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Preparation and properties of SiCN diffusion barrier layer for Cu interconnect in ULSI

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Abstract: SiCN thin films and Cu/SiCN/Si structures were fabricated by magnetron sputtering. And some samples underwent the rapid thermal annealing(RTA) processing. The thin-film surface morphology, crystal structure and electronic properties were characterized by atomic force microscopy(AFM), X-ray diffractometry(XRD), Fourier transform infrared transmission(FTIR) and four-point probe(FPP) analyses. The results reveal the formation of complex networks among the three elements, Si, C and N, and the existence of different chemical bonds in the SiCN films, such as Si—C, Si—N, C—N and C—N. The as-deposited SiCN thin films are amorphous in the Cu/SiCN/Si structures and have good thermal stability, and the SiCN thin films are still able to prevent the diffusion reaction between Cu and Si interface after RTA processing at 600 °C for 5 min.

Key words: SiCN thin film; magnetron sputtering; dielectric diffusion barrier; Cu interconnect for ULSI

1 Introduction

The interconnect resistance-capacitance(RC) delay is a dominant factor in determining the performance of ultra large scale integrated circuits(ULSI) as the minimum feature size device shrinks below 180 nm. Although many low-k (k < 3) materials have been used as interlayer dielectrics (ILD), high-k (k=7-8) materials, such as SiN, SiC and SiCN, are still the primary candidates for the Cu cap barrier and etch stop layer(ESL) required in the Cu damascene process[1-2], which increases the effective k values of stack dielectric films and limits the reduction of the RC delay in ultra large-scale integration[3]. As a result, amorphous silicon carbide(SiC) and amorphous silicon nitricarbide(SiCN) have received much attention for applications as Cu dielectric diffusion barrier and ESL in Cu damascene process[4-6].

The preparation techniques, photoluminescent properties and field emission properties[7] of SiCN thin films have been extensively investigated by many researchers in the recent years. However, very few researches have been carried out on the performance of SiCN thin films as dielectric diffusion barriers in the Cu dual damascene process in ULSI[8–9]. At the same time, the research on diffusion barrier films for Cu interconnect in China focused on refractory metals, nitride refractory metal and their ternary structure diffusion barriers [10–12], and there is hardly reports on dielectric diffusion barrier.

In this work, SiCN thin films and Cu/SiCN/Si structures were fabricated by magnetron sputtering. The chemical bonds, crystal structure and surface morphology of SiCN thin films were discussed, and the performance of SiCN dielectrics as Cu diffusion barriers was also investigated.

2 Experimental

SiCN thin films and Cu/SiCN/Si structures were obtained in a TXZ500-I magnetron sputtering apparatus using a sintered SiC target and a Cu target both with 100 mm in diameter. N-type silicon substrates were used in this experiment. SiCN films grew in an RF-magnetron sputtering system from the planar SiC target, and the substrate was placed at about 6 cm below the target. Firstly, the chamber was evacuated to a base pressure of

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 1.0×10^{-3} Pa, then high-pure N₂ and Ar were introduced into the chamber at different volume ratios of N₂ to Ar. Before each deposition, a 10 min pre-sputtering was performed in order to remove the native oxide layer formed on the target surface. After this pre-sputtering stage, the shutter covering the substrates was removed and then deposition initiated. The RF-power was maintained at 150 W and substrate was not heated during deposition. By choosing appropriate process parameters, a 200 nm Cu overlayer was sputtered onto the SiCN layer in suit. The as-deposited Cu/SiCN/Si systems and SiCN thin films were rapid thermal annealed for 5 min in high-pure N₂ at various temperatures. Table 1 lists the process parameters of the specimens.

The morphology of the thin films was analyzed by NT-MDT type atomic force microscope(AFM). The chemical composition of the thin films was evaluated by energy dispersive spectrometer(EDS). The crystalline structure and the texture of the thin films were measured by X-ray diffraction(XRD) with Cu K_{α} radiation in a standard X-ray diffractometer. Fourier transform infrared transmission(FTIR) was adopted to characterize the



Table 1 Specimen numbers and process parameters

No.	Target	Pressure/ Pa	Volume ratio of N_2 to Ar	Power/ W	Thickness/ nm
1	SiC	0.88	82/100	150	185
2	Cu/SiC	0.88	103/100	150	50
3	Cu/SiC	0.88	82/100	150	50
4	Cu/Si	0.88	20/100	150	50

Cu films were deposited at the same parameters: pressure of 0.9 Pa, power of 100 W, thickness of 200 nm.

microstructures of the thin films in the range of $400-4~000~\text{cm}^{-1}$ with a resolution of $4~\text{cm}^{-1}$. The sheet resistance was measured by four-point probe of SDY-4D type.

3 Results and discussion

3.1 Morphology of surface

The AFM images of as-deposited SiCN thin film (sample No.1) and the Cu/SiCN/Si sandwich structure (sample No.3) before and after annealing at various temperatures for 5 min are shown in Fig.1. From these



Fig.1 AFM images: (a) Sample No.1 as-deposited; (b) Sample No.3 as-deposited; (c) Sample No.3 after RTA at 400 \degree C for 5 min; (d) Sample No.3 after RTA at 600 \degree C for 5 min

images, it can be seen that the SiCN thin films grow in a way of columns or grains and these surfaces are very smooth and compact. These grains are uniform and small and the as-deposited Cu films upon SiCN film are very smooth accordingly with a roughness of 0.846 nm. After RTA process at 400 $^{\circ}$ C for 5 min, large grains emerge, and the Cu films become rough. After RTA at 600 $^{\circ}$ C for 5 min, the surface of the Cu films become rougher with a roughness of 83.054 nm. The latter is double the roughness of the films after RTA at 400 $^{\circ}$ C for 5 min. Moreover, we can see some white spots on the surface that are considered a resultant of some reaction between Cu and Si.

3.2 EDS and FTIR spectroscopy

The chemical composition proportion of sample No.3 (C to N to Si) is evaluated as 10.19:16.053:41.63 by EDS. The FTIR reflectance spectrum of the Cu/SiCN/ Si structure (sample No.3) between 400 and 4 000 cm⁻¹ is shown in Fig.2.



Fig.2 FTIR reflectance spectrum of sample No.3

The spectrum shows absorption bands revealing the presence of components bonds in different vibration modes: asymmetric stretching vibration of Si-N (420-460 cm⁻¹)[13], symmetric stretching vibration of Si-N (820-890 cm⁻¹)[13], vibration (sp³ hybridization) mode of C-N (1 110-1 130 cm⁻¹)[14], stretching vibration $(sp^2 \text{ hybridization})$ of C=N (1 390-1 460 cm⁻¹⁾[13], vibration mode of Si-C (520-613 cm⁻¹)[15], stretching mode of Si-C vibration at 736 cm⁻¹[16] and vibration mode of C=C vibration at 1 625 cm^{-1} [17]. The three components form a complex network. Owing to the complex chemical bonding surrounding each element, the exact vibration frequency is slightly different. And it is easy to find that the absorption intensity of Si-C vibration or C-N vibration is much higher than that of others. Further more, there is a weak absorption peak of C=C bond in Cu/SiCN/Si structure, which indicates that there are C clusters in the sample[17]. The absorption band at 3 360 cm⁻¹ should be correlated to N—H bond resulted from the remnant H₂O in the deposition chamber[18].

3.3 Electrical properties and performances of SiCN thin film in retarding Cu diffusion

The curves of sheet resistance of Cu/SiCN/Si structures vs annealing temperature are presented in Fig.3. It can be seen that before RTA the sheet resistances of these samples are about 0.34 Ω/\Box and below 400 °C these sheet resistances have a trend of decreasing as the annealing temperature increases, which is attributed to the changes of surface roughness, grain size and crystal structure of Cu films after annealing. It is believed that these factors affect the conductance of Cu films largely[19]. After RTA at 500 °C for 5 min, these sheet resistances increase slowly, and then increase abruptly after annealing at 600 °C, indicating that there are strongly mutual diffusion and reactions among multilayered films. We can consider initially that the Cu crystal grains diffuse from the SiCN films into silicon substrate and the dielectric diffusion barrier fails at about 600 °C, which corresponds with the analysis of AFM images. By the XRD analysis, the point will be proved again. Further more, we can find that sample No.3 with the volume ratio of N_2 to Ar of 82/100 has the best diffusion barrier performance among all samples.



Fig.3 Curves of sheet resistance vs RTA temperature

3.4 XRD analysis

Fig.4 shows the XRD patterns of the Cu/SiCN/Si sandwich structures before and after annealing at various temperatures for 5 min. Before annealing there are only diffraction peaks corresponding to $(111)_{Cu}$, $(002)_{Cu}$ and silicon substrate, and the diffraction peak of $(111)_{Cu}$ is stronger than $(002)_{Cu}$, indicating that Cu films growing over the SiCN films have (111) preferred orientation. It has been known that (111)-textured Cu films with large grains would be the most desirable for device metallization as this maximizes electromigration

resistance[19]. Furthermore, there is not any new phase appeared after annealing at 500 $^{\circ}$ C, and the peaks of $(111)_{Cu}$ and $(002)_{Cu}$ become stronger, indicating the Cu grains have grown up and large grain size leads to high conductivity, which has a good agreement with the analysis results of sheet resistance.



Fig.4 X-ray diffraction patterns of Cu(200 nm)/SiCN(50 nm)/Si structures: (a) As-deposited; (b) RTA at 350 $^{\circ}$ C for 5 min; (c) RTA at 400 $^{\circ}$ C for 5 min; (d) RTA at 450 $^{\circ}$ C for 5 min; (e) RTA at 600 $^{\circ}$ C for 5 min; (f) RTA at 800 $^{\circ}$ C for 5 min;

When the annealing temperature is up to 600 $^{\circ}$ C, the diffraction peaks corresponding to (201)_{Cu-Si} and $(030)_{Cu_2Si}$ can be observed at 36.6° and 42.4°, respectively, and the ratio of their intensity, $I_{36.6}$: $I_{42.4}$, is 3.7:1. However, no peak of (300)_{Cu-Si} is found, which usually emerges in the diffraction pattern of Cu₃Si. At the same time, the peaks of $(111)_{Cu}$ and $(002)_{Cu}$ can still be observed, indicating that interdiffusion and reaction between the Cu layer and the Si substrate have taken place when Cu₃Si formed and the SiCN film as diffusion barrier started losing its function. However, just a part of copper ions and atoms diffused towards Si substrate, and the overlayer of the Cu film still kept a continuity, which explains that the sheet resistance kept small. After RTA at 700 °C, we can see the peaks of $(201)_{Cu_2Si}$ and $(300)_{Cu-Si}$, as well as the very weak peak of $(300)_{Cu-Si}$, but still no SiCN crystalline phase.

The metal diffusion barriers have been extensively investigated by many researchers. They found that after annealing, the amorphous barrier film will become crystal, and the grain boundaries in the barrier film are thought as fast diffusion paths generally. The Cu ions and atoms can easily diffuse into barrier layer along the grain boundary defects, even penetrate the barrier layer and reach the Si substrate. In this work, the crystallization temperature of SiCN films is at least higher than 1 000 $^{\circ}$ C. But the SiCN thin films as diffusion barrier already fails after the Cu/SiCN/Si structure is annealed at 600 $^{\circ}$ C, and no SiCN crystalline phases can be observed after the Cu/SiCN/Si structure is annealed even at 700 $^{\circ}$ C. This indicates that the failing mechanism of SiCN film in retarding Cu diffusion is not due to the crystallization of the barrier layer, and there should be other factors causing failing of SiCN film as dielectric diffusion barrier.

4 Conclusions

1) The SiCN thin-film surface is very smooth and compact, and the as-deposited Cu films on SiCN films are very smooth with a roughness of 0.846 nm. The SiCN film possesses a complex network structure. There are complex chemical bonding among Si, N and C components in Cu/SiCN/Si structure. The as-deposited SiCN thin films are amorphous, and Cu films growing over the SiCN films have (111) preferred orientation.

2) SiCN films have a good thermal stability and can prevent the diffusion reaction between Cu and Si interface after RTA below 600 $^{\circ}$ C for 5 min. After annealing at 600 $^{\circ}$ C for 5 min, the sheet resistance of Cu/SiCN/Si structure increases abruptly. This indicates that the SiCN thin films fail as diffusion barrier at the temperature of 600 $^{\circ}$ C.

3) The failing mechanism of barrier layer for Cu diffusion may be not due to the crystallization of the films. As Cu dielectric diffusion barrier, the SiCN has a good performance in preventing Cu diffusion.

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