Improvement of thermal stability of Ta-N film in Cu metallization by a Zr-Si interlayer

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Abstract. Ta-N (10 nm)/Zr (20 nm) film was grown on n-type (100) silicon wafer at various substrate temperatures in a rf magnetron sputtering system, followed by in situ deposition of Cu. The Cu/Ta-N/Zr/Si samples were subjected to thermal annealing up to 800 °C under the protection of pure nitrogen gas. In order to investigate the effect of insertion of a thin Zr layer under Ta-N film on Ta-N diffusion barrier performance in Cu metallization, Cu/Ta-N/Zr/Si contact system was characterized by X-ray diffraction (XRD), four-point probe (FPP) measurement, scanning electron microscopy (SEM), and Auger electron spectroscopy (AES) depth profile. The results reveal that the microstructure of Ta-N films deposited on Zr is amorphous at different substrate temperatures. The barrier breakdown temperature of Ta-N/Zr film is about 100°C higher than that of Ta-N. It can effectively prevent the diffusion of Cu after annealed at 800°C. The improvement of diffusion barrier performance may be due to the production of Zr-Si layer with low contact resistivity after annealed at 800°C.

1 Introduction

Copper metallization has become very popular in the Si industry. Cu possesses significant advantages over Al in terms of RC delay and electromigration [1, 2]. However, Cu reacts with oxides, silicon, and silicides and it is a fast diffuser in these materials due to its high mobility. Therefore, it is necessary to insert a stable diffusion barrier between Cu and Si substrate. Binary transition metal nitrides, especially TaN [3-7] has been widely investigated and used as diffusion barriers for Cu metallization in ULSI devices owing to its high melting point, high thermal stability and good adhesion characteristics. However, the resistivity of TaN is high (180-270 $\mu\Omega\cdot\text{cm}$) [8, 9], therefore, TaN barrier may not well satisfy the need of high speed processing in copper metallization.

Zirconium silicide/silicon interface is a low resistance Ohmic contact and the barrier height (0.55 eV) between the Zr silicide and silicon shows that this contact may be useful for both n-and p-type regions [10]. In addition, Zirconium silicide has a lower resistivity (about 50 nm thick, 32 $\mu\Omega\cdot\text{cm}$) [11] than Ta-N. Cheng and chen have shown that an Zr-Si interlayer was observed just after Zr deposition, increasing in thickness by low temperature annealing below 500 °C [12]. Wang has shown that a reactively sputtered Zr-Si resulted in a promising diffusion barrier for copper metallization [13]. Therefore, in this work, in order to increase the failure temperature and decrease the resistivity of Ta-N diffusion barrier, we developed a new Ta-N/Zr diffusion barrier, investigated its thermal stability in Cu metallization.

2 Experimental

A mirror-polished n-type (100) silicon wafer with resistivity of 3-5 $\Omega\cdot\text{cm}$ was cut into 20×20 mm² pieces and used as substrates. The wafers were progressively cleaned in an ultrasonic bath with acetone, methanol, isopropyl alcohol, and diluted HF solution and then rinsed in de-ionized water before the activation process, in order to remove organic contaminants and native oxide. After cleaning, the Si substrates were loaded in the radio frequency magnetron sputtering chamber that was maintained at a base pressure of 2×10⁻⁵ Pa. The distance between the target and substrate holder was fixed at 80 mm. The sputtered targets were Zr(99.9% purity, Ø60 mm×3 mm), Ta (99.9% purity, Ø60 mm×3 mm) and Cu(99.9% purity, Ø60 mm×3 mm). Both N₂ and Ar gas purity were 99.999%. A Zr layer was deposited by Ar ion sputtering, the sputtering power used for Zr target was 100 W and the flow rate of Ar was 20 sccm. The sputtering pressure was 0.3 Pa. TaN film was deposited on the top of Zr layer by RF reactive sputtering in a mixture of N₂ and Ar and the gas flowrate of N₂/Ar was 2/48 sccm, the sputtering power used for Ta target was 100 W and the sputtering pressure was 0.3 Pa. The thickness of Zr and Ta-N films were maintained at 20 and 10 nm, respectively, by varying deposition time. After deposition of the barrier layers, Cu (100 nm) film was deposited on the barriers without breaking vacuum at the sputtering pressure of 0.1 Pa, the sputtering power used for Cu target was 90 W and the flowrate of Ar was 20 sccm. The substrate's negative bias was fixed at -100V during the whole deposited

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process. The samples were subsequently annealed at different temperatures ranging from 600 to 800°C in N₂ ambient for 1 h.

The sheet resistance was measured by 4-point probe (FPP) for the as-deposited and annealed films. The phase formation was investigated by X-ray diffraction (XRD). The surface topographies of films were inspected by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The element profiles in depth of the as-deposited and annealed samples of Cu/Ta-N(10 nm)/Zr(20 nm)/Si were identified by Auger electron spectroscopy (AES).

3 Results and discussion

3.1 Microstructure of Ta-N/Zr films

Fig.1 shows the XRD pattern for the Ta-N(10 nm)/Zr(20 nm) films deposited at different substrate temperatures. There are only obvious Zr diffraction peaks in the XRD spectrum for the Ta-N(10 nm)/Zr(20 nm) films deposited with different temperatures. No TaN diffraction peaks can be observed, which indicates the typical amorphous structure of the TaN film deposited on Zr film.

Fig.1. XRD patterns of Ta-N(10 nm)/Zr(20 nm)/Si samples deposited at various temperatures: (a) 100 °C and (b) 300 °C

The surface morphology of barrier must be considered seriously because it will directly influence the adhesion strength between barrier and Cu film and barrier properties. It is believed the smoother surface of barrier is, the better barrier capability is [14]. Fig.2 shows the surface morphology of as-deposited Zr/Si and Ta-N/Zr/Si specimens. It can be observed from Fig.2(a) that the surface of Zr film is generally smooth with the surface root mean square (RMS) roughness equal to 2.997 nm. For as-deposited Ta-N/Zr/Si specimens Fig.2(b), the surface root mean square (RMS) roughness decreases to 2.011 nm. The average grain size of Zr film is 18.891nm, which is larger than that of Ta-N/Zr film (12.742 nm). This may be attributed to different microstructure of Zr and Ta-N films. Zr film is polycrystalline structure with larger grain size and Ta-N film is amorphous structure with thin grain size. So the surface of Ta-N/Zr is smoother than that of Zr film. It is

clear that Ta-N/Zr film with low roughness can well meet the requirement of barrier performance.

Fig.2. AFM micrographs of as-deposited samples: (a) Zr/Si and (b) Ta-N/Zr/Si

3.2 Barrier performance of Ta-N/Zr thin films

Before annealing, the sheet resistance of the Cu/Ta-N/Zr/Si system is measured (recorded as R_s). After annealing, the sheet resistance of the sample is measured again and is recorded as R_f . Since the diffusion barrier is very thin, the sheet resistance of the Cu/Ta-N/Zr/Si structure mainly reflects the resistance of Cu. The difference of sheet resistance between the annealed and as-deposited samples ($R_f - R_s$), which is divided by the sheet resistance of as-deposited samples, is called the variation percentage of sheet resistance [15, 16]. Fig.3 shows the variation percentage of sheet resistance with annealing temperature of the Cu/Ta-N/Zr/Si structures. For comparison, that of the Cu (100 nm)/Ta-N (30 nm)/Si structures deposited are also shown in Fig.3. The resistivity of the as-deposited Cu film is about 5.4 $\mu\Omega\cdot\text{cm}$, which is higher than the bulk value (bulk value: 1.678 $\mu\Omega\cdot\text{cm}$). For all of samples, the variation percentage of sheet resistance is a downward trend with the increased annealing temperatures up to 700 °C. This decrease was attributed to the grain growth and defect annihilation of the Cu layer during annealing because the sensing current mainly represents the status of the Cu film. For the Cu/Ta-N (30 nm)/Si sample, annealing at 750 °C results in an abrupt increase in the variation percentage of sheet resistance, indicating a significant reaction involving the Cu layer. It may be caused by copper penetration through the Ta-N layer into Si substrate and reaction with Si. However, the sheet

resistance for Cu/Ta-N (10 nm)/Zr (20 nm)/Si sample annealed at 800°C is still lower than that of the as-deposited sample. Fig.3 indicates clearly that the insertion of a Zr layer under Ta-N layer can effectively improve the thermal stability of Ta-N film.

Fig.4 shows the XRD spectra of the Cu/Ta-N (10 nm)/Zr (20 nm)/Si structures at different annealing temperatures. The results show that peaks from only Cu and ZrSi₂ are identified until annealing at 800 °C. After annealing at this temperature, grain growth of the Cu film is evidently observed from higher intensity and narrower full width at half maximum of Cu (111) peak than that of the as-deposited sample, which corroborates the decrease in the sheet resistance value presented and discussed above. The Zr diffraction peaks disappear at a temperature of 800 °C. It is supposed that the Zr layer may be consumed as a result of the formation of ZrSi₂, which is also a promising diffusion barrier for copper metallization [13]. In addition, the formation of ZrSi₂ decreases the contact resistance between Si and barriers. The predominant reflection line from Cu (111) and those from Cu (200) and Cu (220) with very weak intensity are observed, which indicates that Cu film possesses (111) texture. It has been reported [17] that the (111) texture of Cu films can provide higher electromigration resistance than that of Cu (200) in Cu interconnections. In addition, there is no other crystalline phase like Cu silicide up to 800°C and the Ta-N amorphous structure is stable in entire annealing process. The XRD results indicate that the Zr/Ta-N barrier can prevent copper diffusion up to 800 °C.

Fig.3. Sheet resistance variation of Cu/Ta-N/Zr/Si samples as a function of annealing temperature

Fig.4. XRD patterns of Cu/Ta-N (10 nm)/Zr (20 nm)/Si samples after being annealed at different temperatures

Fig.5 shows the surface morphologies of Cu/Ta-N/Zr/Si samples before and after annealing. For as-deposited sample Fig.5(a), the surface is flat without localized defects. After annealed at 700°C Fig.5(b), the surface of sample shows Cu grain growth, which is consistent with XRD result. Annealing at 800°C Fig.5(c), there are some pinholes in Cu film and Cu film is integrated and free from agglomeration. The origin of the pinholes formation is not connected with the Si-Cu interaction, but is resulted from thermal stress in the Cu film itself. In addition, the surface of the sample annealed at 800°C is probed by AES and the result is shown in Fig. 5(d). It can be observed there is no Cu-Si compound on the surface of sample and the appearance of C and O peaks in sample is attributed to the surface contamination and partial oxidation of Cu.

Fig.5. Surface morphologies and surface elements of Cu/Ta-N/Zr/Si samples: (a) as-deposited, (b) annealed at 700°C, (c) annealed at 800°C, (d) energy spectrum of sample annealed at 800°C

Fig.6. AES depth profiles of Cu/Ta-N(10 nm)/Zr(20 nm)/Si samples: (a) as-deposited and (b) annealed at 800 °C

Fig.6(a) shows the AES depth profile obtained from the as-deposited Cu/Ta-N (10 nm)/Zr (20 nm)/Si specimen. It exhibits a well-separated stacked structure with a sharp transition for all elements at each interface. Fig.6(b) shows the AES depth profiles of the Cu/Ta-N (10 nm)/Zr (20 nm)/Si system upon annealing at 800°C for 1h. A large amount of Cu still remains as the as-deposited samples, which demonstrates the integrity of the barrier. Some of the Zr atoms migrated into the Si substrate but there was no evidence of Si migration through the Ta-N layer into the Cu layer, which indicates the TaN (10 nm)/Zr (20 nm) film has excellent diffusion barrier performance and can prevent the diffusion of Cu atoms up to 800°C. This agrees well with the results of the XRD, FPP and SEM. The oxygen content in the Cu/Ta-N/Zr/Si structures was also investigated by measuring the depth distribution of oxygen in the samples. According to the AES result shown in Fig. 6(a), the as-deposited samples contain a small amount of oxygen. It is also observed that the oxygen is incorporated more with the increasing of the annealing temperature. After annealing at 800°C, oxygen has gone deep into the Cu film and Ta-N/Zr layer. The oxygen comes from the residual oxygen in the annealing ambient and deposited chamber. The oxygen distributed in the sample can stuff the grain boundary of barrier and decrease the diffusion paths of Cu atoms.

4 Conclusion

In conclusion, the effect of insertion of a thin Zr layer under Ta-N film on the Ta-N diffusion barrier performance in Cu metallization has been investigated. It is observed the sheet resistance of Cu/Ta-N (10 nm)/Zr (20 nm)/Si contact system is lower than that of as-deposited specimens even after annealing at 800 °C. XRD data suggest that TaN deposited on Zr film is the typical amorphous structure and Cu silicide cannot be observed up to 800 °C. AES depth profiles of the Cu/Ta-N (10 nm)/Zr (20 nm)/Si sample have no noticeable change except Zr silicide production up to 800°C. These results indicate that the insertion of a thin Zr layer into Ta-N film improves the barrier properties significantly. The reason for that is the formation of ZrSi₂ layer, which is also a promising diffusion barrier and can decrease the contact resistance between Si and barriers. In addition, Cu films on Ta-N/Zr diffusion barrier prefer the (111) crystal orientation, which indicates that Cu(111) texture is not inhibited because of the weak interaction at the Cu/TaN/Zr interface. This Cu (111) texture possess higher electro-migration stability.

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