Extended Abstracts of the 19th Conference on Solid State Devices and Materials, Tokyo, 1987, pp. 423-426 **S-II-6**

Impurity Effect on Reduction in Thermal Stress of Titanium Silicides

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In-situ titanium silicide film stress measurement has been carried out. A thermal stress was found to dominate the film stress. It was also found that an addition of an appropriate amount of impurity (especially boron) was effective in reduction of thermal stress. A tensile stress value after annealing was reduced to $(4.5\text{-}7.6)\times10^{9}$ dyne/cm^2.

1. INTRODUCTION

Titanium silicide ($TiSi_2$) resistivity is as low as 15-20$\mu\Omega$cm, even lower than that for molybdenum silicides ($MoSi_2$: 60-100$\mu\Omega$cm). Therefore, substituting titanium silicides into poly Si is very effective in reducing delay time caused by interconnection resistance. Since Murarka presented papers about Ti polycides[1,2], a lot of papers have been reported on various items. However, there are some problems, like disconnection at the steps, degradation in gate oxide leakage, acid or oxidation resistance, when applying to VLSI processing. Initial average composition for an as deposited silicide is one of the most important factors in applying to interconnection. $TiSi_3$ was chosen to be an appropriate composition, considering a compromise between resistivity and film stress. Stress reduces as Si component increases, however, resistivity increases with Si component enrichment. The resistivity is 22-25 $\mu\Omega$cm and the film tensile stress after annealing is $(1.3\text{-}1.5)\times10^{10}$dyne/cm^2. The stress value is too high for practical use. No thermal stress reduction method has yet been reported.

In this paper, the impurity effect on reduction in film stress is proposed. In order to reduce the stress, it is necessary to clarify whether the dominant factor is thermal stress or intrinsic stress. For clear discrimination between thermal and intrinsic stress, in-situ stress measurement[3-6] was carried out. The thermal stress was found to dominate the film stress. It was found that the addition of an appropriate amount of impurity(especially boron) was effective in stress reduction.

2. EXPERIMENTAL

Initial average composition $TiSi_3$ (0.3μm) films were co-sputtered on a SiO_2(1000-2000Å)/(100)Si or a poly-Si(4000Å)/ SiO_2(1000-2000Å)/(100)Si substrate. DC magnetron sputtering was performed by using a composite target(99.999 % purity). B^+, BF_2^+ or As^+ ions (1×10^{15}-1.5×10^{16} cm^{-2}) were implanted into Ti silicides. Acceleration voltages were chosen so that the projected ranges of ions were about the same as in Ti silicides. Then wafers were annealed at below 1000 ℃ in an Ar ambient in order to avoid oxidation or nitridation. Film stresses were determined by measuring the change in curvature for substrates induced by Ti silicides. The curvature was measured by Newton ring method. Microstructures were studied by

X-ray diffraction and transmission electron microscopy (TEM,TED).

3. RESULTS AND DISCUSSION

(1) Grain size and thermal stress

The change in stress due to film deposition was $(2.25 \pm 0.58) \times 10^9$ dyne/cm^2 in compressive direction, when 3000Å $TiSi_3$ films were deposited on 2000Å SiO_2 / Si(100) substrates. Fig.1 shows the stress value(σ) dependence on temperature (T) in the case of undoped $TiSi_3$ films. The heating rate was 15-20℃/min and cooling rate was 5℃/min. In Fig.1, positive and negative signs in stress values indicate tensile and compressive stresses, respectively. It is clear that most of the tensile stress at room temperature after annealing was thermal stress which was caused by the difference in thermal expansion coefficients between Ti silicides and Si substrates. Initial $TiSi_3$ crystallinity was amorphous and a sudden rise in the stress at around 450℃ was caused by volume shrinkage(5-10%) due to $TiSi_2$(C49) crystlliza-tion. Stress relief occurred at higher temperatures. When the maximum temperature was 980℃, the room temperature stress value was 1.45×10^{10} dyne/cm^2. This was also the case for Ti silicides with a poly Si underlayer. Moreover, the linear temperature dependence of the stress after annealing is reproducible. That is, if the temperature was raised again, the σ-T curve coincided with the previous cooling cycle. The result means that the strain caused by high tensile stress was elastic. A large σ-T difference between A and B in Fig.1, exists in the cooling cycle curve slope. For cases A and B, $-d\sigma/dT$ values are $(2.1\text{-}2.35) \times 10^7$ dyne/cm^2/K and 1.05×10^7 dyne/cm^2/K, respectively. X-ray diffraction shows that orthorhombic $TiSi_2$ and Si eutectic phases exist in both cases, as shown in Fig.2. However, the $TiSi_2$ annealed at 600℃ for 30 minutes was C49 type, and the $TiSi_2$ annealed at 980℃ was C54 type. Moreover, there is a large difference in grain sizes, as shown in Fig.3. Grain sizes ranged from 110 to 390Å for annealing at 600℃ and from 3000-6000Å

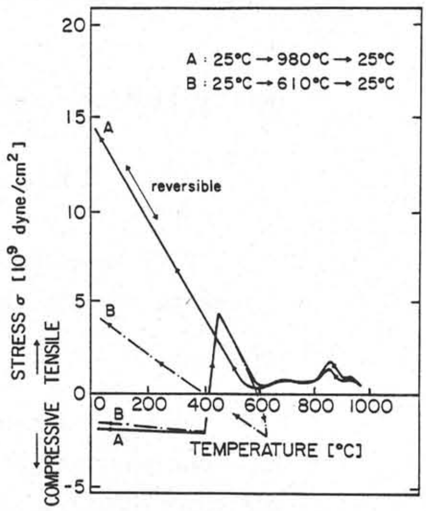


Fig.1 In-situ measured stress values during annealing for undoped $TiSi_3$.

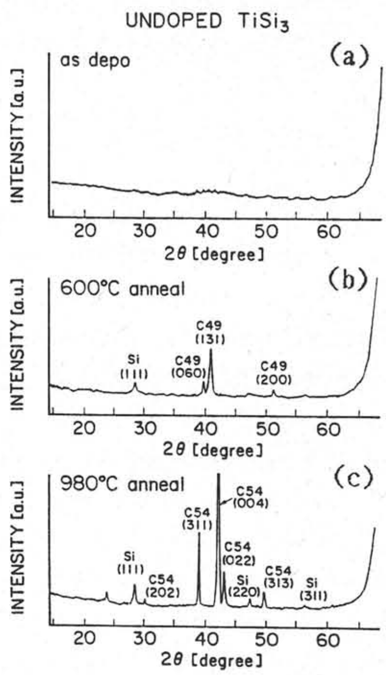


Fig.2 X-ray diffraction patterns for undoped $TiSi_3$. (a) as deposition, (b) 600℃ 30min and (c) 980℃ 30min.

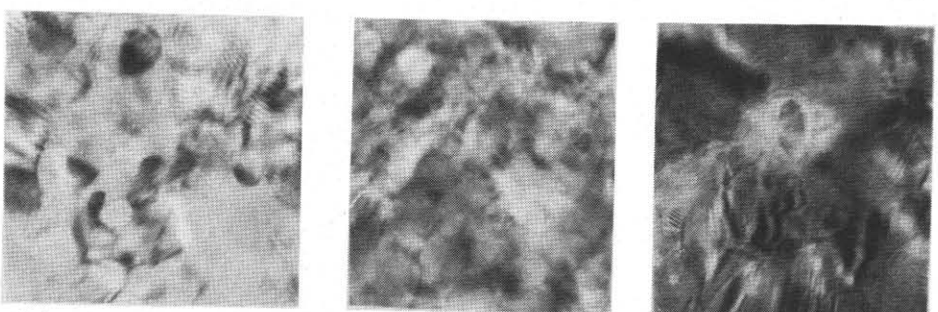
for annealing at 980℃. Fig.4 shows transmission electron diffraction pattern, which agrees well with X-ray diffraction results. A strain at the silicide/SiO_2 interface can be roughly evaluated by the thermal expansion coefficient, Young's modulus and Poisson's ratio. In the case of the 980℃ annealing, contact length between a $TiSi_2$ grain and the substrate is 3000-6000 Å (assumed to be equal to the grain size). Therefore, the strain is 17-34Å for the 600℃ temperature difference. On the other hand, in the case of 600℃ annealing, the contact length is around 110-390Å. Then, the strain is 0.63-2.2Å, which is much smaller than for the higher temperature annealing case. In Si rich Ti silicides, Si would precipitate at the $TiSi_2$ grain boundaries. So, the local strain due to temperature difference is smaller for smaller $TiSi_2$ grain size. A small strain should cause small stress in the films.

(2) Impurity doping effect

Impurity doping has been carried out by using ion implantation, in which dose and doping depth can be controlled. Fig.5 shows σ-T curves for the As^+, B^+, BF_2^+ implanted $TiSi_3$ films on 2000Å SiO_2/Si(100) substrates. Ion implantation with high doses caused 5×10^8-2.7×10^9dyne/cm^2 tensile stress in films. In all cases, the tensile stress values at room temperature after annealing at 980℃ were reduced, compared with undoped $TiSi_3$. The slopes of σ-T curves in a cooling cycle were plotted against implanted doses. As shown in Fig.6, effects of the doping was small for 1×10^{15}cm^{-2} dose, and the slope decreased with ion doses. Furthermore, B^+ or BF_2^+ addition was found to be more effective on tensile stress reduction than As^+ addition. The reason for more reduction in B^+ or BF_2^+ implanted cases is considered as follows. Free energy reduction by compound formation for TiB_2 is 24.7kcal/g atom at 1000℃. It is larger than that for $TiSi_2$ (10.3kcal/g atom). Therefore, the following reaction should occur easily.

$$TiSi_2 + 2B \rightarrow TiB_2 + 2Si \qquad (2)$$

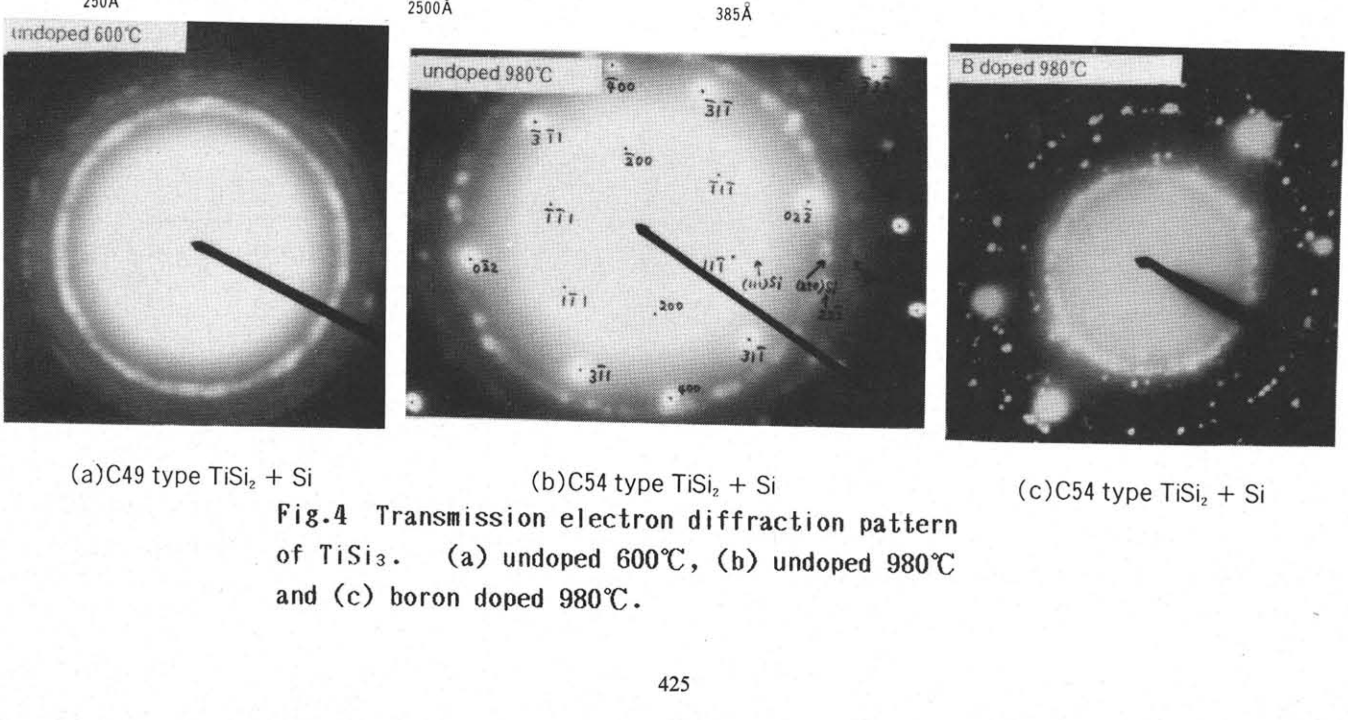
The melting point of TiB_2(2790℃) is twice that of silicide(1500℃). So, stable borides would be formed at grain boundaries of silicides and control the grain growth of $TiSi_2$. Microstructure of boron added Ti silicides is shown in Figures 3, 4 and 7. As shown in Figures 3 and 4, grain sizes for boron doped case were 1/2-1/3 of undoped case. From Fig.7 it was found that the C54 type $TiSi_2$ grains had (001) preferred orientation, however, in the case of impurity doped Ti silicides, (001) preferred orientation became weak, compared with undoped case. TiB_2 will block the $TiSi_2$ grain growth and weaken



(a) undoped 600℃ (b) undoped 980℃ (c) B doped 980℃

250Å 2500Å 385Å

Fig.3 Bright field image of $TiSi_3$.(a) undoped 600℃, (b) undoped 980℃ and (c) boron doped 980℃.



(a)C49 type $TiSi_2$ + Si (b)C54 type $TiSi_2$ + Si (c)C54 type $TiSi_2$ + Si

Fig.4 Transmission electron diffraction pattern of $TiSi_3$. (a) undoped 600℃, (b) undoped 980℃ and (c) boron doped 980℃.

(001) preferred orientation of the grain. These effects caused thermal strain reduction and effective thermal expansion coefficients of $TiSi_3$ were decreased. Therfore, thermal stress was reduced.

4. CONCLUSION

1. Most of the $TiSi_3$ stress after annealing at above 600℃ is thermal stress, which was caused by the thermal expansion coefficient difference between $TiSi_3$ and the substrate. In order to reduce the thermal stress, it is necessary to decrease the temperature gradient for the stress, $|d\sigma/dT|$.

2. For the reduction in $|d\sigma/dT|$, grain size shrinkage and weakening the (001) preferred orientation for $TiSi_2$ was very effective. By adding impurity atoms like boron, arsenic (especially boron), it was possible to reduce $|d\sigma/dT|$. The more doping, the more reduction.

3. By adding boron ($1.5 \times 10^{16} cm^{-2}$) into $TiSi_3$ films (3000Å), the tensile stress (at room temperature) was reduced to 1/2-1/3 of the undoped $TiSi_3$ after annealing above at 900℃. The stress value is $(4.5\text{-}7.6) \times 10^9$ dyne/cm².

4. Reason for the acceleration of reducing thermal stress by boron doping is considered to be due to a stable TiB_2 formation.

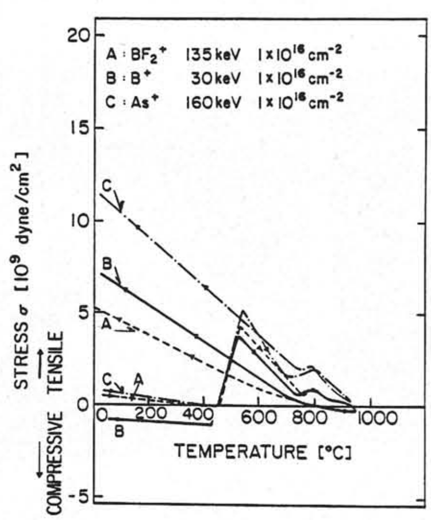


Fig.5 In-situ measured stress values during annealing for impurity doped $TiSi_3$.

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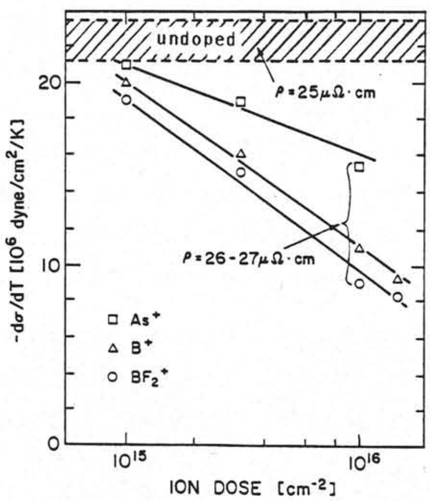

Fig.6 $-d\sigma/dT$ vs. impurity dose.

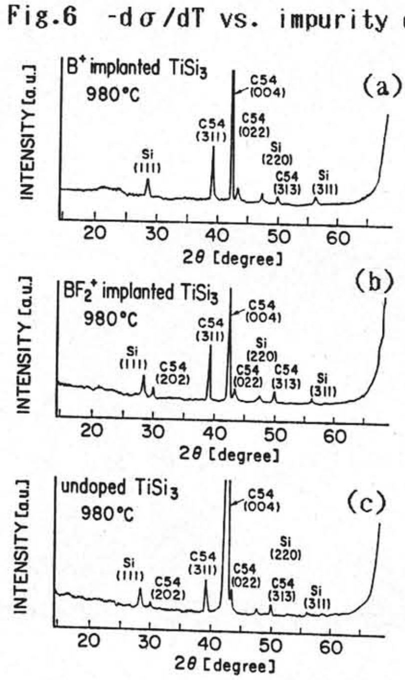

Fig.7 X-ray diffraction patterns for $TiSi_3$ after annealing at 980℃ for 30min. (a) B^+ doped (b) BF_2^+ doped (c) undoped.