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Formation of Ti–Si–N film using low frequency, high density inductively coupled plasma process

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Titanium silicon nitride (Ti–Si–N) has emerged as a strong candidate for next generation diffusion barrier material in copper/low-*k* dielectric back-end-of-line device fabrication. Low frequency, high density inductively coupled plasma process has been developed for the growth of Ti–Si–N film. This work employs the reaction between Ti_xSi_y and the nitrogen plasma. Ti–Si–N films have been successfully grown over different process conditions. Film properties were characterized by Rutherford backscattering spectrometry (RBS), x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectroscopy, x-ray diffraction (XRD), and four-point resistivity probe. RBS reveals that 2–67 at. % of nitrogen can be achieved through the implantation of nitrogen in Ti_xSi_y film. XPS and XRD results show that TiN and Si_3N_4 are successfully formed. As the external bias increases from 100 to 300 V, there is an 80% increase in sheet resistance. Other process conditions investigated do not show a significant effect on film sheet resistance. Increasing argon plasma activation time can significantly increase the implantation depth of nitrogen into Ti_xSi_y substrate. © 2005 American Vacuum Society. [DOI: 10.1116/1.2131080]

I. INTRODUCTION

Copper has been replacing aluminum as the interconnect material for high performance integrated circuit applications. The motivation for this transition comes from the requirements for even lower resistivity and improved electromigration resistance as the electronic device size further shrinks down. However, successful incorporation of copper into sub-micron devices requires improved diffusion barrier. This barrier film should preferably consist of a dense microstructure configuration to prevent Cu from diffusing into silicon devices. More importantly, they must sustain their desirable properties at much reduced thickness to ensure that most of the effective volume of the trench and via structures is occupied by copper.

Conventional barrier material includes TiN, Ta, and TaN. However, due to the down scaling of devices and more stringent reliability requirement, more effective barrier materials have to be found. To this end, a class of refractory, ternary nitrides, such as Ti–Si–N, has been proposed as candidates for the next generation diffusion barrier in copper/low-*k* dielectric back-end-of-line device fabrication.^{1,2} Various research groups have explored the formation of Ti–Si–N films

by physical vapor deposition (PVD), metal-organic chemical-vapor deposition, metal-organic atomic layer deposition (MOALD) techniques, and documented their resulting electrical, structural, and thermal properties.^{3–10}

The current work focuses on an approach by employing low frequency, high density inductively coupled plasma process in the formation of Ti–Si–N. This process is able to control the thickness of Ti–Si–N well. The objective of this work is to investigate the effect of processing parameters on the properties of Ti–Si–N, such as electrical resistivity, film uniformity, and phase composition. The understanding obtained will help selection of appropriate processing parameters for the barrier formation in the back-end-of-line device fabrication.

II. EXPERIMENT

A 50 nm thick Ti_xSi_y film was fabricated by depositing a layer of Ti on *p*-type (100) silicon wafer, followed by rapid thermal annealing at 750 °C (RTA1) and 850 °C (RTA2). The sheet resistance of the formed Ti_xSi_y film was measured to be 6.08 Ω/Sq with a standard deviation of 1.06%. High density nitrogen plasma implantation into the Ti_xSi_y film was conducted in a low frequency inductively coupled plasma reactor for 30 and 60 min. This implantation process was

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TABLE I. $I_{\text{Si}_3\text{N}_4(411)}/I_{\text{TiN}(220)}$ ratio of Ti–Si–N films under various process conditions.

External bias (V)	Ar flow/time (sccm/min)	N ₂ flow/time (sccm/min)	Sample label	Sheet resistance (ohms/Sq)	Standard deviation from sheet resistance (%)	$I_{\text{Si}_3\text{N}_4(411)}/I_{\text{TiN}(220)}$ ratio
/	/	/	Ti _x Si _y	6.08	1.06	/
100	10/5	30/30	A	6.16	1.68	0.91
200	10/5	30/30	B	8.34	2.91	0.88
300	10/5	30/30	C	38.74	8.95	1.47
100	10/20	30/30	I	5.99	1.06	0.63
100	20/20	30/30	K	6.12	2.23	/
100	30/20	30/30	M	5.06	1.62	2.26
100	10/20	30/60	J	5.8	2.81	1.25
100	20/20	30/60	L	5.94	1.36	1.36
100	30/20	30/60	N	5.89	1.35	1.39

preceded by Ar plasma activation. The chamber was evacuated to 1×10^{-4} Torr (base pressure) before the processing gases were introduced. In addition, low frequency (~ 0.5 MHz) was applied for plasma production. During the Ar plasma activation process, the pressure was 2.4×10^{-2} and 9.2×10^{-2} Torr when argon gas flow rate was set at 10 and 30 sccm, respectively. The total gas (Ar, N) pressure during the nitrogen plasma implantation was between 1×10^{-1} to 5×10^{-2} Torr, depending on the combined gas flow rate (Table I). The substrate temperature was between 200 and 300 °C when 2 kW plasma power was used. Process parameters that were varied were external bias, plasma composition, and plasma treatment time. The bias was changed from 100 to 300 V, argon gas flow rate from 10 to 30 sccm, argon plasma activation time from 5 to 20 min, and nitrogen plasma treatment time from 30 to 60 min. Table I summarizes these process parameters. Stoichiometric composition was obtained by Rutherford backscattering spectrometry using a 2.0 MeV $^4\text{He}^+$ beam. Electrical resistivity of Ti–Si–N was measured using four-point resistivity probe, and phase composition was investigated through x-ray diffraction (XRD) using a Shimadzu™ XRD 6000 diffractometer. Implanted nitrogen depth profile was characterized by time-of-flight secondary ion mass spectroscopy (ToF-SIMS) with impact energy of 1 keV Ar^+ ion primary beam. The chemical bonding states of nitrogen were analyzed by x-ray photoelectron spectroscopy (XPS) using 1486.6 eV Al $K\alpha$ irradiation. The x rays and the peak positions were calibrated with respect to C 1s peak at 284.5 eV.

III. RESULTS AND DISCUSSION

RBS analysis shows that there is a gradual change in the nitrogen atomic concentration through the thickness of Ti–Si–N film as shown in Fig. 1. The atomic concentration of N ranges from 2–67 % depends on the implantation depth. In addition, from XPS analysis, nitrogen is found to be bonded to titanium and silicon, forming titanium nitride and silicon nitride, respectively, when N_{1s} peaks are deconvoluted. This result is further confirmed by XRD results shown later. In

general, the results confirm that nitrogen ions have been successfully introduced into Ti_xSi_y lattice through the inductively coupled plasma process, forming a ternary compound of Ti–Si–N. The following sections will discuss the effect of external voltage, argon plasma activation time, argon gas flow rate, and nitrogen plasma treatment time on the properties of Ti–Si–N.

A. Effect of external bias

In copper interconnect technology, the main contributors to interconnect resistance is the barrier resistance. Thus, low resistance in the barrier material is required. As a reference, the sheet resistance of TiN was reported to be 17.12 and 16 Ω/Sq by Yuokoyama *et al.*¹¹ and Olowolafe *et al.*,¹² respectively. For an inductively coupled plasma chemical vapor deposited SiN, Luís da Silva Zambom *et al.*¹³ showed that the sheet resistance was between 10^{13} to 10^{17} Ω/Sq . In the current work, the sheet resistance of the Ti_xSi_y film is 6.08 Ω/Sq . When the external bias is set at 100 V (Fig. 2), the sheet resistance of Ti–Si–N film is 6.16 Ω/Sq with a standard deviation of 1.68% (sample A in Table I). When the bias increases to 300 V (sample C), there is a drastic increase

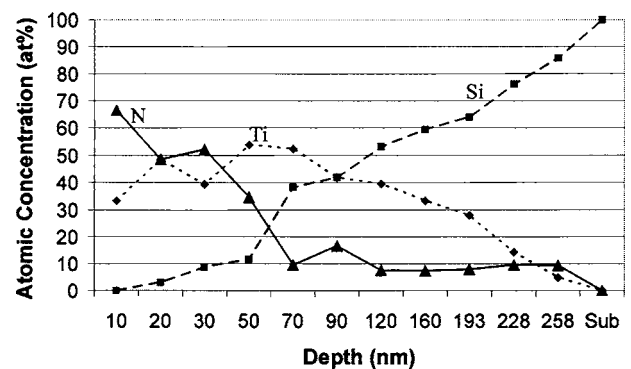


FIG. 1. 2.0 MeV $^4\text{He}^+$ Rutherford backscattering analysis of inductively coupled plasma Ti–Si–N. Nitrogen ions are successfully introduced into Ti_xSi_y .

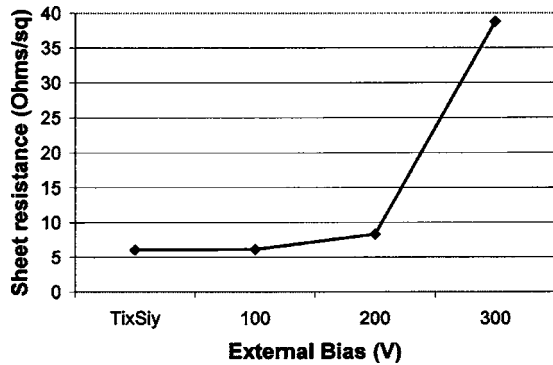


FIG. 2. Sheet resistance of Ti-Si-N films as a function of external bias. The higher the external bias, the higher the sheet resistance of the Ti-Si-N films.

in sheet resistance ($38.74 \Omega/\text{Sq}$), and the standard deviation also increases to 8.95%. The rise in resistance could be explained by the increase in defect density caused by ion bombardment damage under high external bias.

XRD results (Fig. 3) show that both titanium nitride (TiN) and silicon nitride (Si_3N_4) have been formed. Comparing the XRD results with different external bias shown in Fig. 3, it is noticed that the intensity of TiSi_2 peak is reduced when the bias increases from 100 to 300 V (sample A to sample C). At the same time, there is an increase in the intensity ratio between Si_3N_4 (411) peak and TiN (220) peak from 200 to 300 V as shown in Table I. The reduced presence of TiSi_2 could be due to the high bombardment energy which leads to more thorough breakdown of the existing Ti_xSi_y structure. With the presence of nitrogen plasma and the existence of Ti and Si dangling bonds, the formation of TiN and Si_3N_4 are preferred than TiSi_2 when the substrate temperature is between 473 and 573 K. Thermodynamic data¹⁴ show that the enthalpies of formation (ΔH_f) of TiN and Si_3N_4 are -337.45 and -747.56 kJ/mol, respectively at 500 K, compared with those of -134.11 kJ/mol for TiSi_2 . The lower the ΔH_f , the easier the phase can be formed under the same process conditions.

The diffraction intensity ratio between the strongest peak of Si_3N_4 and that of TiN is worth noting. The atomic ratio of Si:Ti in the substrate is fixed in all samples before the nitrogen implantation. The variation in $I_{\text{Si}_3\text{N}_4(411)}/I_{\text{TiN}(220)}$ intensity ratio shown in Table I may be due to a higher degree of crystallization in Si_3N_4 phase. The current implantation of N into dissociated Ti_xSi_y structure is different from vapor deposition or electrochemical deposition where the mobility of adatoms is high on a newly formed surface. However, with limited mobility of dissociated Ti and Si in the substrate, the TiN and Si_3N_4 phases are likely to form where Ti and Si meet the impinging N. Thus, it is possible that there exists a higher percentage of crystalline Si_3N_4 in some of the specimens than others. It is well known that Si_3N_4 formed at relatively low temperatures is in amorphous form.^{3,15-19} However the current experiment clearly shows evidence of crystalline Si_3N_4 . Work is still on going to find out the mechanisms of its formation. In the current work, we attempt to explain the reasons for the higher degree of crystallization.

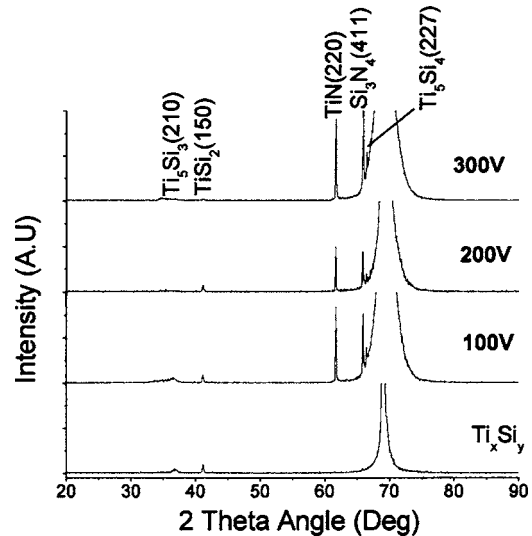


FIG. 3. XRD measurement of the Ti-Si-N film at different external bias. Titanium nitrate and silicon nitrates have been successfully formed through ICP process and the intensity increases at higher bias.

Comparing samples A, B, and C, when external bias increases from 100 to 200 V, the $I_{\text{Si}_3\text{N}_4(411)}/I_{\text{TiN}(220)}$ intensity ratio remains almost the same. From 200 to 300 V, the ratio increases significantly. Cu diffusion study in these formed ternary layers²⁰ finds that for the 300 V treated samples (C), significant diffusion of Cu into the ternary layer has happened after 500°C annealing. On the other hand, the 100 and 200 V (A and B) can prevent Cu diffusion even after 650°C annealing. Besides the reason that high external bias introduces lattice defects into the barrier, another reason could be that when more Si_3N_4 is in crystalline form, Cu diffusion becomes easier.

Figures 4(a) and 4(b) are ToF-SIMS depth profile showing that nitrogen has been successfully implanted to 10 nm deep into the Ti_xSi_y film. It is also found that increasing external bias from 100 to 300 V (sample A to sample C) does not improve the implantation depth of nitrogen. This comparison is made when argon and nitrogen gas flow rate was maintained at 10 and 30 sccm, respectively, and nitrogen plasma treatment time was 30 min. External bias does not seem to affect the N implantation depth in the current work. This indicates the kinetic energy of N atoms or ions is not a key factor for implantation depth; rather, the implantation is achieved by a time-dependant diffusion process.

From the above experimental results and discussion, applying 300 V bias does not improve N implantation depth and will degrade the conductivity significantly. Therefore 100 V is a suitable external bias when film sheet resistance, phase composition and depth profile of nitrogen are considered. From a processing point of view, 100 V bias will not cause much damage to devices. This voltage will be employed in the following experiments.

B. Effect of argon plasma activation time, argon gas flow rate, and nitrogen plasma treatment time

In the range of investigation, argon plasma activation time, argon gas flow rate, and nitrogen plasma treatment time

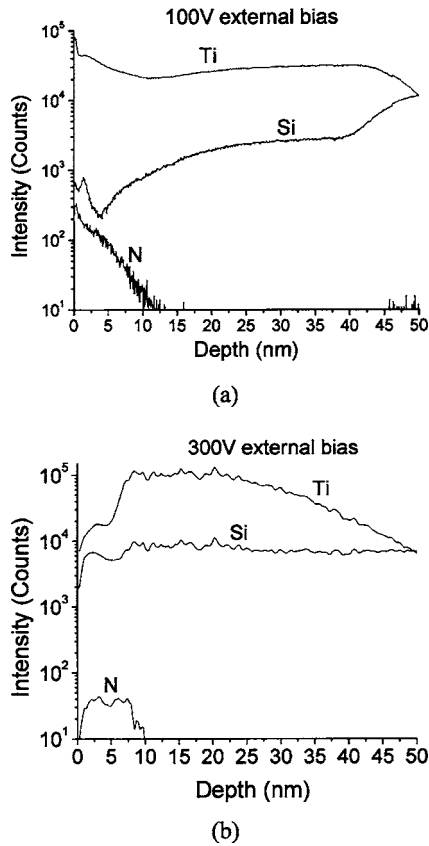


FIG. 4. Depth profile of Ti, Si, and N in the Ti–Si–N film for (a) 100 V, 10 sccm Ar gas flow rate, and 30 min N₂ plasma treatment time (b) 300 V, 10 sccm Ar gas flow rate, and 30 min N₂ plasma treatment time. Sputtering with 1 keV Ar⁺ ions.

do not show a significant effect on sheet resistance. Compared with the reference sheet resistance of 6.08 Ω/Sq, the measured sheet resistance at various process conditions (under fixed bias of 100 V) is within the range of 5.06–6.12 Ω/Sq as shown in Fig. 5. Combined with the results of the effect of external bias discussed above, current work indicates that external bias plays an important role in

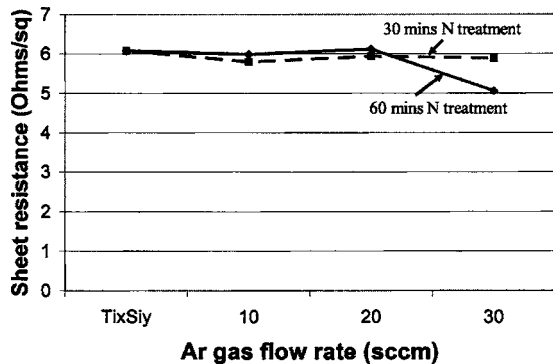


FIG. 5. Sheet resistance of Ti–Si–N films as a function of Ar gas flow rate and N plasma treatment time. No significant change in the sheet resistance is observed.

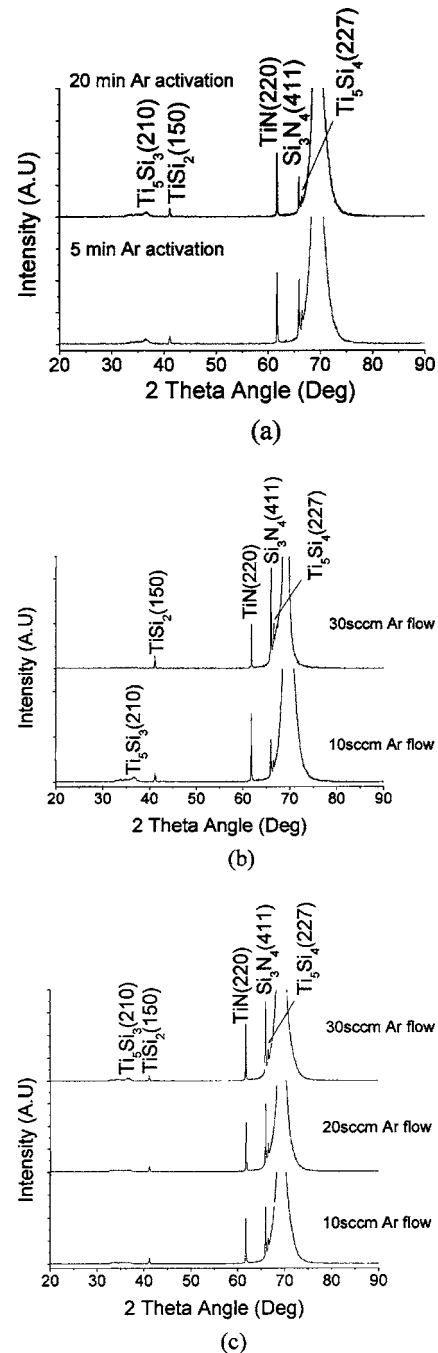


FIG. 6. XRD measurement of Ti–Si–N film subjected to (a) 5 and 20 min argon plasma activation time (b) different argon gas flow rate, 30 min nitrogen plasma treatment time. (c) Different argon gas flow rate, 60 min nitrogen plasma treatment time.

controlling the sheet resistance of Ti–Si–N films: The higher the external bias, the higher the sheet resistance of the Ti–Si–N films.

When argon plasma activation time changes from 5 to 20 min with argon gas flow rate and nitrogen plasma treatment time fixed at 10 sccm and 30 min, respectively, (comparing sample A and sample I), the same phases (TiN, Si₃N₄) are detected as shown in Fig. 6(a). When argon gas flow rate increases from 10 to 30 sccm, with argon plasma

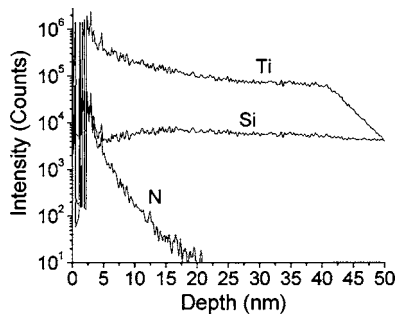


FIG. 7. Depth profile of Ti, Si, and N in Ti–Si–N film for 100 V external bias, 20 min argon activation with 10 sccm Ar gas flow and 30 min nitrogen plasma treatment time. Sputtering with 1 keV Ar⁺ ion.

activation time and nitrogen plasma treatment time fixed (comparing samples I, K, and M), the phase composition remains the same. However the Si₃N₄/TiN intensity ratio increases from 0.63 for sample I to 2.26 for sample M [Table I and Fig. 6(b)]. The trend with argon gas flow rate is much weaker when nitrogen implantation time increases to 60 min as shown in Table I and Fig. 6(c) (comparing samples J, L, and N). As discussed above, this rise in the intensity ratio indicates higher a percentage of Si₃N₄ is crystalline. The reason for the higher degree of crystallization of Si₃N₄ could be due to the higher degree of ionization when argon gas flow rate increases. The higher degree of ionization may also raise the substrate temperature, which enhances element mobility that favors crystalline phase formation. Again, the diffusion study²⁰ shows that sample M, which has the highest $I_{\text{Si}_3\text{N}_4(411)}/I_{\text{TiN}(220)}$ intensity ratio, performs the worst among samples with lower argon gas flow rates while other parameters are fixed (I, K, M).

Figure 4(a) shows the penetration depth of N of 10 nm with sample A subjected to 5 min argon plasma activation while other process parameters are fixed (100 V external bias, 10 sccm argon gas flow rate, and 30 min nitrogen plasma treatment time). When the argon plasma activation time increases to 20 min (sample I), there is a significant rise in the penetration depth of N to 20 nm as shown in Fig. 7. This shows that the penetration depth of nitrogen can be improved by extending argon plasma activation time.

IV. CONCLUSIONS

A low frequency, high density inductively coupled plasma process has been developed for the growth of Ti–Si–N film in which 2–67 at. % of nitrogen is successfully introduced into Ti_xSi_y structure. The Ti–Si–N film is mainly composed

of two major phases, TiN and Si₃N₄. In this work, the effect of various process conditions on the Ti–Si–N film properties has been investigated. It is found that the external bias plays an important role in controlling the sheet resistance of Ti–Si–N film, but not the implantation depth of nitrogen. The diffraction intensity ratio of Si₃N₄ and TiN could be a reflection of the degree of crystallization in the Si₃N₄ phase. Increasing argon plasma activation time will improve the penetration depth of nitrogen into Ti_xSi_y structure. It has been demonstrated that by controlling the process conditions, it is possible to grow Ti–Si–N films with controlled thicknesses and electrical properties.

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