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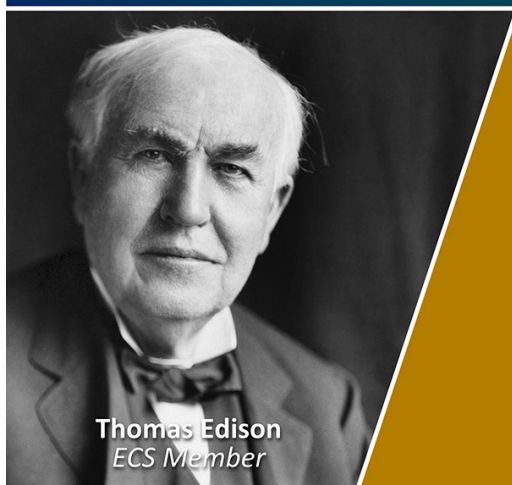
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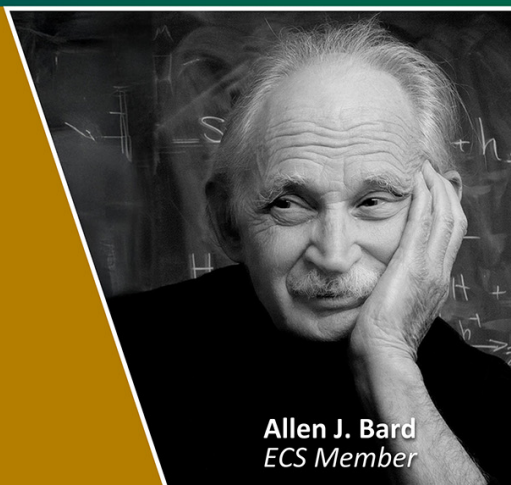


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Self-aligned TiN Formation by N₂ Plasma Bias Treatment of TiSi₂ Deposited by Selective Chemical Vapor Deposition

Kazuyoshi KAMOSHIDA* and Kunio SAITO

NTT System Electronics Laboratories, 3-1 Morinosato Wakamiya, Atsugi-shi, Kanagawa 243-01, Japan

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The titanium nitride (TiN) formation technology described here uses nitrogen plasma bias treatment to form self-aligned TiN only on the diffused layer from titanium silicide (TiSi₂) prepared by selective chemical vapor deposition (CVD). The nitriding was performed using magnetron sputtering equipment with an rf plasma source. Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and etching in 1% HF were used to characterize the samples. The contacts fabricated with the Al-2%Si/TiN/TiSi₂/Si barrier technology exhibit low resistivities of about $10^{-7} \Omega \cdot \text{cm}^2$. No excessive leakage of the 0.2- μm shallow junctions was observed even after thermally stressing the samples at 500°C for 30 min.

KEYWORDS: self-aligned, plasma processing, deposition, titanium nitride, selective CVD, titanium silicide

1. Introduction

The high degree of integration in very-large-scale integration (VLSI) technology has created a great demand for self-aligned processes. Titanium silicide (TiSi₂) can be formed in contact areas in a self-aligned fashion, and this is particularly important for making contact to sub-micron windows, for example a titanium self-aligned silicide (SALICIDE) process.¹⁾ Although self-aligned TiSi₂ has become a widely used low-resistance contact material, it needs a diffusion barrier to suppress the interaction between Al and the Si substrate. Titanium nitride (TiN) is one of the most suitable materials to use as a diffusion barrier between Si and contact metals because of its low resistivity and high chemical stability. Improved thermal stability can be achieved by using a TiN layer as a diffusion barrier between the silicide and the Al. A TiN layer also has the advantage of being resistant to wet etch in buffered HF, used for cleaning contacts after reactive ion etching.

Titanium nitride (TiN) is usually prepared by rf reactive sputtering of pure Ti targets in an Ar-N₂ mixed ambient.²⁾ A TiN/TiSi₂ bilayer structure can be formed by annealing a Ti film on Si in a N₂ or NH₃ atmosphere, which results in simultaneous growth of TiN and TiSi₂.^{3,4)} Alternatively, the silicide can be formed first and the nitriding can be done in a second anneal under N₂ or NH₃.^{4–8)} High-energy nitrogen ion implantation into Ti films followed by annealing at temperatures between 600°C and 800°C has also been used to form TiN/TiSi₂ bilayers on Si.^{9–12)} At such high temperatures, dissociated Si atoms are mobile and can grow epitaxially on the Si substrate, and this regrowth of Si onto the Si substrate may be detrimental to low-resistance ohmic contacts.⁷⁾ The use of a low-energy nitrogen ion beam to transform a TiSi₂ layer on Si to TiN was reported recently.¹³⁾ The advantage of the ion beam method is that the temperatures that can be used are considerably lower than those needed for conventional nitriding.

The selective chemical vapor deposition (CVD) method forms TiSi₂ only on the diffused layer and does not require many processing steps.¹⁴⁾ The nitrogen

plasma bias treatment method combined with the selective CVD TiSi₂ deposition method makes it possible to form self-aligned TiN only on the TiSi₂ surface. In addition, this technology requires fewer processing steps than the conventional two step annealing TiN/TiSi₂ formation technology does.⁸⁾

This paper describes a self-aligned TiN formation process at low temperature and the TiN film characteristics applied to the TiSi₂ contact regions using the selective CVD deposition method of interconnections in VLSIs.

2. Experimental

The process flow for test device fabrication is shown in Fig. 1. (100) oriented p-type and n-type 1–10 $\Omega \cdot \text{cm}$ 6-inch silicon wafers were used to obtain electrical characteristics. A low-energy arsenic ion (As⁺) was implanted to a dose of $4 \times 10^{15} \text{ cm}^{-2}$ to form shallow n⁺/p junctions. A low-energy boron fluoride ion (BF₂⁺) was implanted to a dose of $2 \times 10^{15} \text{ cm}^{-2}$ form shallow p⁺/n junctions. The dopants were activated by a rapid thermal annealing at 950°C for 15 min. Both the n⁺/p and p⁺/n junctions were formed about 0.2 μm deep.

A silicon wafer was dipped in dilute hydrogen fluoride (HF) and rinsed with deionized water. Titanium

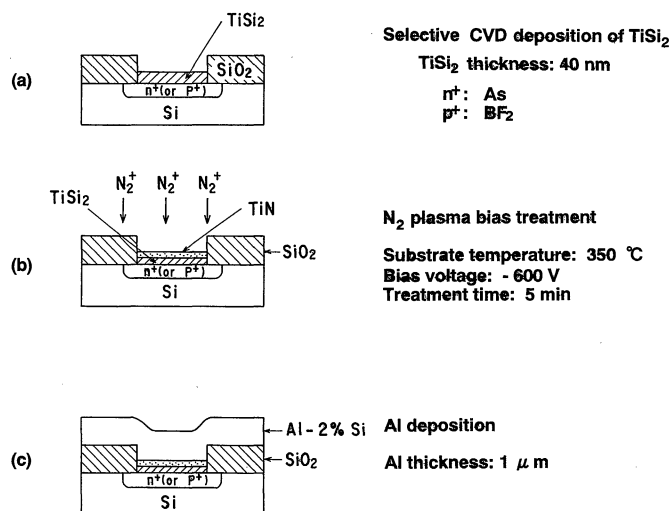


Fig. 1. Process flow for fabricating a test device by N₂ bias treatment of selective CVD TiSi₂.

*E-mail address: kamoshida@aegl.ntt.co.jp

silicide films were selectively grown by the following process using a CVD reactor.¹⁴⁾ First, *in situ* SiH₄ cleaning was performed at about 720°C with an SiH₄ flow rate of 10 sccm and a pressure of 0.5 mTorr (0.067 Pa). Titanium silicide films were selectively grown at 720–740°C with an SiH₄ flow of 20 sccm, a partial SiH₄ gas pressure of 1.9 mTorr (0.25 Pa), and TiCl₄ gas flow rates of 0.20 sccm. Selectively grown TiSi₂ films about 40 nm thick were deposited on the silicon contact for a deposition time of about 80 s. (Fig. 1(a))^{14, 15)}

Nitrogen (N₂) plasma bias treatment of the selective CVD TiSi₂ samples was performed using a sputtering system (Varian 3280) with an rf plasma stage operated in pure nitrogen gas at a pressure of 6.0 mTorr (0.8 Pa). The sputtering system is shown in Fig. 2. The rf system has a substrate table powered at 13.56 MHz during N₂ bias plasma treatment, and a bias voltage was applied to the substrate. The vacuum system was turbo pumped and the base pressure before the experiments was about 1×10^{-7} Torr (1.3×10^{-5} Pa).

The samples were mounted on a resistively heated sample holder using a backside gas flow system. Before they were nitrided, surface oxides and impurities were removed by argon sputtering with a bias voltage of –600 V for 1 min. Backside argon did not flow during this cleaning. This means that low substrate temperatures were maintained during this cleaning. The subsequent nitriding was performed with –600 V N₂ ions at a power density of 0.24 W/cm² to the substrate. We used N₂ bias treatments lasting 5 min at a substrate temperature of 350°C in these experiments (Fig. 1(b)). After nitriding of the TiSi₂ surface, 1-μm thick Al–2%Si alloy films were then deposited continuously and patterned (Fig. 1(c)).

The Auger electron spectra were recorded with a

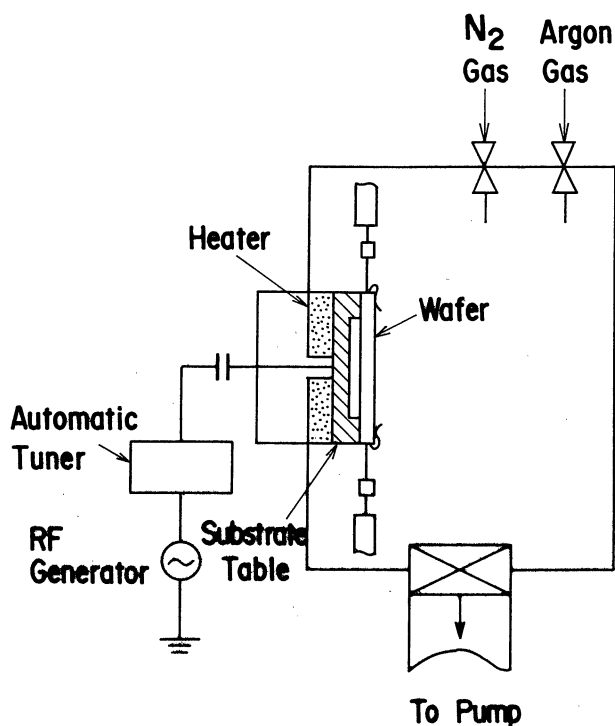


Fig. 2. Schematic diagram of the N₂ plasma bias treatment apparatus.

Phi Auger electron spectroscopy (AES) spectrometer using 5-keV electron beam energy and 6-eV peak-to-peak cylindrical mirror analyzer (CMA) modulation. Depth profiling was performed with 2-eV Ar ions at a current of 0.5-μA. X-ray photoelectron spectroscopy (XPS) analyses were performed in a Phi ESCA 548E spectrometer. XPS was used to analyze the chemical composition of the nitride TiSi₂ surfaces. Nonmonochromatic MgKα radiation (1253.6 eV) was used to excite photoemission. The binding energies of the Ti 2p, N 1s, and Si 2p peaks were calibrated with respect to the C 1s peak at 284.6 eV. Sputter etching was done with a differentially pumped Ar-ion sputter gun. The surface morphology was observed by using a scanning electron microscope (SEM). The etching tests were performed using a 1% HF solution at 22°C. The sheet resistance measurements were performed using standard four-point-probe techniques. The characterized TiSi₂ films were formed on blank Si substrates. Contact resistances were measured using Kelvin resistors.

3. Results and Discussion

3.1 Nitrogen plasma bias treatment process condition

First, the optimum N₂ bias treatment process conditions were determined using an HF solution because the TiN layer was resistant to dilute HF solution but TiSi₂ was not. Figure 3 shows the normalized sheet resistance of 40-nm thick selective TiSi₂ versus bias voltage. The treatment temperature was 350°C and the treatment time was 5 min. The sheet resistance of 40-nm thick selective TiSi₂ films was about 30 Ω/sq. This value was slightly high compared to the thick (≈100 nm) TiSi₂ films because film thickness dependence of sheet resistance and roughly grain growth occurred. But this value was similar to the conventional TiSi₂ films formed by rapid thermal annealing (RTA) in thin (≈40 nm) film thickness.¹⁶⁾ The characterized TiSi₂ films were formed on blank Si substrates. These films were the same as those deposited on the Si contact patterns.¹⁵⁾ The mea-

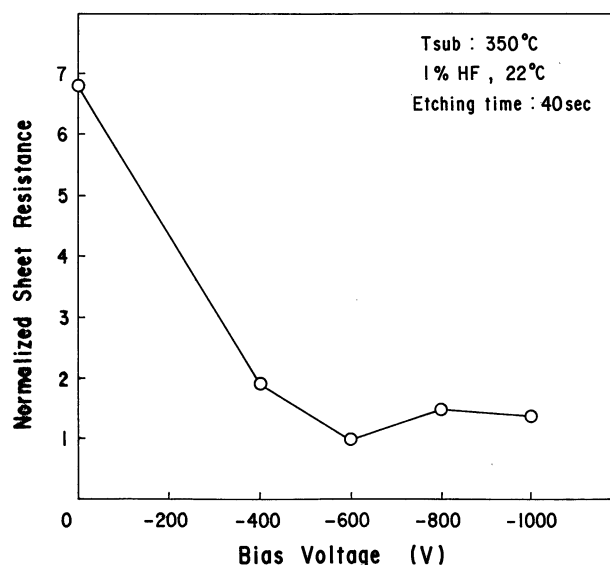


Fig. 3. The normalized sheet resistance of selective TiSi₂ versus bias voltage.

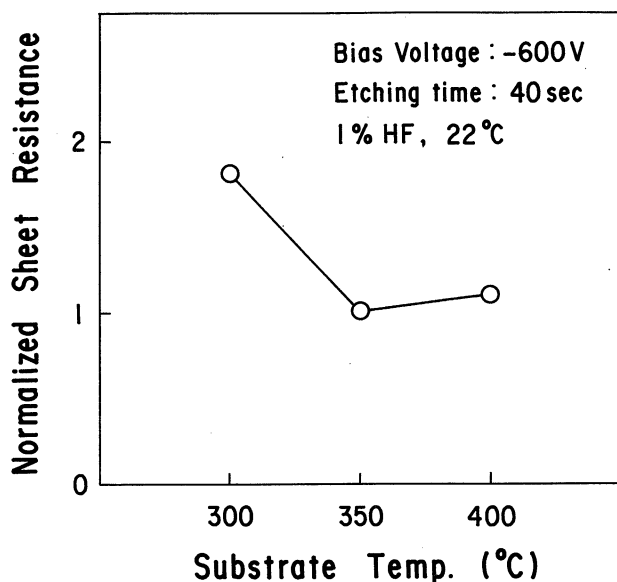


Fig. 4. The normalized sheet resistance of selective TiSi_2 versus substrate temperature.

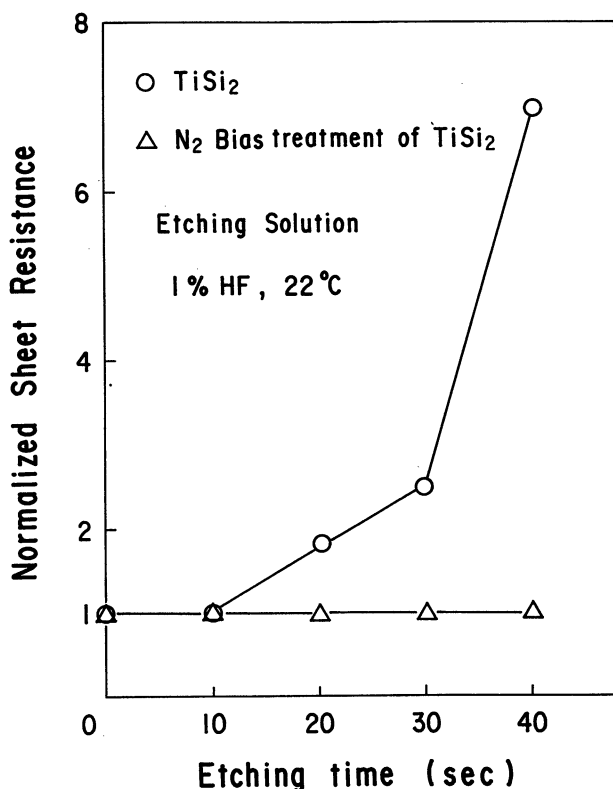


Fig. 5. The normalized sheet resistance of selective TiSi_2 versus etching time in a 1%HF solution at 22°C.

measurements of normalized sheet resistance used in standard film was 40 nm for selective CVD TiSi_2 . The film samples were etched for 40 s in 1%HF solution at 22°C and were rinsed in deionized water for 10 min. The normalized sheet resistance values were lowest at a -600 V bias voltage. When the bias voltage was over -600 V, the normalized sheet resistance values were slightly increased. Figure 4 shows the normalized sheet resistance versus substrate temperature. The normalized sheet re-

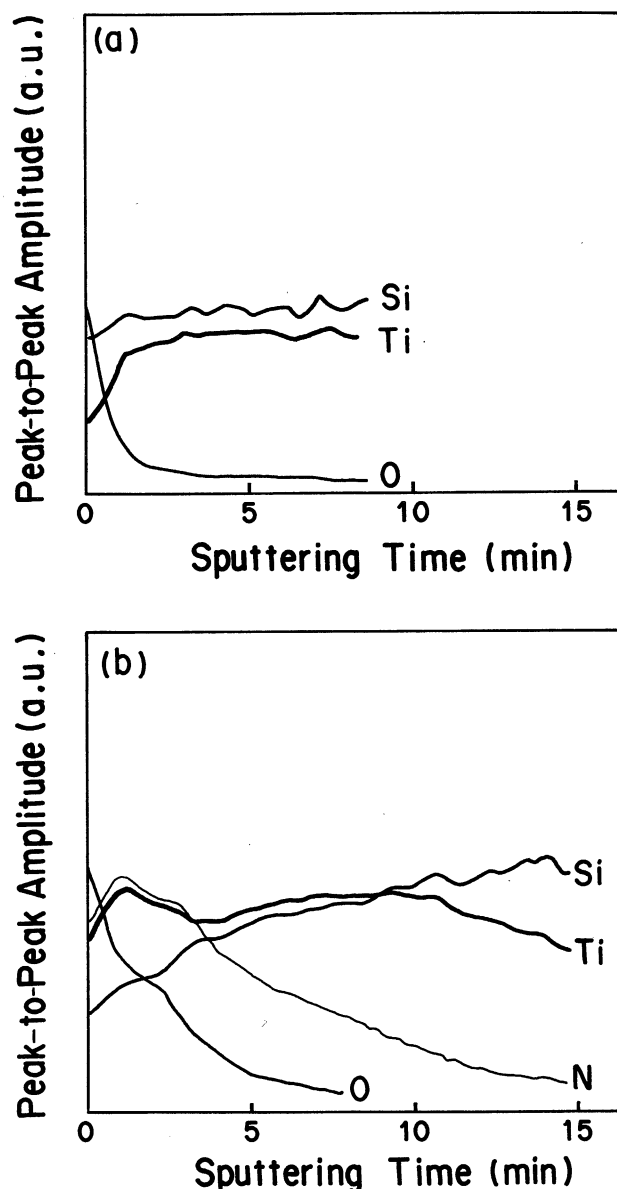


Fig. 6. Auger depth profiles: (a) selective CVD TiSi_2 and (b) the film after N_2 bias treatment at -600 V and 350° for 5 min.

sistance values were about unity at 350°C and 400°C. The optimum conditions for the N_2 bias treatment were an N_2 bias voltage of -600 V, and a substrate temperature of 350°C. The normalized sheet resistance versus etching time with or without N_2 bias treatment in 1% HF solution at 22°C is plotted in Fig. 5. The N_2 bias-treated samples showed greater stability improvement than did the samples that were not treated.

3.2 Auger electron analysis

The Auger electron spectra of TiN are complicated by the overlap of the N ($\text{KL}_{2,3}\text{L}_{2,3}$) and Ti ($\text{L}_{3}\text{M}_{2,3}\text{M}_{2,3}$) transitions at 382 eV kinetic energy. Thus, we used the semiquantitative analysis method.¹⁷⁾ The nitrogen content is characterized by the positive excursion of the combined nitrogen and Ti peak at 382 eV, and the Ti content is characterized by the negative excursion of the Ti peak at 418 eV. Figure 6 shows the AES depth profiles of (a) the selective CVD TiSi_2 , and (b) those of the N_2 bias

treatment of selective CVD TiSi_2 . The profiles of the film prepared by N_2 bias treatment of TiSi_2 are significantly different from those of TiSi_2 . Comparing these two figures reveals that N_2 bias treatment decreases the number of Si atoms and increases the number of N atoms. In the N_2 bias-treated samples, oxygen penetrated deeply into the TiN surface. The relatively long tails of the Ti and N profiles shown in Fig. 6(b) are thought to be due to the surface roughness of the film.

3.3 X-ray photoelectron spectroscopy analysis

Figure 7 shows the Ti $2p$ energy spectra obtained by XPS for films prepared by (a) as-deposited selective CVD TiSi_2 and by (b) -600 V N_2 plasma bias treatment at 350°C for 5 min. As-deposited selective CVD TiSi_2 films were evidently oxidized by residual oxygen in the process chamber or by atmospheric air because the TiO_x peaks (459.0 and 464.6 eV) are apparent in the XPS spectrum. The spectrum of the N_2 plasma bias-treated TiSi_2 sample, on the other hand, showed TiO_2 $2p_{3/2}$ (458.5 eV) and TiO_2 $2p_{1/2}$ (464.2 eV) peaks. Because the more diffuse spectra were observed, the N_2 plasma bias-treated TiSi_2 sample surface was etched using argon sputtering. After sputter etching of the TiSi_2 surface, TiN $2p_{2/3}$ (455.1 eV) and TiN $2p_{1/2}$ (461.0 eV) peaks and mixed TiO_2 peaks were observed.^{18,19} The TiN surface was partially oxidized to form titanium oxide (TiO_2).^{20,21} The Si $2p$ spectrum is shown in Fig. 8. As-deposited selective CVD TiSi_2 films showed the TiSi_2 peak (99.0 eV) and a small peak for oxidized Si (102.6 eV) (Fig. 8(a)). The N_2 bias treatment partially converted TiSi_2 to Si_3N_4 (101.7 eV), but TiSi_2 was still observed (Fig. 8(b)).⁶ Figure 9 shows the N $1s$ spectrum for N_2 plasma bias-treated TiSi_2 samples. The TiN peak (396.8 eV) and a small Si_3N_4

(397.7 eV) peak are evident, but the oxynitride (TiO_xN_y) peak (398.4–399.9 eV)²² cannot be observed. The TiN peak did not shift to a lower binding energy because TiN did not form oxynitride (TiO_xN_y).²¹ Another possible mixed compound such as TiSi_xN_y and $\text{TiSi}_x\text{N}_y\text{O}_z$ would probably not be formed by XPS. Judging from the XPS spectrum, the $\text{TiSi}_x\text{N}_y\text{O}_z$ peak (397.3 eV)²³ would also probably not be observed in our experiment.

From the above results, it was considered that the N_2 plasma treatment of the selective CVD TiSi_2 surface consists of an intimate mixture of TiN, TiO_2 and small amount of Si_3N_4 .

3.4 Contact resistance and leakage currents of N_2 plasma bias-treated selective CVD TiSi_2 samples

The contact resistance for n^+ and p^+ silicon is shown

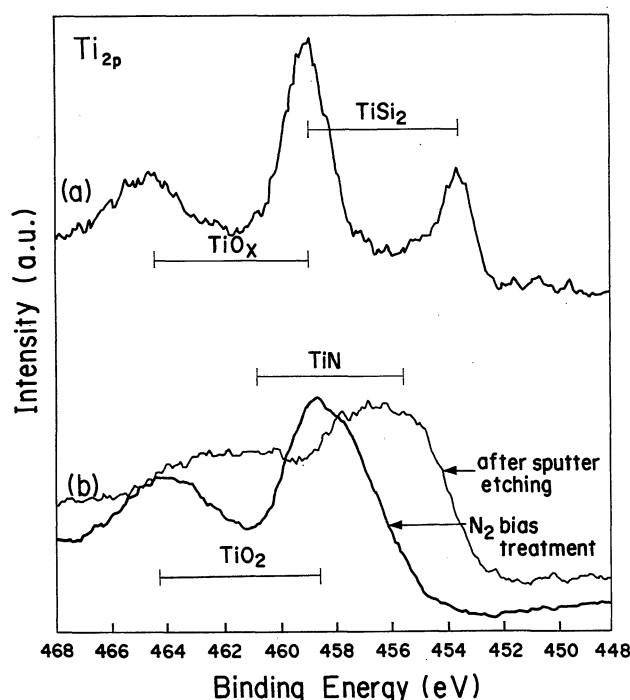


Fig. 7. The Ti $2p$ energy spectra obtained by XPS: (a) selective CVD TiSi_2 and (b) the selective CVD TiSi_2 film after N_2 bias treatment at -600 V and 350° for 5 min.

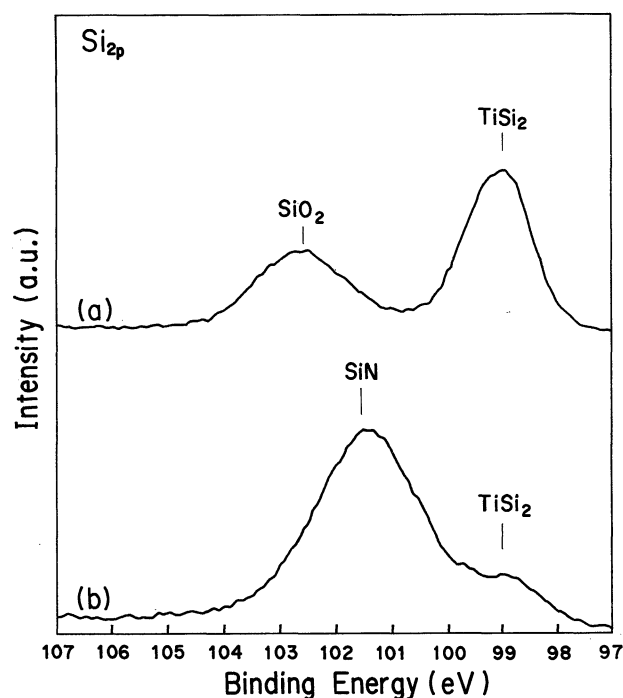


Fig. 8. The Si $2p$ energy spectra obtained by XPS: (a) selective CVD TiSi_2 and (b) the selective CVD TiSi_2 film after N_2 bias treatment at -600 V and 350° for 5 min.

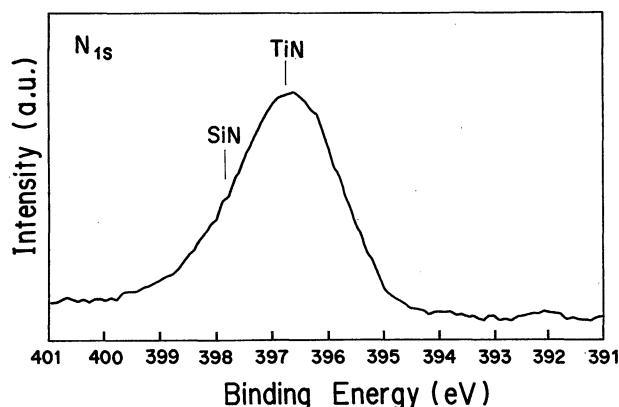


Fig. 9. The N $1s$ energy spectra obtained by XPS for a selective CVD TiSi_2 film after N_2 bias treatment at -600 V and 350° for 5 min.

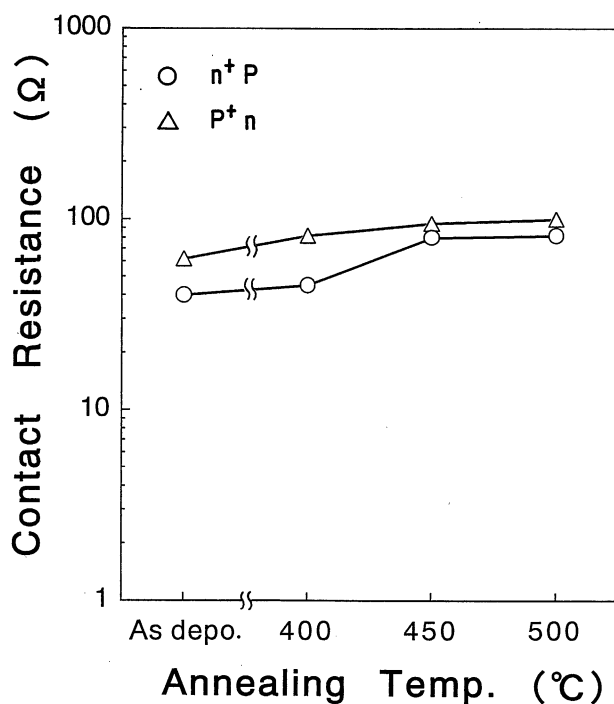


Fig. 10. Contact resistance for n^+ and p^+ silicon as a function of annealing temperature. The contact hole size was $1.0\ \mu\text{m}$ and the aspect ratio was 0.5.

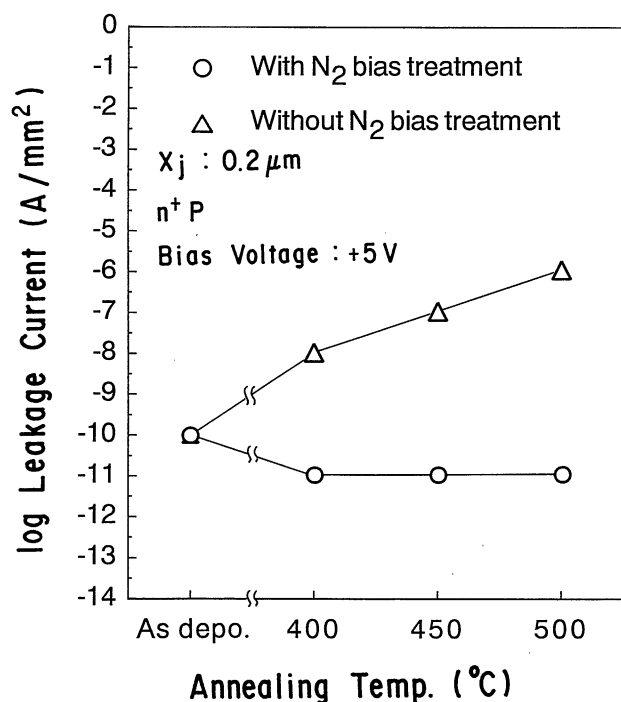
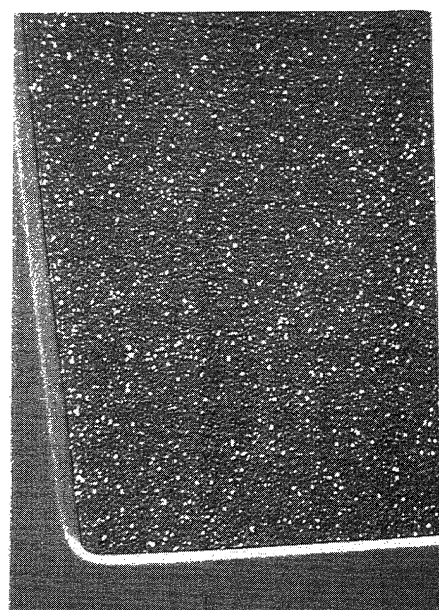
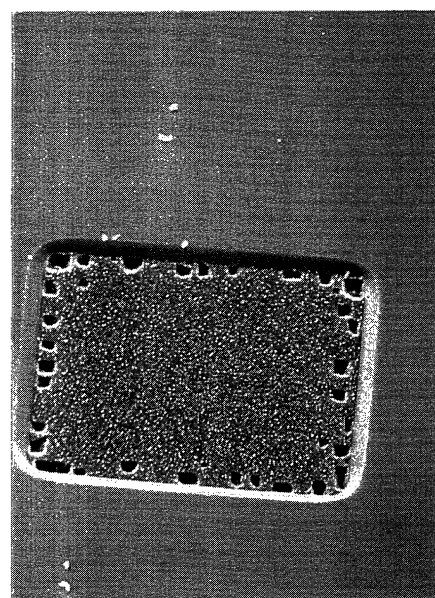


Fig. 11. Junction leakage currents of n^+/p and diodes with $0.2\ \mu\text{m}$ deep shallow junctions as a function of annealing temperature. Annealing time was 30 min.

in Fig. 10 as a function of annealing temperature. In this case, the contact hole size was $1.0\ \mu\text{m}$ and the aspect ratio was 0.5. The contact resistance for these two types of silicon, as-deposited samples are about $40\ \Omega$ for n^+ and $60\ \Omega$ for p^+ . Annealing at 400 – 500°C slightly increases the contact resistance. We inferred that the reason for



(a)



(b) $10\ \mu\text{m}$

Fig. 12. SEM micrographs of (a) $\text{Al-2\%Si/TiN/TiSi}_2/\text{Si}$ and (b) $\text{Al-2\%Si/TiSi}_2/\text{Si}$ contacts, both annealed at 400°C for 30 min and both shown after removal of the top $\text{Al-2\%Si}$ layer.

this was the oxygen being incorporated into the TiN surface. In the sample annealed at 500°C , the n^+/p contact resistance was $80\ \Omega$ and the p^+/n contact resistance was $100\ \Omega$.

The reverse leakage currents of the n^+/p diodes with $0.2\text{-}\mu\text{m}$ deep shallow junctions is shown in Fig. 11 as a function of annealing temperature. The junction areas were 0.1mm^2 for the n^+/p junctions, and the contact areas were about half the junction areas. For the $\text{Al-2\%Si/TiN/selective CVD TiSi}_2/\text{Si}$ contact system, the leakage currents of the junctions were approximately $1 \times 10^{-11}\text{ A}/\text{mm}^2$ at a reverse bias of $+5\text{ V}$. These val-

ues were almost unchanged by annealing at 400–500°C, which indicates that the TiN layer prevents the Al from penetrating the TiSi₂. In the TiSi₂ samples without N₂ plasma bias treatment, on the other hand, a large leakage current was observed increasing with the annealing temperature. In the sample annealed at 400°C, the leakage currents of junctions were approximately 1×10^{-8} A/mm² at a reverse bias of +5 V. To confirm this, we removed the top Al layer and made SEM micrographs. Figure 12 shows the SEM micrographs of samples (a) with the N₂ plasma bias treatment and (b) without the treatment. Both samples were annealed in argon at 400°C for 30 min. Notice that there is pitting around the edges of the contact hole where the Al has diffused into the TiSi₂ of the untreated sample, but interdiffusion is not at all evident in the picture of the treated sample. This indicates that the barrier in the treated sample is very stable.

4. Conclusion

Self-aligned TiN formation technology allows low-temperature N₂ plasma bias treatment with the selective CVD of TiSi₂ and makes it possible to form highly stable ohmic contacts with shallow junctions of multilevel interconnections without any deteriorative problems such as interdiffusion reactions of Al to TiSi₂.

We obtained a highly stable barrier and good resistance to etching in a dilute HF solution. The process is also much simpler than the sputtering deposition process and requires fewer steps. We think that this is a very promising technology for the fabrication of submicron multilevel interconnections.

Acknowledgements

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