffraction angle. In addition, Ta_2O_5 peak appears, which proves the existence of oxygen impurity from the other side. The little amount addition of oxygen is believed to be helpful to improve the diffusion barrier performance [10].

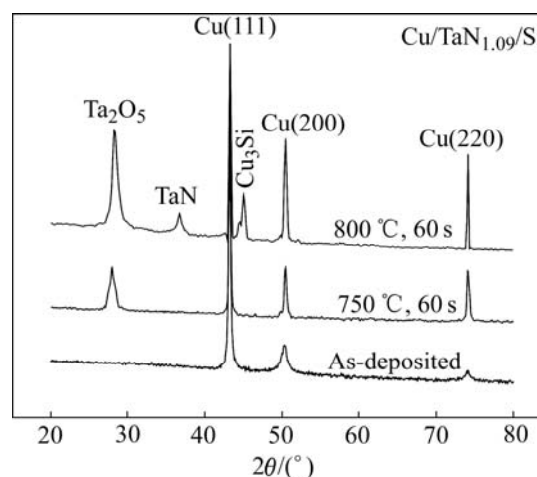


Fig.3 XRD patterns of Cu/ $TaN_{1.09}$ /Si multilayer structure

As a contrast, a kind of Cu/Ta/Si multilayer structure is also deposited. Fig.4 shows the XRD patterns of the Cu/Ta/Si samples annealed at various temperatures. For as-deposited sample, Ta has (202) and (002) orientations. But in Fig.3, $TaN_{1.09}$ remains nano-crystalline/amorphous for as-deposited samples and even if annealed up to 750 °C for 60 s. The deposition parameters for Ta and $TaN_{1.09}$ are the same, except N_2

partial pressure. So it can be concluded that the addition of N delays the TaN_x films to crystallize effectively. As shown in Fig.4, the Cu_3Si peak appears, when the Cu/Ta/Si samples are annealed at 550 °C for 60 s, which indicates that Ta barrier has failed. Furthermore, the interface reaction product $TaSi_2$ is also detected. By comparing Fig.3 with Fig.4, the addition of N not only improves the diffusion barrier property of TaN_x , but also prevents Cu-Si interface reaction, which is usually a common failure mechanism for diffusion barrier.

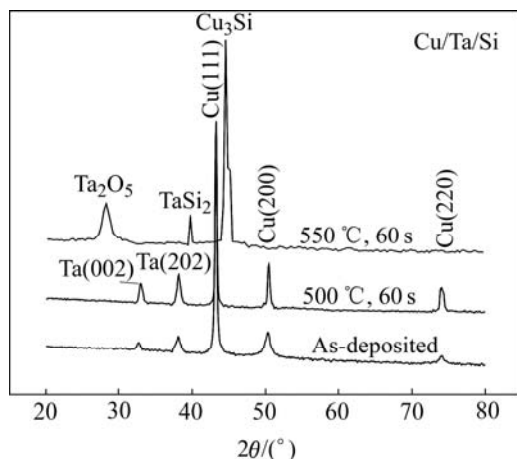


Fig.4 XRD patterns of Cu/Ta/Si multilayer structure

In fact, starting with the columnar-structured polycrystalline thin-films (usually pure refractory metals), there are two ways to reduce their high defect density. The first one is to reduce the amount of grain boundaries, for instance, to deposit giant grains (usually by increasing the adatom mobility), ending up with the fabrication of single crystalline barriers. But to get giant-grained or single crystalline refractory thin-films, the high deposition temperature is required. And this approach does not have any practical application in the semiconductor industry.

The second way is to reduce the defect density by stuffing the existing grain boundaries with light atoms like Si, N and C. This method is to produce nano-crystalline or amorphous-like barrier thin-films by controlling the deposition conditions (gas mixture, ion bombardment, substrate temperature, etc). And this approach is further developed[11].

Fig.5 shows the SEM images of Cu/ $TaN_{1.09}$ /Si surface. Fig.5(a) and Fig.5(b) show flat and smooth surface. It means that the multilayer structures can keep stable up to 650 °C. However, after 700 °C, 60 s RTA process, “black spots” of different diameters are observed by the naked eyes and many “bright spots” appear in the SEM image in Fig.5(c). The origin of the “spots” is probably connected with the following two effects. 1) Cu diffuses along some local defects or grain boundaries in the TaN_x barrier thin-films into Si substrate

and then “voids” remain on the Cu surface. In fact, the interdiffusion between Cu and Si occurs simultaneously and some investigations found that the diffusion velocity of Cu through TaN_x barrier thin-films is higher than that of Si through barrier. Moreover, the diffusion of Cu will do greater harm than that of Si for Cu interconnection [12–13]. 2) Because of the thermal stress in Cu thin-films, there are Cu grain conglomeration and synergistic effect. And then some hillocks and holes occur and develop.

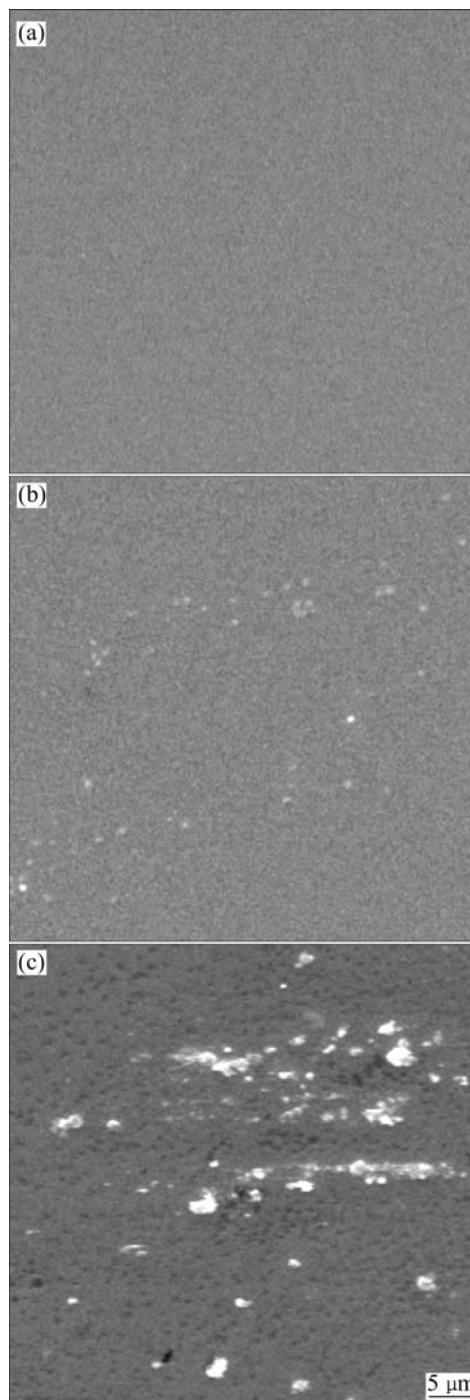


Fig.5 SEM images of Cu/ $TaN_{1.09}$ /Si surface: (a) As-deposited; (b) 650 °C, 60 s RTA; (c) 700 °C, 60 s RTA

Fig.6 shows the 3D AFM images of Cu/TaN_{1.09}/Si surface. Before RTA process, the Cu surface is smooth and the grains are uniformly distributed. With the RTA temperature increasing, Cu grain grows and rougher surface is observed. And after higher temperature RTA process, during which the TaN_{1.09} diffusion barrier is failed, the Cu surface splits into several isolated islands and becomes quite rough.

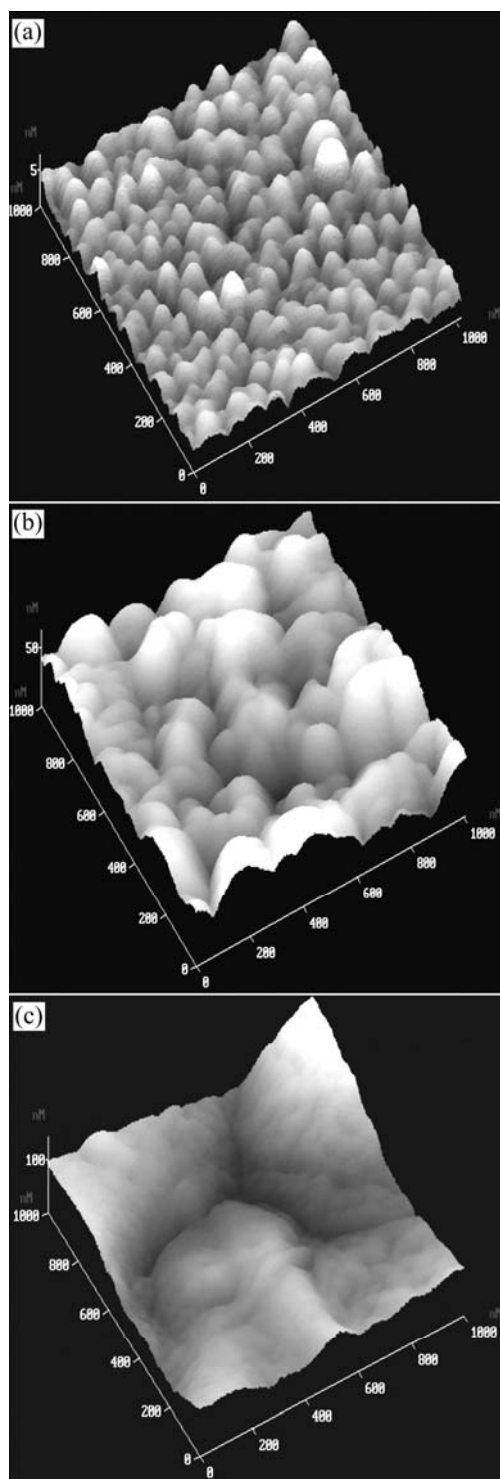


Fig.6 3D AFM images of Cu/TaN_{1.09}/Si surface: (a) As-deposited; (b) 650 °C, 60 s RTA; (c) 700 °C, 60 s RTA

For Cu/TaN_{1.09}/Si multilayer structures, FPP measurement shows that the sheet resistance increases abruptly after 800 °C, 60 s RTA process, and XRD analysis also shows that there are new phase Cu₃Si. Obviously, after 700 °C, 60 s RTA process, many “bright spots” are observed by SEM. And several other analytical techniques were employed to study the diffusion barrier property and failure mechanism of the thin-film[14]. The failure temperatures are determined as follows: for FPP measurement, the temperature, at which sheet resistance starts to increase abruptly, is defined as failure temperature; for XRD analysis, the failure temperature is that at which TaSi₂ or Cu₃Si are observed; and for SEM observation, the failure temperature is that at which the “spots” appear.

In summary, the failure of TaN_x as a Cu diffusion barrier is mainly attributed to the formation of inverse pyramidal Cu₃Si[15–16] on TaN_x/Si interface, which results from Cu diffusion along the grain boundaries of polycrystalline TaN_x.

4 Conclusions

1) The surfaces of as-deposited TaN_x thin-films are smooth. With the increasing of N₂ partial pressure during reactive sputtering, the N atom content and sheet resistance of the TaN_x thin-films increase, the conductivity of the thin-films declines and the deposition rate and RMS decrease.

2) The incorporation of N delays the formation of polycrystalline TaN_x and eliminates the interface reaction at TaN_x/Si. With the increasing of N content in the TaN_x thin-films, the diffusion barrier property of TaN_x thin-films improves. Based on the experimental results, TaN_{1.09} is the best choice for Cu diffusion barrier and it can prevent interdiffusion between Cu and Si effectively, after 650 °C, 60 s RTA process.

3) The failure of TaN_x is mainly attributed to the formation of Cu₃Si on TaN_x/Si interface, which results from Cu diffusion along the grain boundaries of polycrystalline TaN_x.

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