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# TiN/TiSi<sub>2</sub> Formation Using TiN<sub>x</sub> Layer and Its Feasibilities in ULSI

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The new technique on the formation of the TiN/TiSi<sub>2</sub> bilayer from reactive deposition of TiN<sub>x</sub> and subsequent annealing was discribed. The nitrogen atoms in Ti matrix relax the mechanical stress of the deposited film as well as limited the available amount of Ti atoms involved in the silicidation reaction. Through the annealing process, the TiN<sub>x</sub> resulted in the bilayer structure of TiN/TiSi<sub>2</sub> formed between the thickness of the overlying TiN was sufficiently thick and that of TiSi<sub>2</sub> formed between the TiN and Si substrate was rather thin. Moreover, The TiSi<sub>2</sub> showed a well aligned epitaxial structure with an extremely uniform thickness.

## INTRODUCTION

In submicron devices, TiN is used either as barrier layer in combination with an aluminum metallization system or as an adhesion layer in a blanket tungsten(W) deposition process.<sup>11</sup> TiN layer can be formed by reactive sputtering<sup>21</sup> or by chemical vapor deposition techniques.<sup>31</sup> In this study we focussed on another technique: rapid thermal annealing(RTA) of reactively sputtered TiN<sub>x</sub> layer, resulting in the formation of TiN/TiSi<sub>2</sub> bilayer. In deep submicron processes, it is critical to limit the thickness of TiSi<sub>2</sub> formed on the shallow junction contact in order to preserve its contact properties. At the same time the overlying TiN layer has to be sufficiently thick to act as a barrier or etch stop layer. For the formation of TiN/TiSi<sub>2</sub> bilayer from conventional method, however, the relatively thick TiSi<sub>2</sub> with thin TiN layer is considered as a potential draw-back.

This work was aimed to suggest possible solutions to obtain the relatively thin TiSi<sub>2</sub> layer with a relatively thick TiN by using a TiN<sub>x</sub> film, which provides its applicability to submicron era of the today's most popular interconnection system of TiN/AICu/TiN/Ti multilayer lines.

## **EXPERIMENT**

The (100), 10–20  $\mathcal{Q}$ -cm resistivity, p-type Si wafers were used. After a standard cleaning process, TiN<sub>x</sub> films of 50nm thickness were reactively deposited on the substrate by using dc magnetron sputter in mixed gas atmosphere containing Ar and N<sub>2</sub> with nitrogen volume percent(**v**/**o**) ranging from 0% to 50%, and subsequently RTA's at the temperature range of 500–800°C for 20sec were carried out.

The nitrogen atomic percent(a/o) of as-deposited films was analyzed by using Rutherford

backscattering(RBS). The film stress before and after RTA was measured by stress monitor. The phase identification and the crystalline nature of the layers were performed using a X-ray diffraction(XRD). The depth profiles of Ti, Si, O, and N atoms were obtained by Auger electron spectroscopy(AES). The surface of the films was analyzed with scanning electron microscopy(SEM). The structure of annealed films was characterized using primarily transmission electron microscopy (TEM; Hitachi HF2000 FEG).

## **RESULTS and DISCUSSION**

Fig. 1 shows the variation of deposition rate and the a/o in the film as a function of N2 v/o. As the v/o increased up to 20%, the nitrogen content in the as-deposited film linearly increased to yield a stoichiometric TiN above 20v/o of N2. Throughout this paper, the films deposited at 0 v/o of N2, 0%< N<sub>2</sub> v/o <20%, and N<sub>2</sub> v/o > 20% are termed Ti. TiNx, and TiN, respectively. The mechanical stress of the films was found to be decreased with increasing the N2 v/o, showing no stress at 15 v/o[Fig. 2]. Furthermore, the surface and the cross sectional structure of TiNx(15 N2 v/o) was extremely smooth even after RTA, as shown in Fig. 3. This could be explaned by XRD data[Fig. 4]. That is, the lattice constant of the Ti matrix increased with increasing the N2 v/o, which eventually relaxed the tensile stress of the deposited film. However, above 20% of N2 v/o, the film showed the stoichiometric TiN, with (200) texture, which is consistent with the Fig. 1.

After RTA, as shown in Fig. 5, the peaks of Ti mainly consisted of random oriented TiSi<sub>2</sub> with the weak peak of (111)TiN. The only peak of (311)TiSi<sub>2</sub> with strong (111)TiN was observed in the case of 15 v/o TiN<sub>x</sub>. Finally, the TiN(at 20 v/o) showed the

more developed (200)TiN texture. This observation suggests that the nitrogen atoms in Ti matrix limit the available amount of Ti atoms involved in the silicidation process of Ti. The (111) preferred TiN texture could be due to the fact that atomic arrangement and interatomic distance of (002)Ti plane is very close to those of (111)TiN plane.

Atomic redistributions before and after themal annealing for the Ti and the TiN<sub>x</sub> films are shown in Figs. 6 and 7. The as-deposited pure Ti(or TiN<sub>x</sub>) films showed strong oxygen peak at the surface, owing to the chemisorbed oxygen (i.e., formation of Ti-O compound) during air exposure. This layer limited the nitrogen diffusion during RTA and allowed the silicon and Ti to interaction, resulting in the formation of relatively thicker TiSi<sub>2</sub> layer. On the contrary, in the case of TiN<sub>x</sub>, a layer with prominant nitrogen intensity which was identified as TiN was formed on the upper half of the film, and a thin TiSi<sub>2</sub> layer was formed below the TiN layer. Thicker nitride was formed as the annealing temperature decreased, because the nitridation is faster than the silicidation at lower temperature(not shown here)."

In the case of the Ti, most of Ti was used to form TiSi<sub>2</sub> during the annealing, and the TiSi<sub>2</sub>/Si interface was very irregular[Fig. 8(a)]. Also, the film did not show the continuous TiN layer on the surface but the dispersion of many precipitates, which were identified as TiN. Whereas, TiN<sub>x</sub> film provides an uniform bilayer of TiN/TiSi<sub>2</sub>. More interestingly, the lattice image associated with the epitaxial growth in large-lattice mismatch system appears at the TiSi<sub>2</sub>/Si interface[Fig. 8(b)].(wedge indicated) High resolution TEM obviously shows the misfit dislocation at the interface and well aligned TiSi<sub>2</sub> lattice image on the Si(100) substrate, which indicates the formation of the epitaxial TiSi<sub>2</sub> layer on the Si substrate[Fig. 8(c)]. In addition, the thickness of the overlying TiN increased with increasing N<sub>2</sub> v/o. As appearing in Fig. 9, the map of the normalized thickness of TiN, TiN+TiSi<sub>2</sub>, and TiSi<sub>2</sub> after RTA at 800°C as a function of N<sub>2</sub> v/o. Here, TiN+TiSi<sub>2</sub> means the thickness of TiSi<sub>2</sub> at which the TiN precipitates were dispersed. It means that the individual thicknesses could be controlled by the modification of process conditions, and the TiN<sub>x</sub> could satisfy the qualification for contact metallization of deep submicron devices.

#### CONCLUSION

High quality contact structure of TiN/TISI<sub>2</sub> bilayer on Si substrate, using the reactive TiN<sub>x</sub> and subsequent annealing, has been developed, in which the overlying TiN was sufficiently thick and the TiSi<sub>2</sub> was relatively thin. This process would bring about the improvement in the contact technology for future VLSI's.

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Fig. 1. Variation of deposition rate and nitrogen concentration in the as-deposited layer as a function of  $N_2$  v/o.



Fig. 2. Stress variation of deposited TiNx films with increasing  $N_{2}$  v/o.





Fig. 4. XRD spectra of the Fig. 5. XRD spectra after RTA at as-deposited (a) Ti, (b)  $TiN_x(at 800^\circC: (a) pure Ti, (b) TiN_x(at 15v/o), and (c) TiN(at 20v/o).$ 

Fig. 3. Surface of the as-deposited (a) Ti and (b) TiNx, and RTA treated (c) Ti and (d) TiNx at  $800^{\circ}C$ .



Fig. 6. AES profiles of pure Ti Fig. 7. AES profiles of TiNx film film (a) before and (b) after RTA (a) before and (b) after RTA at at 800 °C.



9. Normalized thickness of TiSi2, TiSi2+TiN, TiN after RTA at 800°C as a function of N2  $\,$ Fig. and v/o.



Fig. 8. TEM pictures after RTA at 800°C in N<sub>2</sub> ambient; (a) pure Ti, (b) TiN<sub>x</sub>(at 15 v/o), showing uniform TiN/TiSi<sub>2</sub> layer and the periodic contrast interface(wedge image with semicoherent interface(wedge indicated), and (c) HRTEM of sample (b), showing a TiSi2 lattice image with misfit dislocation.