1996

Microstructure and chemistry of thermal oxide on titanium silicide thin film

Kaynam Chun
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DOI: <https://doi.org/10.31979/etd.vqpq-9tr2>
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**Microstructure and Chemistry
of Thermal Oxide on Titanium Silicide Thin Film**

**A Thesis
Presented to
The Faculty of the Department of Materials Engineering
San Jose State University**

**In Partial Fulfillment
of the Requirements for the Degree
Master of Science**

**by
Kaynam Chun
May 1996**

UMI Number: 1379329

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ABSTRACT

Microstructure and Chemistry of Thermal Oxide on Titanium Silicide Thin Film

by Kaynam Chun

This research addresses the chemistry and the microstructure of thermal oxide on titanium silicide thin film on Si single crystal substrate. The multilayer oxide film structure was studied with Transmission Electron Microscopy (TEM), Fourier-Transmission Infrared Spectroscopy (FT-IR), Auger Electron Spectroscopy (AES), and Angle Resolved X-ray Photoelectron Spectroscopy (ARXPS).

The native oxide on as prepared titanium silicide was silicon oxide containing 0.4 atomic percent of titanium oxide. The multilayer oxide films represented the interfaces between silicon oxide, titanium oxide, and titanium silicide, in agreement with previous studies. No evidence of reaction between silicon oxide and titanium oxide at low, intermediate, and high temperature oxidations was obtained. TEM results of high temperature oxide films showed that the low temperature annealed titanium silicide (C49 phase) resulted in smaller titanium oxide precipitates than high temperature annealed titanium silicide (C54 phase). Selected Area Diffraction (SAD) patterns suggested that crystalline precipitates in high temperature oxide films was anatase and rutile.

ACKNOWLEDGEMENTS

The author wishes to thank his thesis advisor, Dr. Guna Selvaduray, Professor, Department of Materials Engineering, for his guidance and perseverance throughout this work. Special thanks to Dr. Peter Gwozdz, Professor, College of Engineering, for his valuable advice and for chairing the author's thesis committee. The author is grateful to Dr. Alex Payne, Censtor Corporation, for serving on the thesis committee, and for his valuable input that served to improve this work.

A special thanks is due to Mr. Dave Lopes at Hewlett-Packard Palo Alto Laboratory, Dr. Peiching Ling and Mr. Harry Kawayoshi at Advanced Materials Engineering Research, Mark Crockett, Dolores Miller, and Dave Nieman at IBM Almaden Research Center. Their support was necessary for this study.

The author thanks his parents, Mrs. Seung-won Shin, Mr. and Mrs. Sung-whan Chai. The author specially thanks his wife, Soon-mi and his daughter, Jane, for their patience throughout this study.

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I. INTRODUCTION

Transition metal silicides have been used for source, drain, and gate electrode materials in VLSI circuits.⁽¹⁾ The desirable features of silicides for VLSI applications are low resistivity, easy formation, easy patterning with high precision, good thermal stability, mechanical stability (good adherence to substrate), smooth surface, and low-resistance contacts with silicon. For VLSI application, the formation, properties, and oxidation of silicides have been investigated. An important issue for VLSI applications is the formation of pure SiO_2 dielectric films on silicide interfaces, in order to form a self-passivation layer.⁽¹⁻²⁾

In titanium silicide, the kinetics of oxidation and the oxidation mechanism were investigated in order to understand its oxidation behavior and to prepare metal-free silicon oxide on titanium silicide.⁽¹⁻²⁾ In particular, the effect of oxidation conditions on the kinetics and the formation of oxide have been of keen interest since the composition, microstructure, and growth kinetics of the oxide film on titanium silicide are dependent on oxidation conditions.⁽³⁻⁹⁾

Previous investigations showed that the oxidation of titanium silicide follows a linear-parabolic rate law and that pure silicon oxide film can be prepared at high temperatures when Si diffusion from the Si substrate is fast. Other studies showed that the decomposition of titanium silicide occurred during oxidation at intermediate temperatures and resulted in a mixed oxide (TiO_2 - SiO_2). These studies demonstrated that Si is the dominant element that diffuses during the oxidation and the formation of titanium silicide.⁽³⁻¹⁴⁾

Despite extensive work in this area, several aspects require further investigation. First, the oxidation products at low temperatures, when Si diffusion is not possible, is rarely known. The oxide which forms from titanium and silicon at low temperature are

unknown. In order to understand how the oxidation reaction occurs and what reaction mechanism controls the oxidation process at low temperatures, or at the early stage of oxidation, the chemical binding energies of Ti and Si in oxide film need to be determined. The crystalline phase of the various phases and microstructure have also not been identified according to oxidation temperature; this affects the diffusivity of silicon and the oxidants. Knowledge of the chemical bond and the crystalline structure of the oxide are important for understanding the kinetics and the thermodynamics of the oxidation of titanium silicide. Identification of the oxide phase according to oxidation temperature provides an understanding of the oxidation mechanism at early, intermediate, and later stages.

It has been considered that the oxidation of titanium silicide at low temperatures proceeds with the decomposition of titanium silicide.⁽³⁻⁵⁾ Partial decomposition of titanium silicide has been rejected because other silicide phases (e.g. TiSi) have not been observed near the oxide-titanium silicide interface during oxidation.⁽⁶⁾ Once the decomposition of titanium silicide occurs, free Ti and Si atoms will react with oxidants. Therefore, it is expected that titanium, with a higher standard Gibbs free energy than its oxide, will oxidize first. However, it is known that the oxidation of as prepared titanium silicide deviates from the ideal case since as prepared titanium silicide is polycrystalline and contains excess silicon over the ideal stoichiometric ratio of titanium disilicide. In this situation, it is interesting to know how as prepared titanium silicide reacts with oxidants, especially at the early stage where the oxidation reaction is strongly dependent on the chemistry and the microstructure of polycrystalline titanium silicide. Even at high temperatures, previous oxidation studies did not clearly explain the crystalline phase of titanium oxide but simply referred to it as TiO_x or titanium oxide.^(3,6) Some investigators have referred to the oxide as TiO_2 without presenting data on the crystalline structure.⁽¹⁴⁾ A recent study by G. J. Huang and L. J. Chen⁽¹²⁾ showed that orthorhombic TiO_2 (brookite) was formed by high temperature oxidation above 880°C. However, their result

seems to be questionable since amorphous titanium oxide from a pure chemical reaction (e.g. thin film reaction or sol-gel process) generally transforms to anatase first at low temperature and then transforms to rutile at higher temperature.⁽¹⁵⁻²⁰⁾ The oxidation of titanium silicide also can be considered as a pure chemical reaction unless impurities are involved in the oxidation reaction. It is known that the brookite phase has been found as a natural ore, containing some impurities. The transformation of titanium oxide in the sol-gel process and vapor-phase synthesis showed that titanium oxide is amorphous below 400°C and transforms to anatase above 400°C, and to rutile about 600°C.

A recent study by M. K. Akhtar et al. showed that the addition of SiCl_4 (5 - 10 mol%) or POCl_4 (8 - 15 mol%) to TiCl_4 made anatase phase stable even at 1227°C.⁽²¹⁾ Their results showed that the lattice parameters in a- and c-axis of Si- or B-doped titanium oxide increased with the addition of SiCl_4 or POCl_4 , suggesting that Si^{4+} and P^{5+} incorporation into the structure of titanium oxide occurred.

Inversely, the incorporation of Ti^{4+} into silicon oxide has been a topic of interest in solid state chemistry.^(22 - 25) Recently, D. C. Allan and M. P. Teter studied the titanium bond in α - quartz when one of the six silicon atoms (17 v/o) in the doubled quartz unit cell was replaced by one titanium.⁽²⁶⁾ Their *ab initio* theoretical study suggests that the replacement of silicon in α - quartz by titanium is possible. They found that the titanium atom has stable tetrahedral bonding as a replacement for silicon, with Ti-O bond length of about 0.18 nm, which is slightly elongated over the Si-O length of about 0.16 nm. The Ti-O bond length in rutile is about 0.195 to 0.198 nm. Their results suggest that the incorporation of Ti^{4+} into the silica network is possible and a partial solid solution in the TiO_2 - SiO_2 system may exist.

Similarly, the reaction between amorphous silica and amorphous titania during the oxidation of titanium silicide may be possible. It is interesting to know whether a Ti-O-Si molecular bond is formed during the oxidation of titanium silicide. If titanium oxide and

silicon oxide react, the most probable compound would be titanium silicate which has a Ti-O-Si bridge bond as a primary molecular bond. Titanium silicate containing Ti-O-Si bonds has been known well in titania-silica sol-gel systems.^(22, 27-31) The Ti-O-Si bridging bond is stable up to approximately 400°C; above that temperature, Ti-O-Si bond becomes unstable.⁽²⁷⁻²⁹⁾

Titanium disilicide, TiSi_2 , has two crystalline phases, C54 and C49.⁽³²⁾ C54 is thermodynamically stable and has a face-centered orthorhombic structure ($a=8.252 \text{ \AA}$, $b=4.783 \text{ \AA}$, $c=8.540 \text{ \AA}$).⁽³³⁾ C49 is a metastable phase and has a base-centered orthorhombic structure ($a=3.62 \text{ \AA}$, $b=13.76 \text{ \AA}$, $c=3.61 \text{ \AA}$).^(33,34) If the decomposition of titanium silicide during oxidation is dependent on the thermodynamic stability of its structure, it can be expected that the oxide microstructure of the C54 and C49 structures would have different crystal sizes and/or oxide film thicknesses.

The purpose of this study was to investigate the mass transport phenomena and the thermodynamics of the oxidation of titanium silicide on a silicon substrate. In an attempt to find evidence supporting a proposed mass transport and thermodynamic theory, the microstructure and the phase of oxide were analyzed according to oxidation temperature. The chemistry of oxide film and its crystallinity were also investigated. From the result of oxide chemistry and its crystallinity, the reactivity between TiO_2 and SiO_2 was inferred. Based upon the results in this study, three distinct stages of the oxidation of titanium silicide are proposed and a model of oxide layer structure is presented to show how the oxide film grows at various oxidation stages. The difference between C54 and C49 titanium silicide in oxide microstructure is also presented.

II. LITERATURE REVIEW

2.1. Ti-Si Intermetallic System

The phase diagram of Ti - Si intermetallic system is shown in Figure 1.⁽³⁵⁾ The five intermetallic phases in the Ti-Si system are Ti_3Si , Ti_5Si_3 , Ti_5Si_4 , TiSi , and TiSi_2 . Ti_5Si_3 has the highest melting point and TiSi_2 has the lowest melting point. As shown in the Ti-Si phase diagram, titanium silicide is a line compound. This means that TiSi_2 can coexist with either the Si or TiSi phase. S.P. Murarka reported that TiSi_2 containing some excess silicon had the lowest resistivity, as shown in Figure 2.⁽³⁶⁾ The Si/Ti ratio for the lowest resistivity film was close to 2.5, based on Rutherford backscattering (RBS) analysis. X-ray diffraction analysis of this film revealed only TiSi_2 .⁽³⁶⁾ The exact ratio of Si/Ti = 2.5 corresponds to one excess silicon atom per two TiSi_2 formula units, or four excess silicon atoms per unit cell of TiSi_2 . More than four Si atoms per unit cell cannot be accommodated and at higher Si/Ti ratios silicon is rejected and may be crystallized as a second phase in a matrix.⁽³⁶⁾

The formation of titanium silicide by reaction between sputtered or E-beam evaporated Ti and Si substrate has been extensively investigated.⁽³⁷⁻⁴³⁾ R.R. De Avillez et al.⁽⁴⁴⁾ investigated the phase formation in titanium-amorphous silicon multilayers. They showed that the amorphous phase was formed when the multilayer was heated to 427°C and the amorphous titanium silicide transformed to a metastable C49 crystalline phase near 587°C. They also noted that low temperature annealing (~400°C) resulted in a small amount of unreacted titanium layers in multilayers.

Figure 1. Ti-Si phase diagram. (After W.G. Moffat ⁽³⁵⁾)

Figure 2. Resistivity of co-sputtered films on oxide before and after sintering at 900°C for 30 min in hydrogen as a function of the nominal Si/Ti ratio in the film. The figure shows that the minimum resistivity is near the nominal Si/Ti ratio 2.5 - 3 and a film near the minimum resistivity contains excess silicon.(After S.P. Murarka ⁽³⁶⁾)

2.2. Structure and Property of TiSi_2

TiSi_2 has two crystalline phases, a metastable C49 phase and a stable C54 phase. The C49 phase has a base-centered orthorhombic structure (similar to ZrSi_2 structure, space group $D_{2h}^{17} = Cmc$) and is formed by reaction between Ti and Si at a low temperature of around 500°C . The C54 phase has a face-centered orthorhombic structure and is prepared at a high temperature of around 700°C . The C49 phase has four formula units in its unit cell and the C54 phase has eight formula units in its unit cell.⁽³⁴⁾ The lattice parameters of C54- TiSi_2 are $a = 8.2668 \text{ \AA}$, $b = 4.7897 \text{ \AA}$ and $c = 8.5503 \text{ \AA}$.^(32 - 34) The lattice parameters of C49- TiSi_2 are $a = 3.62 \text{ \AA}$, $b = 13.76 \text{ \AA}$ and $c = 3.606 \text{ \AA}$.⁽³²⁻³⁴⁾ Figures 3 and 4 show the unit cells of C54 and C49 TiSi_2 , respectively.

Figure 3. (a) a unit cell of C54- TiSi_2 is shown. (b) the arrangement of Ti atoms in $[010]$ direction, indicating four equivalent stacking positions, $A'B'C'D'$. Ti atoms on different lattice sites in (a) are noted by different symbols. (After T.C. Chou et al.⁽³⁴⁾)

Figure 4. (a) a unit cell of C49-TiSi₂ is shown in (a). (b) is a corresponding structure of the same unit cell. Ti atoms of different orthorhombics are indicated by different symbols. (After T.C. Chou et al. ⁽³⁴⁾)

R. Beyer ⁽³³⁾ and T. Chou et al. ⁽³⁴⁾ explained that the low temperature annealed C49 phase has heavily faulted grains and the high temperature annealed C54 phase has an equiaxed grains. The atomic positions of Ti in the C54 phase are similar to those of Si in the diamond cubic lattice. ⁽³⁴⁾ It is known that the low temperature annealed C49 phase shows higher resistivity (60 - 300 $\mu\Omega\text{cm}$) than high temperature annealed C54 phase (15 $\mu\Omega\text{cm}$). ⁽³³⁾ Typically, the C49 phase has a smaller grain size than an equilibrium C54 phase.

2.3. Kinetics of Oxidation

It has been reported that the oxidation of titanium silicide follows a linear-parabolic rate law which is similar to the oxidation of silicon.^(3, 5, 10, 45 - 47) The linear parabolic rate law can be expressed as followings:

$$X^2 + AX = B(t + \tau) \quad [1]$$

where X and t are oxide thickness and time, respectively. B is a parabolic rate constant and B/A is a linear rate constant. τ is a correction term that accounts for initial oxide thickness. Previous investigations showed that the diffusion of oxidants through the growing oxide film is the rate-determining step in a parabolic rate region, and a linear rate constant is related to the initial oxidation reaction.^(3, 4, 14)

The activation energy of the oxidation of titanium silicide in the linear rate region has been reported as 2.06 eV (199 KJ/mol); for the parabolic rate region the value reported was 1.5 eV (144.97KJ/mol).^(3, 47) J. R. Chen et al. showed that the formation of small amounts of titanium oxide did not influence the activation energies in the linear and parabolic regions.⁽³⁾ More recently, G.J. Huang and L.J. Chen⁽¹²⁾ showed that the activation energy of the oxidation of titanium silicide in wet atmospheres was slightly less than that for oxidation in dry atmospheres. A lower activation energy in wet atmospheres indicates that titanium silicide was more reactive to H_2O than O_2 . The lower activation energy in wet oxidation has been also observed in the oxidation of silicon and the oxidation of various silicides.⁽⁴⁷⁾ The similarity between the oxidation of titanium silicide and the oxidation of silicon can be shown in Arrhenius plots of linear and parabolic rate constants for the oxidation of titanium silicide and the oxidation of silicon, as shown in Figure 5, 6, 7, and 8 respectively. These Arrhenius plots represent oxidation above 700°C.

Figure 5. Arrhenius plot of the linear rate constant for the oxidation of titanium silicide in wet atmospheres. (After J.R. Chen et al. ⁽³⁾)

Figure 6 Arrhenius plot of the parabolic rate constant for the oxidation of titanium silicide in wet atmosphere. (After J.R. Chen et al. ⁽³⁾)

Figure 7. Arrhenius plot of the linear rate constant for the oxidation of silicon in wet and dry atmospheres. (After B.E. Deal and A.S. Grove et al.⁽⁴⁵⁾)

Figure 8. Arrhenius plot of the parabolic rate constant for the oxidation of silicon in dry and wet atmospheres. (After B.E. Deal and A.S. Grove et al.⁽⁴⁵⁾)

2.4. Mass Transport During Oxidation

M. Barter ⁽¹⁰⁾ explained that four distinct types of mass transport occur during the oxidation of titanium silicide. The proposed mass transport mechanisms during the oxidation of titanium disilicide are shown in Figure 9. First, oxidants diffuse through the growing oxide layer. Second, the oxidation reaction occurs at the silicide-oxide interface. Third, net transport of silicon atoms, with respect to metal atoms, occurs in the silicide. Fourth, the reaction also occurs at the silicide-silicon interface.

Figure 9. Four distinct mass transports in the oxidation process.(After M. Bartur ⁽¹⁰⁾)

To investigate the mass transport mechanism in the oxidation of titanium silicide, inert marker or radioactive tracer methods have been used. ^(4, 5, 14) Previous investigators explained that silicon is supplied rapidly through the silicide matrix at high temperatures. In Table 1, the dominant diffusing species during oxidation and the formation of silicide are shown. ^(10, 14) Most silicides, except CrSi₂, have the same diffusing element for both

oxidation and silicide formation. Radioactive tracer experiments using ^{31}Si showed that silicon atoms from the Si substrate diffuses through the titanium silicide layer via grain boundary or interstitial diffusion during oxidation.⁽⁴⁾ In the case of titanium silicide, it is known that the diffusivity of Si affects the growth rate of the oxide at high temperatures.

Table 1. Dominant mobile species in the formation and the oxidation of silicide.^(10, 14)

Silicide	Moving species in silicide formation	Moving species in silicide oxidation
TiSi_2	Si	Si
CoSi_2	Co	Co
NiSi	Ni	Ni
NiSi_2	Ni	Ni
Pd_2Si	Pd,Si	Pd,Si
PdSi	Pd,Si	Pd
PtSi	Pt	Pt
CrSi_2	Si	Cr

2.5. Thermodynamics of Oxidation and Phase Equilibria in Ti-Si-O System

The formation of oxide on titanium silicide films has been explained based upon the enthalpy of formation of an oxide.^(10, 11, 14) Due to inaccuracy or incompleteness in published thermodynamic data, only qualitative predictions have been made by previous investigators. Previous studies on the oxidation of titanium silicide showed that the oxidation of titanium silicide resulted in silicon oxide with or without titanium oxide depending on the oxidation temperature. H. Jiang et al.⁽¹⁴⁾ emphasized two facts regarding the oxidation of titanium silicide. First, some discrepancy between experimental results and thermodynamic prediction may exist because of inaccurate data on the formation enthalpy of oxides. Second, the kinetics of oxidants and Si play a major role at high temperature.⁽¹⁴⁾ The formation of oxide at high temperature is affected by fast Si diffusion from the Si substrate. In the case of oxidation at intermediate or low temperatures, where Si diffusion is not rapid, thermodynamic predictions for oxidation seem possible since only thermodynamic factors affect the formation of oxides. Since three elements (silicon, oxygen and titanium) are involved in a reaction at the oxide-silicide interface, the phase equilibria in the Ti-Si-O system has been another approach to understand the oxidation mechanism, oxidation products, and the reaction condition at the oxide-silicide interface. R. Beyers^(48, 49) proposed the phase diagram shown in Figure 10 for the Ti-Si-O system. It shows the presence of stable tie lines at the TiSi_2 - SiO_2 and TiO_2 - SiO_2 interfaces in the temperature range of 700 - 1000°C. This suggests that SiO_2 is a stable phase which coexist with TiSi_2 or TiO_2 . On the other hand, the absence of a TiSi_2 - TiO_2 tie line suggests that TiO_2 reacts with TiSi_2 . The proposed phase diagram also shows that most of the titanium oxides have stable tie lines with SiO_2 . It is interesting to know if the proposed phase diagram is correct at the proposed temperature range and if it

is also applicable at lower temperature ranges below 700°C. The oxide phase analysis and molecular bond analysis of oxidation products should reveal the phase equilibria in the Ti-Si-O system.

Figure 10. Calculated phase diagram for Ti-Si-O system in the temperature range 700 - 1000°C. (After R. Beyers et al. ^(48,49))

2.6. Titanium Silicide Formation Process

2.6.1. Effect of Oxygen Impurity

Oxygen impurity during the silicidation process has been found to result in an entrapped oxide in as prepared titanium silicide.^(39, 43, 48, 50) Four contamination sources have been known: poor vacuum condition during titanium deposition, adsorption of oxygen during air exposure, oxygen contamination in nitrogen for rapid thermal annealing (RTA) process, and native oxide on silicon substrate due to inadequate chemical cleaning.^(1, 40 - 43, 50) Oxygen impurity affects the formation and the growth of titanium silicide in the solid state reaction between silicon and titanium.

P. Merchant and Jun Amano⁽⁴³⁾ investigated oxygen redistribution in sputtered titanium films on silicon during ultra high vacuum (UHV) sintering. Using Rutherford Backscattering Spectroscopy (RBS) with a detection limit of 1.5×10^{20} oxygen/cm³, they observed that as-deposited Ti film had exponential oxygen distribution, decreasing from the titanium film surface, and that this exponentially distributed oxygen moved into the film during low temperature vacuum sintering at 450°C. Later, the distribution of oxygen became uniform throughout the film thickness. For high temperature reaction (800°C, 30 min) between titanium and silicon, they observed that the uniformly distributed oxygen at low temperature was snow-plowed back toward the surface while titanium silicide is formed, and is completely driven away from the TiSi₂ film after high temperature annealing. Their results imply that oxygen incorporation into titanium silicide does not occur, or is below the RBS detection limit of 1.5×10^{20} oxygen/cm³. The low sheet resistance (5.8Ω/sq) of as prepared titanium silicide proves that oxygen impurity in the structure of titanium silicide is very low.⁽⁴³⁾

In cosputtered Ti + Si films, R. Beyer et. al. have shown that the trapped oxygen in the film accumulates at the titanium silicide-silicon interface and forms SiO_2 .⁽⁴⁸⁾ Their results also indicated that oxygen incorporation into titanium silicide does not occur. Additionally, the formation of SiO_2 at the silicide-silicon interface suggests that titanium silicide forms a stable interface with silicon oxide. Tie lines in the calculated phase diagram of the Ti-Si-O system in Figure 10 suggest that a stable interface exists between TiO_2 and SiO_2 and also between TiSi_2 and SiO_2 in the temperature range of 700 - 1000°C.

In TiO_2/Si and $\text{Ti/TiO}_2/\text{Si}$ films, M. Berti et. al. investigated the formation of titanium silicide under vacuum ($<5 \times 10^{-7}$ Torr).⁽³⁹⁾ They observed that the TiO_2/Si interface was stable up to 900°C and in $\text{Ti/TiO}_2/\text{Si}$ films, metallic titanium reacted with TiO_2 film above 400°C and a uniform oxygen solid solution was formed at 600°C. They observed that in $\text{Ti/TiO}_2/\text{Si}$ system, Ti_5Si_3 formed at 650°C and was stable up to 750°C; above 750°C TiSi_2 formed rapidly while an outward oxygen diffusion toward the surface of growing titanium silicide occurred. Oxygen diffusion toward the outer surface of the growing titanium silicide suggested that titanium silicide did not accommodate oxygen impurity into its structure.

The formation of TiO_2 - SiO_2 mixed oxide on oxidized titanium silicide film and the formation of entrapped silicon oxide at the silicide-silicon interface suggested that the calculated phase diagram in Figure 10 predicted the phase equilibria (or interfacial condition) in the Ti-Si-O system quite well. However, it is uncertain that the calculated phase diagram can be applied to lower temperature regions below 700°C. Phase analysis of the interface of low temperature oxide films should address this question.

2.6.2. As Prepared Titanium Silicide

In the previous section, the effect of oxygen contamination on the formation of titanium silicide was discussed. For a solid state reaction between silicon and sputtered titanium, rapid thermal annealing under nitrogen atmosphere has been widely used. During the process the top surface of the sputtered titanium film reacts with nitrogen and forms a TiN layer. If oxygen impurity exists either in the sputtered Ti film or in the annealing atmosphere, a TiON film is formed on the surface.⁽⁴⁰⁾ However, titanium containing layers can be removed by selective chemical etching.^(38 - 43, 50) It was reported that selective chemical etching left an amorphous oxide layer on the surface of titanium silicide. The formation mechanism of an amorphous oxide is not clear. It was assumed that excess Si in as-prepared titanium silicide was oxidized during the selective etching.

R. Beyers et al. reported that the amorphous oxide on titanium silicide was silicon oxide. Based upon their observation, R. Beyers et al. proposed the following. First, during rapid thermal annealing a transition layer containing titanium, silicon, nitrogen and oxygen was formed between the top TiN layer and titanium silicide underlayer. Next, the selective chemical etching removed the top TiN layer and also selectively removed titanium and nitrogen from a transition layer and then formed an amorphous silicon oxide. The selective chemical etching did not change the thickness of the annealed titanium silicide. Titanium oxide (possibly Ti_2O_3) can then be formed on the as-annealed silicide but can be removed by selective chemical etching. If elemental silicon did not exist in the transition layer or in the micro-crystalline titanium silicide, the decomposition of micro-crystalline titanium silicide should occur to supply silicon to form an amorphous oxide during selective chemical etching.

The calculated Ti-Si-N phase diagram in Figure 11 can explain how amorphous silicon oxide was formed during selective chemical etching after rapid thermal annealing.^{(38,}

⁴⁹⁾ The Ti-Si-N phase diagram shows that TiN, rather than Si_3N_4 , is the stable nitride in contact with TiSi_2 . Hence, even though silicon diffusion in TiSi_2 is very rapid at high temperatures (above 700°C), the formation of a Si_3N_4 layer on TiSi_2 is not anticipated. Instead, the formation of TiN occurs at the surface of TiSi_2 , and TiN coexists with the free Si from the decomposition of TiSi_2 in a nitrogen atmosphere. ⁽³⁸⁾ This reaction can be written as the following reaction:

Therefore, it can be concluded that free silicon exists in the transition layer or in the micro-crystalline titanium silicide just below the top TiN layer during rapid thermal annealing.

Figure 11. Calculated phase diagram for Ti-Si-N system at $700 - 1000^\circ\text{C}$
(After R. Beyers ⁽⁴⁹⁾)

In addition, even after proper selective chemical etching, a high Si/Ti ratio of over 2 has been observed. S. J. Rosner et al. reported that as prepared titanium silicide had a Si/Ti ratio of 2.2 ~ 2.3 if the titanium silicide film is prepared by the reaction of sputtered Ti metal with a Si substrate.⁽⁷⁾ If as prepared titanium silicide contains excess Si after RTA process, excess Si in titanium silicide will affect the early stage of the oxidation of titanium silicide. M.A. Taubenblatt and C. R. Helms also observed a Si/Ti ratio of 2.5 from the silicide film annealed at 700°C.⁽⁵¹⁾ A.E.T. Kuiper et al. reported that small amounts of silicon in as-prepared titanium silicide films tend to segregate at grain boundaries or top surfaces of titanium silicide during the initial oxidation at low temperatures below 800°C.⁽⁵²⁾ These previous results explain that titanium silicide contains some amount of excess Si and it tends to diffuse out to the surface of the titanium silicide under oxidizing conditions.

2.7. Oxidation Products on Titanium Silicide

The chemistry and the microstructure of oxide films on titanium silicide are dependent on the microstructure and composition of as prepared titanium silicide and on the oxidation conditions. Table 2 shows the oxidation products according to the results of previous investigations. The results in Table 2 clearly show that oxidation at low temperatures (300 ~ 800°C) resulted in a mixed oxide ($\text{TiO}_x - \text{SiO}_2$) and that high temperature oxidation above 800°C resulted in pure SiO_2 . Table 2 shows that the oxidation products from temperatures below 300°C have rarely been studied.

Table 2. Effect of oxidation temperature on oxidation products of titanium silicide.

Investigator	Atmosphere	RT	300°C	600°C	700°C	800°C	1000°C
W.Y. Yang et al. ⁽⁶⁾	Air ambient	SiO ₂	TiO _x - SiO ₂ mixed oxide				pure SiO ₂
S.J. Rosner et al. ⁽⁷⁾	Steam, high pressure	Si rich mixed oxide				pure SiO ₂	
T.Sandwick (52)	dry oxygen ambient	TiO _x - SiO ₂ mixed oxide					
R. Perez et al. ⁽⁵³⁾	Oxygen plasma	TiO ₂ - SiO ₂ mixed oxide		Pure SiO ₂			
T. Huang and S. Lee ⁽⁹⁾	H ₂ O ambient					Ti-Si-O layer	

W. Y. Yang et. al. ⁽⁶⁾ studied the oxidation products from room temperature to 1000°C using X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). Their results showed that as prepared titanium silicide (C54-TiSi₂) was covered with silicon oxide and the relative atomic ratio of Si to Ti in TiSi₂ was about 2.5 ~ 3.1. They explained that surface silicon oxide was formed by the reaction between the residual oxygen in the vacuum system and silicon which was supplied from the substrate by grain boundary or lattice diffusion.

W.Y. Yang et al. also observed that titanium oxide was formed with silicon oxide between 100°C and 800°C. The formation of titanium oxide with silicon oxide at intermediate temperature regions below 800°C requires a source of titanium. The source of titanium should be free Ti metal from the complete decomposition of titanium silicide unless unreacted Ti exists in as prepared titanium silicide after RTA.

In addition, the formation of a mixed oxide (TiO₂ - SiO₂) implies that no chemical reaction occurred between titanium oxide and silicon oxide, and titanium oxide formed a stable interface with silicon oxide, as predicted from the calculated phase diagram in Figure 10. The phase diagram shows that silicon oxide has stable interfaces with various titanium oxides except TiO. Unless TiO is formed during the oxidation of titanium silicide, the oxidation products will be a mixed oxide if the proposed diagram is correct.

Since the decomposition of titanium silicide was expected to be the source of free Ti for oxidation at intermediate temperatures, the phase stability of titanium silicide during its oxidation has been of great interest.^(4-6, 9, 11, 52) W. Y. Yang et al. ⁽⁶⁾ explained that the complete decomposition of titanium silicide occurs during oxidation since they did not observe other silicides (ex. TiSi or Ti₅Si₃) in oxidized TiSi₂. Supporting W.Y. Yang et al.'s report, the transformation of titanium silicide to lower Si-content silicide during the oxidation has never been reported.

The stoichiometry and the phase of titanium oxide, as oxidation products at intermediate temperatures, have been well identified.^(3-9,52) Recently, G. J. Huang and L. J. Chen⁽¹²⁾ reported that wet oxidation above 880°C for 5 - 70 min resulted in a mixed silicon oxide - orthorhombic TiO₂. However, dry oxidation up to 6 hr at the same temperature region did not form TiO₂ with silicon oxide. Only extended dry oxidation over 10 - 15 hr above 920°C resulted in the formation of TiO₂ with silicon oxide. They explained that the nucleation barrier for the formation of TiO₂ during wet oxidation is lower than that during dry oxidation.

However, the formation of orthorhombic TiO₂ with silicon oxide seems to be exceptional since the orthorhombic phase (brookite) has been generally observed only as a natural ore which normally contains impurities. Since the oxidation of titanium silicide can be considered as a pure chemical reaction in which only titanium, silicon, and oxygen are involved, the formation of the orthorhombic phase needs to be confirmed. It is noted that a pure chemical reaction like the titania sol-gel process resulted in an amorphous phase at low annealing temperatures, anatase at intermediate temperatures (400°C - 700°C), and rutile at high temperatures.⁽¹⁶⁻²⁰⁾ It is known that the phase transformation in titanium oxide is affected by additives and preparation procedures.

2.8. Chemical Binding Energy of Titanium and Oxygen

In the previous sections, the oxidation products were reviewed. It was shown that while high temperature oxidation has been extensively investigated, the oxidation products of low temperature oxidation or early stage oxidation have been rarely studied. It is known that the chemical binding energy of metallic titanium is very sensitive to its valence state. If the chemical binding energy of titanium in oxide is measured, its valence state can be determined indirectly. H. Bender et al.⁽³⁷⁾ observed that the binding energy of Ti 2p_{3/2} increased when Ti reacted with other elements to form ionic or covalent compounds. Table 3 shows the chemical binding energy of Ti 2p_{3/2} of various titanium compounds, which shows the results to be similar to those of H. Bender et al. Pure metallic titanium has a binding energy of 453.8 eV. Titanium in titanium silicide has a binding energy of 453.2 ~ 454.2 eV, depending on the preparation method. The binding energy of titanium in thermodynamically stable titanium dioxide is 458.1 eV. Table 3 clearly shows that Ti 2p_{3/2} from ionic or covalent bonds is higher than that from the Ti metallic bond. J. P. Lu and R. Raj⁽⁵⁴⁾ who studied titanium oxide from gas pyrolysis observed the binding energy of titanium in titanium oxide as being 458.9 eV, which was very similar to W.Y. Yang et al.'s results, as shown in Table 3. It shows that titanium oxide on oxidized titanium silicide also has very similar chemical bond characteristics to titanium dioxide. In addition, the chemical binding energy of Ti in titanium oxide on oxidized titanium silicide was also very similar to the binding energy (458.4 eV) of titanium oxide on oxidized TiN.⁽⁵⁵⁾ N.C. Saha and H.G. Tompkins⁽⁵⁵⁾ reported that the binding energy of Ti in titanium oxide increased with oxidation temperature, suggesting that the binding energy of Ti in titanium oxide is dependent on the crystalline stability of titanium oxide, or the degree of ionic/covalent bonding in titanium oxide. When the oxidation temperature increased from 350°C to 450°C, the binding energy of Ti in titanium oxide increased from 458.6 eV to 459.1 eV.

Table 3. XPS peak positions of Ti2p_{3/2} in previous investigations.

Sample	Binding Energy (eV)	Reference
TiO _x in oxidized TiSi ₂	458.8	6, 37
TiO ₂	458.1	6, 37
TiO ₂ by gas pyrolysis	458.9	54
TiO ₂ on oxidized TiN	459.1	55, 56
RTA TiSi _x	454.2	37
TiSi ₂	453.2	6
Sputtered TiSi ₂	453.3	6
TiO _x N _y	454.7	37
Ti	453.8	6, 37

The binding energy of O1s of SiO₂ and TiO₂ have also been studied by earlier investigators. W.Y. Yang et al. ⁽⁶⁾ observed 533 eV O1s peak of titanium dioxide in oxidized titanium silicide. N.C. Saha and H.G.Tompkins ⁽⁵⁵⁾ observed 530 eV O1s peak of native titanium oxide on TiN film. J.P. Lu and R. Raj ⁽⁵⁴⁾ observed 530.3 eV O1s peak from CVD titanium oxide annealed at 400°C for 20 min.

The binding energy of Si2p has been also measured by previous investigators. It has been known that Si2p of titanium silicide, elemental silicon, and silicon oxide are 98.8, 99.2, and 103.5 eV respectively. Table 4 shows the binding energy of Si2p in the previous investigations. It suggests that the binding energy of Si2p is also sensitive to the chemical bond type of the compound.

Table 4. Chemical binding energy of Si2p.

Sample	Binding Energy (eV)	Reference
Elemental Si	99.2	37, 56
SiO ₂	103.5	6, 37, 56
TiSi _x	98.8	37
TiSi ₂	98.3	6, 37

III. RESEARCH OBJECTIVES

The previous sections showed that the oxidation of titanium silicide is affected by Si diffusion and the initial composition of the as-prepared titanium silicide. The stoichiometry and the crystal structure of titanium oxide in oxide film on titanium silicide has also been found to be unclear. Questions were raised if the previously proposed Ti-Si-O phase diagram can estimate the oxidation products and the interface condition at low temperature region.

To answer the above questions, the microstructure, chemistry, and crystalline phases of oxide films on titanium silicide were investigated. In order to explain the microstructure of the growing oxide layer and its interfacial condition at the oxide-silicide interface, oxide films were analyzed according to various oxidation stages, namely early, intermediate, and high temperature. To understand the formation of the oxide at the early stage or very low temperatures, native oxide films on as prepared titanium silicide were selected and the chemical binding energy of Ti, Si, and O were measured.

In an attempt to find microstructural evidence to explain the thermodynamics of oxidation reactions and the interface conditions (or phase equilibria) in the Ti-Si-O system, the microstructure of oxide films and their crystalline phase were analyzed. The oxidation temperatures and times for this study are shown in Table 5. For the early stage of oxidation, native oxide film was selected and analyzed. For the intermediate stage, oxide films at 300°C - 600°C were studied. For high temperature oxidation, oxide films at 800°C were analyzed.

Table 5. Experimental matrix for the oxidation of titanium silicide in this study.

Temp. (°C)	RT	300	400	500	600	700	800	900	1000
Time (Hr)		5	5	----	----	----	----	----	----
		20	20	20	20	20	20	20	20
		100	----	----	----	----	----	----	----

IV. EXPERIMENTAL PROCEDURE

4.1. Preparation of Titanium Silicide

Two crystalline titanium silicide films were prepared by rapid thermal annealing of sputtered Ti on p-type Si(100) single crystals. C49 titanium silicide was prepared by a single step rapid thermal annealing at 655°C for 30 sec in a nitrogen atmosphere. C54 titanium silicide was prepared by a two-step rapid thermal annealing at 850°C for 20 sec after the first step annealing at 655°C for 30 sec in a nitrogen atmosphere. Chemical selective etching with a 2:1 H_2SO_4 : H_2O_2 solution was used to remove the surface layer containing N, Si, and Ti from the as-prepared titanium silicide, after rapid thermal annealing.

4.2. Silicide Phase Analysis

The sheet resistances of sputtered Ti film, low temperature annealed film (C49) and high temperature annealed film (C54) were measured by a four point probe after each annealing step in order to confirm the formation of the C49 and C54 phases. An Eclipse Auto probe 280 was used for the sheet resistance measurement. The probe pressure was 60 grams and the reading interval was 10 mm. A total of 52 points per wafer were measured and averaged.

The crystal structure and the grain size of the as-prepared titanium silicide and oxidized titanium silicide were determined by X-ray diffraction (XRD). The diffraction angle and d spacing were corrected against the (004) peak of a Si single crystal substrate. The lattice parameters of the as-prepared titanium silicide were calculated. The crystal

sizes of C49 and C54 titanium silicide were calculated using Scherrer's method after a full-width at half-maximum (FWHM) of the main peaks of the C49 and C54 were obtained.⁽⁵⁸⁾

Selected area diffraction (SAD) analysis from a TEM planar view was performed to determine the crystalline phase in the oxide films on oxidized titanium silicide at high temperatures. The calculated d-spacings were compared with Joint Committee on Powder Diffraction Standards (JCPDS) files for titanium silicide, silicon oxide, and the various titanium oxides.⁽³²⁾

4.3. Oxidation

The oxidation of titanium silicide was carried out inside an electrical tube furnace in air ambient atmosphere. The furnace temperature was monitored with a K type thermocouple near the hot zone. The oxidation temperature was maintained within ± 2 °C. 1×1 in² specimens were cut from a 4" wafer. All specimens were etched with 20:1 diluted HF for about 30 sec to remove the native oxide film and then rinsed with ethanol. Immediately after the ethanol rinse, the specimens were dried with nitrogen gas and placed on a fused silica plate and loaded into the tube furnace which was already maintained at the pre-determined oxidation temperature. The specimens reached the hot zone of the furnace within 30 sec. The estimated specimen heating rate was 300 °C/min. Since the specimen size was small enough to avoid any breakage due to rapid thermal shock, all oxidized specimens were recovered after oxidation without any damage.

4.4. Analysis of Native Oxide Film

Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) analyses were performed to determine the chemical composition of the native oxide and to determine the valence states of Ti and Si in the native oxide on the as-prepared C49 and C54 titanium silicide. It was expected that the results would help determine how the initial or early stage of oxidation reaction is affected by the ratio of Si/Ti and the oxidation temperature.

AES depth-profiling was performed with a current density of $0.2 \mu\text{A}/\text{mm}^2$ at 3.0 KeV until oxygen was not detected. The spectra were recorded in the $E^*N(E)$ mode and were numerically differentiated to get $dN(E)/dE$ corresponding to the Si $L_{2,3}V_1V_2$ Auger line.

The binding energies of Ti2p, Si2p, and O1s of the native oxide film were measured by XPS. The measured peak positions of Ti2p, Si2p, and O1s were calibrated against the C1s peak at 284.6 eV which corresponds to natural hydrocarbon contamination on the surface. The spot size for XPS analysis was about 600 μm . The number of scans was controlled depending on scan range, number of detected electrons, and incident angle. For a brief scan over a wide range of binding energies, 1 or 2 scans were used. For strong Si2p or O1s peaks, 5 or 10 scans were used. For weak Ti2p peaks, the number of scans were increased up to 200. The XPS incident angle was fixed at 10 and 60 degrees in order to analyze the oxide film from different depths. From the peak analysis, the Ti2p peak for the titanium oxide and the Si2p peak for the silicon oxide were separated from those of metallic Ti and elemental Si. The film compositions were determined after normalization with respect to the relative atomic concentration of Si, Ti, and O based upon the integrated intensity of each highly resolved peak.

4.5. TEM Microstructure Analysis

Planar-views and SAD patterns of thermally grown oxide films were obtained using a Philips 400T Transmission Electron Microscope. Approximately $3 \times 3 \text{ mm}^2$ size specimens were prepared from a 4" wafer and then placed onto a molten wax film on a slide glass. The side containing the oxide film was placed down on a slide glass. After the molten wax film was solidified, a part of the Si substrate was removed by rough grinding and polishing. Then, the slide glass with the polished sample was placed on a chemical spray etcher, and the back side of the sample was chemically etched. A light was shone onto the center of the sample, from the bottom of the slide, in order to stop chemical etching at the moment when a tiny hole appeared at the center of the sample. 5:1 HNO_3 : HF was used as the chemical etchant. Once a tiny hole was obtained, the specimen was removed from the slide glass by dissolving the wax in a warm solution of trichloroethylene. The specimen was then cleaned with acetone and mounted on a TEM sample holder.

Ion milling was used for further thinning very near the perforation, to analyze the top layer of the oxide film. After ion milling, bright-field and dark-field images near the perforation were taken to find how the oxide film structure changes sequentially from the top layer and also to find what crystalline phases had formed on the oxidized film.

From SAD analysis, d spacings of the crystalline phases in oxide films were calculated, with the known camera constant, and compared with JCPDS reference files. Diffraction planes were assigned with the best-fit d spacing in the JCPDS file when visual relative intensities of SAD ring patterns also showed the same order of relative intensity (I/I_0) in the JCPDS file.

4.6. FT-IR Analysis

FT-IR analysis has been very useful to determine oxide molecular structures.^(59,60) FT-IR analysis has been widely used for Ti-O-Si oxide bond analysis in TiO_2 - SiO_2 systems.^(22 - 24, 27 - 29) Unfortunately, normal IR analysis for thin oxide films on titanium silicide is very difficult because IR absorption in thin oxide layers is very small. Attenuated total reflectance (ATR) spectroscopy has been known as a better way to obtain more absorption in a thin sample. The IR penetration depth in the ATR method is a function of the ATR-plate material (or relative ratio of refractive index), angle of incidence, and wavenumber.⁽⁶¹⁾ The depth of penetration is decreased by increasing the angle of incidence or using an ATR plate with a higher refractive index.

For ATR analysis one KRS-5 (a mixed crystal of 42% thallium bromide and 58% thallium iodide) crystal was inserted between two plates of a sample to obtain IR reflection at the titanium silicide-oxide interfaces. IR absorption was measured in the wavenumber range of $580 - 4000 \text{ cm}^{-1}$ and absorption peaks were compared with previous reports to determine if the thermal oxide on titanium silicide contains Ti-O-Si bridging bonds, which is a primary molecular bond in titanium silicate, a binary oxide in the TiO_2 - SiO_2 system.

V. RESULTS AND DISCUSSION

5.1. Properties and Crystalline Structure of Titanium Silicide

The sheet resistances of as sputtered Ti film and as annealed titanium silicide films are shown in Figure 5. The sheet resistance of low temperature annealed titanium silicide (C49 phase) was 5.267 Ohms/sq. The sheet resistance of high temperature annealed titanium silicide (C54 phase) was 0.917 Ohms/sq, which corresponds to a resistivity of $12.8 \mu\Omega\text{cm}$. It is previously reported that as-prepared titanium silicide has the normal resistivity of $15 - 20 \mu\Omega\text{cm}$.^(33, 70, 72) This sheet resistance of the C54 phase is lower than the minimum resistivity ($27 - 40 \mu\Omega\text{cm}$) of the high temperature annealed co-sputtered Ti+Si film shown in Figure 2. The sheet resistance of as-prepared C49 and as-prepared C54 phase in this study were very similar to previous values, as shown in Table 6.^(9, 33, 36, 38, 43, 70, 71, 72)

Table 6. Sheet resistance of C49 and C54 titanium silicide in previous studies.

Investigator	C54, Sheet Resistance (Ω/sq)	C49, Sheet Resistance (Ω/sq)	Si Substrate
T.Huang ⁽⁹⁾	1	6	single crystal
R. Beyer et al. ⁽³³⁾	1.5	6	single crystal
S. P. Murarka ⁽³⁶⁾	0.6 - 0.8	4.2	Poly-Si
P. Murchant ⁽⁴³⁾	-	5.8	single crystal
H. Koster et al. ⁽⁷⁰⁾	0.8	-	co-sputter film
C.D. Lien ⁽⁷¹⁾	1	-	single crystal
This study	0.92	5.27	single crystal

Figure 12. Sheet resistances of as-sputtered Ti, as-prepared C49, and as-prepared C54 titanium silicide in this study.

The crystal structures of as-prepared C49 and C54 titanium silicide were examined by XRD. The results are shown in Figures 13 and 14. Figure 13 shows the diffraction patterns of as-prepared C49 titanium silicide. There are 2 peaks near the diffraction angles of $2\theta = 33$ and $2\theta = 41$. The peak at $2\theta = 41.19$ ($d = 0.2196$ nm) corresponds to (131) C49 ($d = 0.220$ nm)⁽³³⁾ and the peak at $2\theta = 33.07$ ($d = 0.271$ nm) corresponds to Si (002). Figure 14 shows the diffraction patterns of as-prepared C54 titanium silicide. The five peaks at 2θ values of 39.3, 42.4, 43.4, 50.1, and 30.2 correspond to (311), (004), (022), (313), and (202) C54 respectively.⁽³²⁾

The lattice parameters of C49 were calculated based upon the d-spacings of (131) and other minor peaks which were detected by XRD but are not clearly shown in Figure 13.

The lattice parameters of C54 were calculated using the d-spacings of (311), (004), and (022) peaks. The lattice parameters of the C49 phase in this study were $a = 0.357$ nm, $b = 1.346$ nm, and $c = 0.357$ nm. The C54 phase in this study had the lattice parameters of $a = 0.825$ nm, $b = 0.479$ nm, and $c = 0.854$ nm. The lattice parameters of C49 in this study were slightly smaller than those reported by P.G. Cotter et al.⁽⁶²⁾ but were similar to those reported by R. Beyers and R. Sinclair as shown in Table 7.⁽³³⁾

Table 7. Lattice parameters of C49 and C54 titanium silicide.

Investigators	C49, Lattice parameter (nm)	C54, Lattice parameter (nm)
R. Beyers, R. Sinclair ⁽³³⁾	-	a=0.356, b=1.361, c=0.356
P. G. Cotter ⁽⁶²⁾	-	a=0.362, b=1.376, c=0.361
F. Dietrich et al. ⁽⁷³⁾	a= 0.825, b=0.479, c=0.854	-
This study	a=0.824, b=0.478, c=0.854	a=0.357, b=1.346, c=0.357

The crystalline grain sizes of both as prepared C49 and C54 titanium silicide were also calculated by the Scherrer method.⁽⁵⁸⁾ The crystalline grain size of the as-prepared C49 phase was about 37 - 49 nm. The crystalline grain size of the as-prepared C54 phase was about 65 - 120 nm. It was found that the crystalline grain sizes of as-prepared C49 and C54 in this study were smaller than previous results.⁽³³⁾ R. Beyer and R. Sinclair⁽³³⁾ reported that C49 has an average grain size of 0.2 μm and C54 has an average grain size of 0.7 μm . Difference in grain size determining methods most probably resulted in this difference. Nevertheless, the smaller crystalline grain size of the as-prepared C49 phase suggests that C49 titanium silicide has a larger grain boundary area than C54. Therefore, it is expected that the oxidation of C49 titanium silicide will be

enhanced by grain boundary oxidation and the oxide film thickness on the C49 film will be thicker than that on the C54 film.

Figure 13. X-ray diffraction pattern of as-prepared C49 titanium silicide.

Figure 14. X-ray diffraction pattern of as-prepared C54 titanium silicide.

5.2. Thermodynamics of Titanium Silicide Oxidation

The overall oxidation of titanium silicide can be expressed by the following reaction:

Reaction (3) can be expressed as a set of sub-reactions, as shown in Table 6, to explain which reaction will be thermodynamically favorable and to compare the oxidation products with the theoretical estimation. Reactions (A-1) and (A-2) explain that the oxidation of free Si in titanium silicide occurs first and elemental titanium freed by reaction (A-1) oxidizes later. Reaction (F-1) and (F-2) explain that the oxidation of metallic Ti in titanium silicide occurs first and elemental silicon freed by reaction (F-1) oxidized later. Reactions (B-1), (B-2), and (B-3) indicate the decomposition of titanium silicide into its elemental forms first, followed by the oxidation of silicon and titanium. Reaction (B) has been proposed by previous investigators for the oxidation reaction in the intermediate temperature region.^(3, 5, 6, 7.) Reactions (C-1), (C-2), and (C-3) show that titanium silicide transforms to TiSi (lower Si content silicide) through selective Si oxidation. Reactions (D-1), (D-2), and (D-3) explain that oxidation proceeds with the formation of SiO as an intermediate product. Reactions (E-1), (E-2), (E-3), and (E-4) represent a combination of reactions (C) and (D).

Even though the standard Gibbs free energies for the overall oxidation reactions are exactly the same, namely, - 2458 KJ/mol at 298 K, the standard Gibbs free energies of the individual sub-reactions are different from each other, as shown in Figure 15. The standard Gibbs free energies of the overall oxidation reaction and individual sub-reactions are listed in the Appendix. When the Gibbs free energy of each sub-reaction is compared,

the most favorable reaction in the oxidation of C49 and C54 titanium silicide can be estimated theoretically.

Table 8. Stepwise reactions for the oxidation of TiSi_2 .

Oxidation Reactions	Note
(A) $\text{TiSi}_2 + 2 \text{O}_2 \rightarrow \text{Ti} + 2 \text{SiO}_2$ (A-1) $\text{Ti} + \text{O}_2 \rightarrow \text{TiO}_2$ (A-2)	Si oxidation is preferred
(B) $\text{TiSi}_2 \rightarrow \text{Ti} + 2 \text{Si}$ (B-1) $\text{Ti} + \text{O}_2 \rightarrow \text{TiO}_2$ (B-2) $2\text{Si} + 2 \text{O}_2 \rightarrow 2 \text{SiO}_2$ (B-3)	TiSi_2 decomposition
(C) $\text{TiSi}_2 + \text{O}_2 \rightarrow \text{TiSi} + \text{SiO}_2$ (C-1) $\text{TiSi} + \text{O}_2 \rightarrow \text{Ti} + \text{SiO}_2$ (C-2) $\text{Ti} + \text{O}_2 \rightarrow \text{TiO}_2$ (C-3)	Dissociation of TiSi_2 to lower content
(D) $\text{TiSi}_2 + \text{O}_2 \rightarrow \text{Ti} + 2 \text{SiO}(\text{g})$ (D-1) $2\text{SiO}(\text{g}) + \text{O}_2 \rightarrow 2 \text{SiO}_2$ (D-2) $\text{Ti} + \text{O}_2 \rightarrow \text{TiO}_2$ (D-3)	Formation of silicon monoxide Oxidation of silicon monoxide
(E) $\text{TiSi}_2 + 1/2 \text{O}_2 \rightarrow \text{TiSi} + \text{SiO}$ (E-1) $\text{TiSi} + 1/2 \text{O}_2 \rightarrow \text{Ti} + \text{SiO}$ (E-2) $2 \text{SiO} + \text{O}_2 \rightarrow 2 \text{SiO}_2$ (E-3) $\text{Ti} + \text{O}_2 \rightarrow \text{TiO}_2$ (E-4)	Formation of silicon monoxide
(F) $\text{TiSi}_2 + \text{O}_2 \rightarrow \text{TiO}_2 + 2 \text{Si}$ (F-1) $2 \text{Si} + 2 \text{O}_2 \rightarrow 2 \text{SiO}_2$ (F-2)	Ti oxidation is preferred

Figure 15. Standard Gibbs free energies of selected sub-reactions shown in Table 8.

Figure 15 shows that thermodynamically the most favorable reaction is the reaction (A-1). The most unfavorable reaction would be the reaction (B-1) which is endothermic. However, the standard Gibbs free energy change for reaction (B-1) is about 126 ~ 132 (KJ/mol) and it can be driven if heat is provided. The oxidation of titanium silicide via SiO formation (reaction D-1, E-1) is thermodynamically less favorable than the other sub-reactions (A-1, C-1, F-1). If the oxidation occurs through the formation of SiO, the gas phase SiO will leave from the surface and the surface layer of titanium silicide will become titanium rich and therefore the oxide film will be a titanium oxide rich. This hypothesis is contrary to the results of previous reports, as shown in Table 2, which did not show titanium oxide rich film as an oxidation product.

The dissociation of titanium silicide via the formation of TiSi (reaction C-1) is thermodynamically favorable. If reaction (C-1) occurs during the oxidation of titanium silicide, the TiSi phase would be observed at the oxide-silicide interface. However, previous studies did not show the presence of TiSi in oxide on titanium silicide or at the oxide-silicide interface.

The decomposition of titanium silicide (reaction B-1) has been accepted as the main mechanism for the oxidation of titanium silicide in the intermediate temperature region. Previous investigators explained that the complete decomposition of titanium silicide occurred when Si diffusion from the Si substrate was slow. This hypothesis has been supported by analytical evidence from the previous investigations. W.Y. Yang et. al.⁽⁶⁾ performed XPS analysis to explain the decomposition of titanium silicide according to oxidation temperature. Their XPS results showed that the intensity of Ti2p and Si2p peak due to titanium silicide was diminished significantly near 300°C, suggesting that the decomposition of titanium silicide occurred. In their results, the relative intensity of Si2p to Ti2p corresponding to oxide was constant from 300°C to 600°C. This means that the Ti and Si in the oxide came from the decomposition of titanium silicide. Above 600°C, the intensity of Si2p increased but the intensity of Ti2p decreased. Therefore, the Si in silicon oxide comes from the Si substrate and not from the silicide. In addition, their XPS result also implied that the decomposition of titanium silicide might occur below 300°C. This result well explained the above thermodynamic interpretation that reaction (B-1) can be driven very easily.

As an extreme example of the early stage oxidation, the formation of the native oxide on titanium silicide can be explained by the standard Gibbs free energy change of reaction (B-1) at room temperature and the results of chemical analysis. The standard Gibbs free energy change of reaction (B-1) at 298K was + 132 KJ/mol, suggesting that the decomposition of titanium silicide at room temperature is theoretically impossible.

Therefore, it is clear that the native surface oxide on titanium silicide at room temperature was not formed by the decomposition of titanium silicide, but by some other mechanism. It is considered that the formation of the native oxide film is mainly affected by the presence of excess Si in as prepared titanium silicide. In Section 5.4., the analytical results to support this explanation are presented.

Previously in this section, it was explained that the decomposition of titanium silicide is the main mechanism to supply free Ti and Si for the oxidation of titanium silicide. For native oxides, it is interesting to estimate theoretically what oxide will be formed. It is estimated that a compound having a higher standard Gibbs free energy of formation will be formed first. The standard Gibbs free energy of TiO_2 (reaction F-1) is slightly larger (~4%) than that of SiO_2 (reaction A-1).^(65, 66) (ΔG_f° of TiO_2 at 298 K = - 877.6 KJ mol⁻¹, ΔG_f° of SiO_2 at 298 K = - 856.5 KJ mol⁻¹) It indicates that the formation of titanium dioxide is thermodynamically preferred rather than the formation of silicon oxide. However, the difference of ~4% is very small.

It is also important to consider that the oxidation of titanium silicide is also dependent on the chemical activity of Si and Ti at the surface of the titanium silicide. Previous investigators reported that as prepared titanium silicide showed a higher Si/Ti ratio than 2. The phase diagram in Figure 1 indicates that there is no solid solution between titanium silicide and silicon, suggesting that if the ratio of Si/Ti is over 2, excess silicon will exist as free Si in the matrix or at the grain boundaries of titanium silicide. Since titanium silicide ($T_m = 1540^\circ\text{C}$) has a higher melting point than silicon ($T_m = 1410^\circ\text{C}$), it is estimated that the free silicon has a higher than ideal activity. The activity of the free silicon will also be higher than the activity of the silicon bound as the silicide. Therefore, when as-prepared titanium silicide contains excess silicon, the oxidation reaction will be dominated by the oxidation of the excess Si and the decomposition of titanium silicide will be either prevented or retarded.

To know the Si/Ti ratio of as prepared titanium silicide, qualitative EDS analysis was performed. It showed that as-prepared titanium silicide in this study showed also a high Si/Ti ratio (~6.2). It is considered that the excess Si near the surface of as-prepared titanium silicide was already oxidized to form silicon oxide film on the samples and resulted in a very high ratio.

In summary, the oxidation reaction can be explained as follows:

For the very early stage of the oxidation,

In the intermediate temperature region when the decomposition of titanium silicide occurs,

When fast Si diffusion occurs at high temperature,

Titanium silicide is thermodynamically stable at room temperature but can be decomposed at low temperatures under an oxidizing atmosphere. It is known that as-prepared titanium silicide contains excess free silicon. Free silicon in titanium silicide is oxidized first either at the early stage of the oxidation or low temperatures before the decomposition of titanium silicide occurs. The decomposition of titanium silicide is a dominant reaction mechanism at intermediate temperatures when excess silicon in titanium silicide is not available or also when Si is not supplied through the grain boundary diffusion from the Si substrate. Once the decomposition of titanium silicide occurs, titanium oxide is formed with silicon oxide and results in a mixed titanium oxide-silicon oxide. When Si atoms are supplied via the grain boundary diffusion to the oxide-silicide interface, pure silicon oxide is formed at the interface without the decomposition of titanium silicide .

After considering kinetic factors (Si diffusion) and thermodynamic (standard Gibbs free energy of formation) factors together, S. L. Zhang et al. explained that a pure silicon oxide layer can be obtained if the activity of silicon at the silicide-oxide interface is larger

than $\exp(-\Delta G_{f, \text{SiO}_2}^\circ/RT)$ and less than 1. If excess Si exists in as prepared titanium silicide, the activity of Si on the surface or near the silicide-oxide interface will be 1. Then, the oxidation of titanium silicide at the oxide-silicide interface is dominated by the oxidation of excess Si until the excess Si is completely oxidized.

5.3. Mass Transport: Diffusion Coefficients of Reactants

In Section 5.2, it was explained that the oxidation of titanium silicide is dependent on the Si activity at the oxide-silicide interface. It was also explained that the initial composition of as prepared titanium silicide and the Si diffusivity through the silicide matrix affect the oxidation products. In this section, the diffusion coefficients of each reactant, according to oxidation temperature, will be presented to support the results in Section 5.2.

5.3.1. Silicon

Silicon is a dominant diffusion element during the formation and the oxidation of titanium silicide. It was reported that the diffusion coefficient of silicon through the silicide matrix, at temperatures above 700°C, is very rapid.⁽¹⁰⁾ The diffusion coefficient of silicon in titanium silicide from the previous studies is tabulated in Table 9 and plotted in Figure 16. With an estimated diffusion coefficient of $D \sim 10^{-19} \text{ cm}^2/\text{sec}$ at room temperature, extrapolated from the reported values, the required time ($t \sim x^2/D$) for silicon diffusion from the silicon substrate to the top surface of as-prepared titanium silicide was estimated for room temperature. With an estimated 1400Å thickness⁽³⁶⁾ of the as-prepared

Table 9. Diffusion coefficient of silicon in titanium silicide in previous studies.

Temperature (°C)	D (cm ² /sec)	Reference
350	1.24×10^{-15}	R.R. De Avillez ⁽⁴⁴⁾
375	2.29×10^{-15}	"
400	5.60×10^{-15}	"
550	3×10^{-14}	P. Gas et al. ⁽⁶⁴⁾
600	1.3×10^{-13}	L.S. Hung et al. ⁽⁶³⁾
700	1.5×10^{-12}	"
800	1.1×10^{-11}	"

Figure 16. Diffusion coefficient of silicon in titanium silicide from previous studies. ^{(44,}

63, 64)

titanium silicide in this study, the required time for silicon diffusion from the substrate to the surface of the silicide is about 62 years. Therefore, it is considered that silicon diffusion through the titanium silicide, from the silicon substrate, at room temperature is practically impossible or negligible. In light of this, the formation of the native oxide will be dependent only on the initial composition of the as prepared titanium silicide.

5.3.2. Oxygen

The diffusivity of oxygen in fused silicon oxide for high temperatures has been determined.^(67, 68) The previous results are plotted in Figure 17. As shown in Figure 17, the diffusivity of oxygen at 900°C is $2.8 \times 10^{-9} \text{ cm}^2/\text{sec}$. The activation energy for oxygen diffusion in fused silica is 27 Kcal/mol (1.16eV).

Recently, D.A. Gulino et al.⁽⁶⁷⁾ reported that the diffusivity of oxygen in silicon dioxide at 50°C is on the order of $10^{-15} \text{ cm}^2/\text{sec}$. If we simply accept this data for room temperature, it is evident that the oxygen diffusivity in silicon oxide at room temperature seems to be higher than the diffusivity of silicon in titanium silicide. This result indicates that room temperature oxidation or low temperature oxidation is governed by oxygen diffusion.

Figure 17. The diffusivity of oxygen in fused silica as a function of temperature.
(after B. E. Deal and A. S. Grove⁽⁶⁸⁾ D. A. Guliano et al.⁽⁶⁷⁾)

5.3.3. Water

Figure 17 showed the diffusivity of water in silicon oxide in previous studies.^(67, 69) At 900°C, the diffusivity is $4 \times 10^{-10} \text{ cm}^2/\text{sec}$, which is one magnitude smaller than that of oxygen. At high temperature water diffusion is slower than that of oxygen. It is known that the activation energy of water diffusion in silicon oxide is about 18.3 Kcal/mol (0.79 eV). The low activation energy for water diffusion suggests that wet oxidation is easier than dry oxidation.

Figure 18. The diffusivity of water in silica glass as a function of temperature in previous studies (after H. Wakabayashi and M. Tomozawa⁽⁶⁹⁾)

Recently, H. Wakabayashi and M. Tomozawa measured the diffusivity of water in amorphous silica glass.⁽⁶⁹⁾ Their results are plotted in Figure 18, which shows that the activation energy of water diffusion in silica glass shows a change near 550°C. From Figure 18, the diffusion coefficient of water at room temperature was obtained by linear extrapolation. The diffusivity of water in silica glass near room temperature is expected to be on the order of 10^{-16} cm²/sec. This value is at least 100 times higher than that of silicon in titanium silicide at room temperature. Therefore, it is concluded that low temperature oxidation proceeds with oxidant diffusion, not Si diffusion.

Based upon the diffusion coefficients of the reactants discussed above, it can be concluded that the native surface oxide is formed by the reaction of oxidant with as-prepared titanium silicide through oxidant absorption and surface reaction. Since the Si supply from Si substrate is negligible and the decomposition of titanium silicide is impossible at room temperature, the native oxide on as-prepared titanium silicide is the result of the oxidation of either excess Si ^(7,51) or unreacted Ti ⁽³³⁾ in as-prepared titanium silicide. It is also evident that once the surface oxide is formed, the extended oxidation of titanium silicide at room temperature or low temperatures should be rate-limited by the diffusion of oxidants through the surface oxide layer. The oxidation reaction will also be stopped until the decomposition of titanium silicide occurs. Once the decomposition of titanium silicide has occurred at low temperature, but before fast Si diffusion occurs, the oxidation products will be a mixed titanium oxide-silicon oxide. It is also estimated that once the native oxide is formed, the oxide film growth will occur at the oxide-silicide interface and therefore the growing oxide film can be a multilayer film if one sample experiences different oxidation stages. G. Valyi et al. ⁽⁸⁾ and T. Sandwick and K. Rajan ⁽⁵²⁾ observed a multilayer oxide film which had a layered sequence of silicon oxide top layer / a mixed silicon oxide-titanium oxide layer / silicon oxide layer / titanium silicide.

5.4. Native Oxide on As prepared C49 and C54 Titanium Silicide

In Section 5.2 and 5.3, it was indicated that the oxide film on titanium silicide can be a multilayer because the presence of excess Si or unreacted Ti in as-prepared titanium silicide affects the initial oxidation reaction and the decomposition of titanium silicide occurs at intermediate temperature. In this section, the results of AES and XPS analysis of as-prepared C49 and C54 titanium silicide are presented to explain the composition and the chemical bonding nature of titanium silicide near the surface of as-prepared titanium silicide.

5.4.1. AES Analysis

AES depth profiles of as-prepared C49 and as-prepared C54-titanium silicide are shown in Figures 19 and 20, respectively. They show very similar AES depth profiles except for the Auger intensity profile of Ti and Si near the oxide-silicide interface. The AES depth profile of low temperature annealed C49 titanium silicide in Figure 19 shows a higher Ti signal near the oxide-silicide interface than C54 titanium silicide. It possibly indicates that as-prepared C49 titanium silicide contains either unreacted Ti and more titanium oxide near the surface. Figure 19 also shows a gradual decrease of the oxygen signal and a gradual increase of Ti and Si signals which means that the oxide-silicide interface is not sharp. In other words, as-prepared titanium silicide is polycrystalline, with oxidation at the grain boundaries.

Apparently, the sputter etch time to expose titanium silicide surface is very similar in both types of titanium silicide which means that the native oxides on the as-prepared C49 and C54 titanium silicide have similar thicknesses. The AES depth profiles proved that

Figure 19. AES depth profile near the surface of as-prepared C49 titanium silicide.

Figure 20. AES depth profile near the surface of as-prepared C54 titanium silicide.

the native oxide films on as-prepared C49 and as-prepared C54 titanium silicide are primarily silicon oxide with a small amount of titanium oxide. This result is in agreement with the results of previous investigations that as-prepared titanium silicide contains excess Si.

In order to understand the chemical bonding nature of Si, the shape of the Si Auger peak of as-prepared titanium silicide with native oxide was examined, and is shown in Figure 21. The pure Si has one peak at 92 eV.^(8, 56,57) Figure 21 shows two major peaks at 76 and 88.4 eV. The 76 eV peak corresponds to the Auger peak of oxidized Si.^(8,,51,56,57) The 88.4 eV peak corresponds to Si in titanium silicide.⁽³⁷⁾ Figure 21 also shows three shoulder peaks near 76 eV, at 74.4, 77, and 80.4 eV. The 80.4 eV peak is due to oxidized Si. The two minor peaks at 74.4 and 77 eV seem to indicate different oxidation states of Si, possibly indicating the silicon hydroxyl bond (Si-OH). The absence of the 92 eV peak suggests that near the oxide-silicide interface there is no free elemental Si. M.A.Taubenblatt and C.R. Helms studied the change in the Si Auger peak position when silicon oxide reacts with an electron-beam evaporated monolayer of Ti.⁽⁵¹⁾ They observed that titanium bonds to oxygen in silicon oxide and reduces a surface layer of silicon oxide, thus freeing Si from its oxidized state. They observed that the intensity of the 80 eV peak (oxidized Si) decreased with increasing intensity of the 92 eV peak (unoxidized Si). They explained that the monolayer of Ti on silicon oxide reduced the silicon oxide, thus freeing Si from its oxidized state.⁽⁵¹⁾

Figure 21. Si Auger spectra of a surface oxide on as-prepared C54 titanium silicide.

5.4.2. XPS Analysis

In Section 5.4.1, AES results showing that the native oxide on as-prepared titanium silicide is mainly silicon oxide, with a small amount of titanium oxide was presented. In this section, the results of XPS analysis are presented, to explain the chemical bonds of Si and Ti in the native oxide on as-prepared titanium silicide. Once the chemical bonds of Ti and Si are determined, the oxide form of Ti and Si can be determined and therefore the reactivity between titanium oxide and silicon oxide can be also examined.

The incident angle for XPS analyses were set at 10° and 60° to analyze the oxide films at approximately 15 Å and 70 Å detection depths, respectively. The chemical binding energy of Ti in titanium oxide on as prepared C49 titanium silicide are shown in Figure 22 for 15 Å and Figure 23 for 70 Å detection depth. As shown in Figure 22, the Ti 2p spectrum intensity from the very top surface of C49 titanium silicide is slightly higher than that of C54 titanium silicide. This means that as-prepared C49 titanium silicide has a slightly higher volume of titanium oxide near the surface. This is possibly due to the fine grain structures of C49 titanium silicide, or due to the possible presence of unreacted Ti in a low temperature annealed C49 titanium silicide.⁽³³⁾ It was mentioned in Section 5.1 that the grain size of as-prepared C49 is about two times smaller than that of as-prepared C54 and therefore C49 titanium silicide has more grain boundary area than C54 titanium silicide.

The atomic concentration of the surface oxide on as-prepared titanium silicide was calculated after unoxidized Ti, unoxidized Si, oxidized Ti, and oxidized Si peaks were identified individually. In Figures 22 and 23, Ti 2p_{3/2} of oxidized Ti appears near 459 eV and Ti 2p_{3/2} of unoxidized Ti appears near 453.5 eV.

Figure 22. $Ti2p_{3/2}$ and $Ti2p_{1/2}$ spectra of as-prepared C49 titanium silicide showing the presence of a small amount of titanium oxide in native oxide. Dashed lines indicate individual peaks after peak deconvolution.

Figure 23. $\text{Ti}2p_{3/2}$ and $\text{Ti}2p_{1/2}$ spectra of as-prepared C54 titanium silicide showing the presence of a small amount of titanium oxide in native oxide. Dashed lines indicate individual peaks after peak deconvolution.

The peak near 460 eV is a combined peak of $Ti2p_{1/2}$ of unoxidized Ti and oxidized Ti. Assuming that the peaks have a Gaussian distribution, the peaks near 460 eV were deconvoluted and then normalized to calculate the atomic concentrations of Si, Ti, and O near the surface of as-prepared titanium silicide. The results are shown in Table 10.

Table 10. Normalized atomic concentration of thin surface oxide on as-prepared C49 and C54 titanium silicide at 15Å and 70Å XPS detection depth level.

(unit: atomic percent)

Sample	XPS angle	Si(ox)	O	Ti(ox)	Si°	Ti°
C54	10	29.00	70.76	0.18	0.01	0.05
	60	30.64	68.44	0.31	0.54	0.07
C49	10	28.15	71.58	0.23	0.01	0.01
	60	29.53	69.77	0.39	0.23	0.04

Table 10 shows that the native oxides on as-prepared C49 and C54 titanium silicide are almost pure silicon oxide (> over 99 a/o) and contain only tiny amounts of titanium oxide. Table 10 also shows that the amount of titanium oxide increased with XPS detection depth. This suggests that titanium oxide exists in the subsurface close to the oxide-silicide interface and silicon oxide covers titanium oxide, which probably exists at the grain boundaries of the titanium silicide. Table 10 also shows that as-prepared C49 titanium silicide has slightly more titanium oxide (0.1 a/o) than as-prepared C54 titanium

silicide. The difference in the amount of titanium oxide is insufficient to distinguish the difference in grain boundary area and crystal stability between C49 and C54 titanium silicide, as indicated previously in Section 5.1.

5.4.3. Binding Energy of Ti, Si, and O in Native Oxide

AES results showed that the native oxide on as-prepared titanium silicide is silicon oxide, as reported in Section 5.4.1. In this section, the oxidation states of titanium and silicon in native oxide are explained based upon the chemical binding energy of titanium and silicon because the valence state of titanium and silicon in the native oxide are closely related to the oxidation states of titanium and silicon.^(9, 39) The valence state of titanium in the native oxide on as-prepared C49 and C54 titanium silicide is a clue to determining the type of titanium oxide, because the stoichiometric ratio of titanium to oxygen is dependent on the valence state of titanium.

The chemical binding energies of $Ti2p_{3/2}$ for titanium oxide on as-prepared C49 and C54 titanium silicide are tabulated in Table 11. The binding energy of $Ti 2p_{3/2}$ for titanium oxide from 15Å detection depth level was slightly higher (0.3 eV) than those from 70Å detection depth level. In addition, the binding energy of $Ti2p_{3/2}$ for titanium oxide on as-prepared C49 is slightly higher (0.38 eV at 10° and 0.45 eV at 60°) than those of C54 titanium silicide.

W.Y. Yang et al. reported that the chemical binding energy of $Ti2p_{3/2}$ for titanium oxide in oxidized titanium silicide film was 458.8 eV ⁽⁶⁾ J. Lu and R. Raj ⁽⁵⁴⁾ observed that the chemical binding energy of titanium dioxide prepared by chemical vapor deposition at 400°C was 458.9 eV. Since the binding energy of $Ti2p_{3/2}$ for titanium oxide in native oxide is very similar to previous results, it is considered that titanium oxide in native oxide on as prepared titanium silicide is titanium dioxide.

Table 11. The binding energy of $Ti2p_{3/2}$ for titanium oxide in native oxide on C49 and C54 titanium silicide.

Sample	XPS Angle	Binding Energy (eV)
C54	10	459.13
	60	458.81
C49	10	459.51
	60	459.26

N. C. Saha and H. G. Tompkins⁽⁵⁵⁾ investigated the oxidation of TiN films and measured the chemical binding energy of $Ti2p_{3/2}$ in the native oxide and thermal oxides at 350°C and 450°C. They observed that the $Ti2p_{3/2}$ peak was shifted from low binding energy to high binding energy, with increasing temperature. They also observed that the binding energy (459.1 eV) of crystalline TiO_2 (anatase or rutile) was higher (458.4 eV) than that of amorphous TiO_2 , suggesting that the stable titanium oxide phase has a higher binding energy. Their results showed that the binding energy of $Ti 2P_{3/2}$ is sensitive to crystallinity of titanium oxide. It is unclear why titanium oxide on C49 titanium silicide (metastable phase) showed slightly higher binding energy than that on C54 titanium silicide (stable phase).

J. P. Lu and R. Raj⁽⁵⁴⁾ reported that the peak position and the peak separation between $Ti2p_{3/2}$ and $Ti2p_{1/2}$ of titanium oxide is very sensitive to its stoichiometry. It was reported that titanium dioxide (+4 valence state for Ti) had 5.6 eV peak separation between $Ti2p_{3/2}$ and $Ti2p_{1/2}$.⁽⁵⁴⁾ The peak separation between $Ti 2p_{3/2}$ and $Ti 2p_{1/2}$ is tabulated in Table 12.

Table 12. Peak separation between $Ti2p_{3/2}$ and $Ti2p_{1/2}$ of metallic Ti and oxidized Ti near the native oxide-silicide interface.

Sample	XPS Angle	Peak	Binding E. (eV)	ΔE (Ti2p)
C54	10	ox-Ti $2p_{3/2}$	459.13	5.3
		ox-Ti $2p_{1/2}$	464.44	
	60	e-Ti $2p_{3/2}$	453.59	6.1
		e-Ti $2p_{1/2}$	459.69	
		ox-Ti $2p_{3/2}$	458.81	5.7
		ox-Ti $2p_{1/2}$	464.51	
C49	10	ox-Ti $2p_{3/2}$	459.51	5.6
		ox-Ti $2p_{1/2}$	465.10	
	60	e-Ti $2p_{3/2}$	453.27	6.2
		e-Ti $2p_{1/2}$	459.47	
		ox-Ti $2p_{3/2}$	459.26	5.7
		ox-Ti $2p_{1/2}$	464.96	

The peak separation between $Ti2p_{3/2}$ and $Ti2p_{1/2}$ for both metallic titanium and titanium oxide are shown in Table 12. The peak separation between $Ti2p_{3/2}$ and $Ti2p_{1/2}$ of titanium oxide is 5.6 - 5.7 eV. This indicates that titanium oxide in native oxide on as-prepared titanium silicide has +4 valence state. Table 12 also shows that the peak separation between $Ti2p_{3/2}$ and $Ti2p_{1/2}$ of metallic titanium was consistently 6.1 - 6.2 eV. This 6 eV peak separation corresponds to titanium in titanium silicide since free metallic titanium near the oxide-silicide interface is already oxidized.

To find the oxidation state of Si at the early stage of oxidation of as prepared titanium silicide, the binding energy of Si2p was measured. The chemical binding energy of Si2p of as-prepared C49 and C54 titanium silicide are shown in Figure 24 and tabulated in Table 13. Previously, it was reported that the binding energy of Si2p for SiO₂ is 103.3 - 103.5 eV.⁽³⁶⁾ and that the binding energy of Si2p for titanium silicide is 98.8 eV.⁽⁶⁾ The binding energy of Si2p for silicon oxide (103.4 eV) and titanium silicide (98.6 eV) in this study was very similar to the previous results (103.5 eV for silicon oxide, 98.8 eV for TiSi_x)⁽³⁷⁾, and suggests that the silicon in the silicon oxide has a +4 valence state and interfaces with titanium silicide.

Table 13. Binding energies of Si2p for titanium silicide and silicon oxide near the oxide-silicide interface.

Sample	XPS Angle	Binding E.(eV)	Peak
C54	10	103.43	ox-Si2p
	60	98.62	e-Si2p
		103.38	ox-Si2p
C49	10	103.46	ox-Si2p
	60	98.72	e-Si2p
		103.55	ox-Si2p

The binding energy of O1s from the native oxide is shown in Table 14. The binding energy of O1s from the native oxide in this study deviates from the known values of silicon dioxide (533 eV)⁽⁶⁾ and titanium dioxide (530 eV).^(6, 54) This indicates that the oxygen bonds in the native oxide are different from the oxygen bonds in silicon dioxide or titanium dioxide. It is interpreted that moisture enters into the silica glass network to form Si(OH)₄.⁽⁶⁹⁾

Figure 24. Si2p spectra obtained from the native oxide on (a) as-prepared C54 and (b) C49 titanium silicide film. It is noted that the peak positions in this figure should be read after the peak correction.

Table 14. Binding energy of O1s for native oxide on as-prepared titanium silicide.

Sample	XPS Angle	Binding E. (eV)	Deviation from SiO ₂	Deviation from TiO ₂
C54	10	532.43	0.57	2.43
	60	532.39	-	-
C49	10	532.48	0.48	2.48
	60	532.50	-	-

5.5. Molecular Structure of Oxide

The previous sections explained that native oxides on C49 and C54 titanium silicide were mainly silicon oxide and tiny amount of titanium dioxide existed near the oxide-silicide interface. XPS and AES results showed that native oxide on C49 and C54 titanium silicide was a mixed oxide TiO₂ - SiO₂. It indicated that there was no reaction between silicon oxide and titanium oxide. This result supports R. Beyer's assumption for his theoretical phase diagram of Ti-Si-O system which is shown in Figure 10.^(48, 49) R. Beyer assumed that there is no ternary phase in the Ti-Si-O system. A ternary phase in the Ti-Si-O system is titanium silicate which has Ti-O-Si bridging bonds in its molecular structure.

In this section, the results of FT-IR analysis are presented to explain the molecular bonds in the oxide film. Since the native oxide is too thin for FT-IR analysis, and is mainly silicon oxide, low temperature oxide films were analyzed in order to check if there is a reaction between silicon oxide and titanium oxide during the oxidation. If the decomposition of titanium silicide occurred at low temperature, free Ti, Si, and O can react and possibly form Ti-O-Si bonds.

Oxide films at 300, 400, and 800°C were examined by FT-IR and a representative IR spectra for C49 film oxidized at 300°C for 24 hrs is shown in Figure 25. There were no characteristic absorption peaks near the wavenumbers of 919 - 926 cm^{-1} , which corresponds to Ti-O-Si bridging bonds. ^(15, 22) The absorption spectra in Figure 25 showed Ti-O and Si-O stretching bonds at 827 cm^{-1} and 1093 cm^{-1} , respectively. The absorption peaks at 1625 cm^{-1} and 1400 cm^{-1} correspond to absorbed moisture and carbonate on the sample surface.

Figure 25. FT-IR absorption spectra of an oxidized C49 film at 300°C, 24hrs. It is noted that no characteristic Ti-O-Si absorption peaks at 926 cm^{-1} was observed.

The absence of Ti-O-Si absorption peaks in the oxide films at 300, 400, and 800°C indicates that Ti-O-Si bonds cannot be formed by the oxidation of titanium silicide, or suggests that the amount of Ti-O-Si bridging bonds in the growing oxide film is negligible. The FT-IR results proved that there was no reaction between silicon oxide and titanium oxide while the oxidation of titanium silicide occurs.

The absence of Ti-O-Si bonds in the oxide film on titanium silicide can be interpreted also as a result of chemical immiscibility between silicon dioxide and titanium dioxide. B.E. Yoldas indicated that Ti-O-Si bridging bonds can be formed only when an intimate mixing of elemental Ti and Si exists.⁽¹⁵⁾ Previous investigators showed that Ti-O-Si bridging bonds could be formed by either the sol-gel process or the spray-pyrolysis process.^(15,21,27,28,30,54) Therefore, it is considered that the formation of Ti-O-Si bonds during the oxidation of titanium silicide is impossible because titanium silicide already has an ordered structure (either C49, base-centered orthorhombic structure or C54, face-centered orthorhombic structure) and therefore, intimate mixing of Ti and Si atoms through their rearrangement after the decomposition of titanium silicide is very difficult to occur.

Another explanation for the absence of Ti-O-Si bridging bonds is the instability of the Ti-O-Si bridging bonds in a humid environment. Matsuda et al.⁽²⁹⁾ reported that the intensity of the Ti-O-Si absorption peak at 950 cm⁻¹ was decreased after 150 hr exposure at 135°C, 90%RH and that the intensity of the Ti-O-Si absorption peak was not recovered after heat treatment at 350°C for 30 min. The overall reaction steps can be expressed as follows:

If the above reactions can occur in the previously formed Ti-O-Si bonds, water vapor reacted with unstable Ti-O-Si bridging bonds in titanium silicate and induced a phase separation between titanium oxide and silicon oxide. Nevertheless, it is concluded that Ti-O-Si bridging bonds do not exist in the thermal oxide on titanium silicide. Therefore, it is considered that the proposed phase diagram in Figure 7 is also valid for low temperature regions. XPS and AES results in Section 5.4 already proved that Ti-O-Si bridging bonds were not formed during the oxidation of titanium silicide.

5.6. Phase Analysis of Titanium Oxide in the Oxide Layer by TEM

The previous sections showed that a small amount of titanium oxide in the native oxide film on titanium silicide has a +4 valence state. Since titanium oxide can have various crystalline phases, depending on the formation temperature, the crystalline phases of titanium oxide in oxide films from various oxidation temperatures were analyzed. In previous investigations, the stoichiometric ratio of titanium oxide was not explained and simply named as Ti_xO_y or TiO_2 .^(3, 6, 8, 11, 52) In this section, the crystalline structure of titanium oxide in a mixed oxide film on titanium silicide is explained. In addition, the oxide microstructures on C54 and on C49 titanium silicide are explained.

Recently, T. Sandwick and Krishna Rajan observed crystalline oxide precipitates in thermal oxide film on titanium silicide on Si substrate. The sample preparation and oxidation process in their study were very similar to this study. Their results showed that the size of precipitates was about 10 to 100 nm and the precipitates showed faulted grains. They called these faulted grains as crystalline precipitates, Ti_xO_y .

The SAD pattern of the oxidized C49 titanium silicide at 300°C 24hr is shown in Figure 26. It shows a broad diffraction ring. This result indicates that a semi-crystalline phase may exist in the low temperature oxide film. The calculated d spacing of the inner

broad ring was close to the d spacing of anatase TiO_2 (101). The bright and dark field images of oxidized C49 titanium silicide at 300°C / 24hr are shown in Figures 27 and 28, respectively. In the dark field image in Figure 28, the crystalline phase is shown as white spots. The average size of the crystalline phase was about $75\text{\AA}$. In Figure 28, the individual crystalline precipitates (white spots) show contours of titanium silicide grains, which is about $0.1\text{ }\mu\text{m}$. It suggests that semi-crystalline oxide precipitates were formed at the grain boundary of C49 titanium silicide. It is interesting that a semi-crystalline phase was obtained at 300°C / 24hr oxidation even though the oxidation time was long and C49 titanium silicide is metastable.

Figure 26. SAD pattern of oxidized C49 titanium silicide at 300°C / 24hr. Two outer rings correspond to C49 (131) and (171, 081) respectively. The wide, inner diffused ring corresponds to micro-crystalline titanium oxide, probably anatase TiO₂ (101). The corresponded bright and dark-filed images are shown in Figures 27 and 28.

Figure 27. Planar view of oxidized C49 titanium silicide at 300°C / 24hr. The arrow indicates oxide precipitates ($\sim 100\text{\AA}$) preferentially formed at the grain boundary of titanium silicide. These oxide precipitates are semi-crystalline (x167,000)

Figure 28. TEM dark-field image of oxidized C49 titanium silicide at 300°C / 24hr. White lines or spots indicates the presence of crystalline phase. It is considered that micro-crystalline titanium oxide ($\sim 100\text{\AA}$) exists preferentially at the grain boundary of titanium silicide. Chemical etching removed titanium silicide matrix and left oxide at the original grain boundary of titanium silicide ($\times 167,000$)

Even in the titania-silica sol-gel process, it has been known that a crystalline phase (anatase) was generally obtained above 450°C.⁽¹⁵⁾ It is considered that C49 titanium silicide was very reactive to oxidants, and that the high reactivity of C49 titanium silicide is attributable to crystalline defects inside C49 titanium silicide.^(33, 34)

In Figure 29, the SAD pattern of oxidized C49 titanium silicide at 800°C / 20hr is shown. The SAD pattern shows that the high temperature oxide film contains the rutile phase of titanium oxide. From the results of SAD analysis shown in Figures 26 and 29, it is clear that the semi-crystalline phase was obtained from low temperature oxidation and later this crystalline phase transformed to anatase or rutile.

In Figures 30 and 31, the planar views of oxidized C49 and C54 titanium silicide at 800°C / 20hr are shown. Figures 30 and 31 clearly show the difference in the size of the crystalline titanium oxide precipitates, i.e. the black precipitates. TEM images were obtained from the C49 and the C54 titanium silicide which were oxidized at the same time inside a furnace. The figures clearly show that the titanium oxide precipitates on oxidized C49 titanium silicide is finer than the precipitates on oxidized C54 titanium silicide. The size of the titanium oxide precipitates on oxidized C49 titanium silicide was about 16nm. However, the size of the oxide precipitates on C54 titanium silicide was about 47nm, which is about three times larger than those on C49 titanium silicide. The size difference is attributable to the difference in microstructure and reactivity between low temperature annealed C49 phase and high temperature annealed C54 phase.

Figure 29. SAD pattern of oxidized C49 titanium silicide at 800°C / 20hr. The diffraction rings can be indexed as follow; (1) (100) TiO_2 -Rutile (R) or Anatase (A), (2) (101) TiO_2 -R, (3) (100) TiSi_2 -C49, (4) (211) TiO_2 -R or (200) TiSi_2 -C49, (5) (002) TiO_2 -R or (213)-A or (171) (181) (132) TiSi_2 -C49, (6) (221) TiO_2 -R or (116) TiO_2 - A

Figure 30. TEM planar view (bright field image) of oxidized C49 titanium silicide at 800°C 20hr. It is noted that micro-crystalline titanium oxide precipitates are uniformly distributed in the oxide film. (x100,000)

Figure 31. TEM planar view of oxidized C54 titanium silicide at 800°C / 20 hr. It is noted that titanium oxide precipitates are coarse and the distribution is not uniform. (x100,000)

It is likely that the unreacted Ti which is finely dispersed in low temperature annealed C49 film was oxidized and resulted in the finely dispersed titanium oxide precipitates. On the other hand, the oxidation of C54 titanium silicide seemed to occur preferentially at the grain boundary area since high temperature annealed C54 titanium silicide is a stable phase and does not contain unreacted Ti. In the oxidation of the C54 film, crystalline titanium oxide can be formed only when titanium silicide is decomposed and free metallic Ti is available. Decomposition and the oxidation of C54 titanium silicide therefore most probably occurred preferentially at the grain boundaries. Preferential oxidation resulted in a wide distribution of titanium oxide precipitates in a mixed oxide layer film.

In Section 5.4, the ARXPS results suggested that the oxide film on titanium silicide has a multilayer structure. The formation of this multilayer oxide film is evidence that the oxidation mechanism of titanium silicide changed over several oxidation stages. In Section 5.4, native oxide films were analyzed as an example of the early stage oxidation or the low temperature oxidation. In the first part of this section, TEM results of oxidized C49 titanium silicide at 300°C / 24 hr was presented as an example of intermediate oxidation stage where the decomposition of titanium silicide occurs since Si diffusion from Si substrate is slow. Since the oxide film thickness of oxidized C49 titanium silicide at 300°C / 24 hr was not thick enough to show a multilayer structure, one of high temperature oxide film from later stage of oxidation was selected and analyzed using two step ion-milling in order to survey a multilayer oxide film through its thickness.

The bright and dark-field images of oxidized C49 titanium silicide at 800°C / 20hr are shown in Figures 32 and 33, respectively. Figures 32-a and 32-b represents the oxide microstructure very near the oxidation reaction interface, the oxide-silicide interface. It was obtained after the first 4 min of ion milling. Figures 33-a and 33-b shows the

oxide microstructure away from the oxide-silicide interface (near the top surface) which was obtained after the second 4 min of ion milling.

Figure 32-a. Bright-field image of oxidized C49 titanium silicide at 800°C 20hr. The image was obtained by a combined 4 min ion milling and chemical etching. (x100,000)

Figure 32-b. Dark-field image of oxidized C49 titanium silicide at 800°C 20hr. (x100,000)

Figure 33-a. Bright-field image of oxidized C49 titanium silicide at 800°C 20hr. The image was obtained after the second ion milling focused on the same location where the images in Fig.32-a and 32-b were obtained (x100,000)

Figure 33-b. Dark-field image of oxidized C49 titanium silicide at 800°C 20hr. (x100,000)

Figures 32-a and 32-b show clearly that titanium oxide precipitates widely distributed in the sub-surface oxide layer. In Figures 33-a and 33-b, after the second 4 min ion milling, the area near the ion-milled hole does not show titanium oxide precipitates. This means that the very top layer of the thermal oxide is amorphous silicon oxide, and crystalline titanium oxide precipitates exist underneath the surface of the silicon oxide. In Section 5.4.1 and 5.4.2, it was explained that the very thin native oxide on as-prepared C49 and C54 titanium silicide also has similar layer sequence. The ARXPS results showed that a small amount of titanium oxide exists underneath the surface silicon oxide. Since the oxide microstructure at high temperature also showed a similar oxide layer sequence from top to bottom, it is concluded that the oxide film grows outward and the oxidation reaction interface is the oxide-silicide interface. Previous investigation suggested that the reaction interface is the oxide-silicide interface.^(7, 8, 10, 13, 14, 46, 47) The TEM results in this study supports the previous investigations. Therefore, it is concluded that the oxidation of titanium silicide is dependent on the inward diffusion of oxidant and the oxide growth becomes linear-parabolic rate dependent, as reported previously.^(3-5, 12-14)

Following the first and second ion-milling, the intensity of each ring of SAD pattern from C49 titanium silicide oxidized at 800°C / 24 hr was carefully monitored. The results are summarized in Table 15. In Table 13, d_m , d_r , R and A represent the measured lattice spacing, JCPDS reference lattice spacing, rutile phase, and anatase phase, respectively. Table 15 shows that the relative intensity of the rutile phase and C49 phase were slightly decreased after the second ion milling. It possibly indicates that the anatase phase exists near the top surface. It is unclear why the anatase phase exists near the outside surface of the oxide, away from the oxide-silicide interface.

Table 15. SAD results after 1st and 2nd ion-milling of oxidized C49 film at 800°C 20hr.

1st ion milling				2nd ion milling				Note
dm	I/Io	dj	phase	dm	I/Io	dj	phase	
3.2260	VS	3.2460	R (110)	3.543	S	3.563	A (101)	New decreased by ion mill
		3.262	C49 (021)	3.2260	W	3.246	R (110)	
2.4843	VS	2.4873	R (101)	2.4843	S	2.4873	R (101)	decreased by ion mill
						2.4343	A (103)	
2.1032	M	2.0232	R (111)	-	-	-	-	disappear
1.8795	VW	1.949	C49 (200)	1.8795	VW	1.8895	A (200)	
						1.949	C49 (200)	
1.6886	VS	1.6898	R (211)	1.6886	S	1.6786	A (105)	
						1.6898	R (211)	
1.4604	M	1.4680	R (310)	1.4604	M	1.4804	A (204)	
		1.5004	C49 (260)			1.4611	R (002)	
1.3509	S	1.3598	R (301)	1.3509	M	1.3409	A (116)	
						1.342	R (301)	

Considering that anatase is stable at lower temperatures and rutile is stable at higher temperatures, it is interpreted that the anatase phase near the top surface was formed at either low or intermediate temperatures and then was pushed away from the oxide-silicide interface while high temperature oxidation, at the later stage oxidation, resulted in the rutile phase near the oxide-silicide interface.

TEM, AES, and XPS results suggest that the oxide layer on titanium silicide has a multilayer structure. The results from this study agree well with previous reports.^(6, 8, 52) AES depth profile study done by G. Valyi et al. showed a similar multilayer structure.^(8, 52) As a summary, the oxide layer structures from the various oxidation stages are schematically shown in Figure 34.

(a)

(b)

Figure 34. Schematic drawings to show how the oxide film is formed on titanium silicide at various oxidation stages. (a) shows mass transport and (b) shows the multilayer at various stage of oxidation.

V. CONCLUSION

As prepared titanium silicide films (C49 and C54) which were exposed at ambient room temperature had pure silicon oxide containing negligible titanium oxide, less than 0.4 atomic percent. The formation of silicon oxide on as-prepared C49 and C54 titanium silicide proved that the early stage oxidation of titanium silicide at room temperature was mainly due to the initial high Si/Ti ratio of the as-prepared titanium silicide. This means that the early stage oxidation depends on the high activity of silicon at the surface of titanium silicide, and is not dependent on the standard Gibbs free energy of formation of the oxide. The source of silicon to form silicon oxide is excess silicon in as-prepared titanium silicide since the decomposition reaction of titanium silicide at room temperature is thermodynamically impossible and also since Si diffusivity at room temperature is extremely slow. (D is on order of 10^{-19} cm²/sec)

AES and XPS results showed that the native oxide on as prepared C49 and C54 titanium silicide contains titanium oxide. Angle-resolved XPS analysis showed that titanium oxide existed near titanium silicide and beneath the top surface silicon oxide. The native oxide film on a low temperature annealed titanium silicide (C49 phase) showed more titanium oxide than high temperature annealed titanium silicide (C54 phase).

The binding energy of Ti2p for titanium oxide showed that the titanium in titanium oxide in native oxide has a +4 valence state. This means that the stoichiometric ratio of titanium to oxygen is close to 2:1. The chemical binding energy of Ti2p for titanium oxide on C49 titanium silicide was higher than that of titanium oxide on C54 titanium silicide, meaning that the oxide film on C49 titanium silicide had a stronger screening effect on escaping photoelectrons than that on C54 titanium silicide. This suggests that a metastable titanium silicide (C49 phase) had a thicker oxide film than a stable titanium silicide (C54 phase). This is also possibly due to the presence of unreacted Ti or TiSi

(which is not detected by XRD) in low temperature annealed C49 titanium silicide. The higher sheet resistance of the C49 phase explains that the low temperature annealed film has more electron scattering sites than C54 phase.

The molecular bond in the oxide films on titanium silicide was investigated to examine the reactivity between titanium oxide and silicon oxide. FT-IR results showed that there was no reaction between titanium oxide and silicon oxide during the oxidation of titanium silicide. No characteristic IR absorption peaks corresponding to Ti-O-Si bridging bonds were found. It proved that the oxide films on C49 and C54 titanium silicide are TiO_2 - SiO_2 mixed oxide. This result also suggests that a stable interface exists between titanium oxide and silicon oxide. The results in this study support the previous studies on the phase equilibria in Ti-Si-O system.

The oxide layer structure and the crystalline phase of titanium oxide from intermediate and later stage oxidation were investigated by TEM. Titanium oxide precipitates in the oxide films on C49 titanium silicide was smaller than those on C54 titanium silicide. TEM dark-field image of titanium oxide precipitates showed that titanium oxide precipitates are preferentially located on the grain boundary of titanium silicide. TEM results from two step ion-beam milling showed that titanium oxide precipitates were sandwiched between the top surface silicon oxide and the bottom silicon oxide, which was formed later and interfaced with titanium silicide. The sandwiched structure suggested that the oxidation reaction occurred at the oxide-silicide interface and the surface oxide formed earlier was pushed away from the reaction interface. This result supports the previous results that the oxide growth is rate-limited by inward oxidant diffusion and outward Si diffusion. TEM results also showed that titanium silicide forms a stable interface with silicon oxide, not with titanium oxide.

The crystalline phase of titanium oxide in oxidized C54 and C49 titanium silicide at 800°C were examined by SAD. Titanium oxide on oxidized C54 and C49 titanium silicide

had two crystalline forms, which are anatase and rutile. Silicon oxide in a mixed oxide film was amorphous. In a multilayer oxide structure, the anatase titanium oxide formed earlier existed near the top surface and the rutile titanium oxide formed later existed near the oxide-silicide interface.

In summary, the thermal oxide film in this study was a multilayer film which shows that the oxidation of titanium silicide proceeds in various distinct stages. First, the early stage, which is affected by excess Si or unreacted Ti in as prepared titanium silicide. Second, the intermediate stage when the decomposition of titanium silicide is necessary for the oxidation reaction to be continued. Third, the later stage when fast Si diffusion from the Si substrate is possible and the decomposition of titanium silicide does not occur. No ternary phase existed in the Ti-Si-O system, even at low temperatures below 700°C, suggesting that there was no reaction between titanium oxide and silicon oxide during the oxidation of titanium silicide.

REFERENCES

1. T. Yoshida et al., " Thermally Stable, Low-Leakage Self-Aligned Titanium Silicide Junctions," *J. Electrochem. Soc.*, Vol.137, No.6, June 1990, pp.1914 - 1917.
2. S.M. Sze, pp. 106 - 107 in "VLSI Technology "
3. J. R. Chen et al., " Oxidation of Titanium Disilicide on Polycrystalline Silicon, " *J. Electron. Mat.*, Vol. 11, No. 2, pp.355 - 389, 1982.
4. J. R. Chen et al., " Investigation of TiSi_2 Thin-Film Oxidation by Radioactive Tracer Technique," *Appl. Phys. Lett.*, Vol.40, No.3, 1 February 1982, pp. 263 - 265.
5. J.R. Chen et al., " Oxidation Mechanisms in TiSi_2 Films on Single Crystal Silicon Substrates, " *Appl. Phys. Lett.*, Vol. 37, No.9, 1 November 1980, pp. 824 - 826.
6. W. Y. Yang et al., " Study of Oxidation of TiSi_2 Thin Film by XPS, " *Jpn. J. Appl. Phys.*, Vol.23, No.12, 1984, pp. 1560 - 1567.
7. S. J. Rosner et al., " High-Pressure Oxidation of Titanium Disilicide/Polycrystalline Silicon Composite Films," *J. Appl. Phys.* Vol.65, No.4, 15 February, 1989, pp. 1729 - 1732.
8. G. Valyi et al. , " Oxidation Behavior of Double Layers of TiSi_2 on Polycrystalline Silicon," *Thin Solid Films*, Vol.116, pp.383 - 390, 1984.
9. T. L. Huang and S. T. Lee, " Formation and Oxidation of Titanium Silicide," *Mat. Res. Soc. Symp. Proc.*, Vol.77, 1987, pp.339 - 344.
10. M. Bartur, " Thermal Oxidation of Transition Metal Silicides:The Role of Mass Transport," *Thin Solid Films*, Vol.107, 1983, pp. 55 - 65.
11. W. J. Strydom et al., " Thermal Oxidation of The Silicides CoSi_2 , CrSi_2 , NiSi_2 , PtSi , TiSi_2 , and ZrSi_2 ," *Thin Solid Films*, Vol. 131, 1985, pp. 215- 231.
12. G. J. Huang and L. J. Chen, " Investigation of the Oxidation Kinetics of C54- TiSi_2 on (001) Si by Transmission Electron Microscopy, " *J. Appl. Phys.* Vol. 72, No. 7, 1 October 1992, pp. 3143 - 3149.
13. S.L. Zhang, R. Ghez, and F. M. d'Heurle, " A Mathematical Model for Silicide Oxidation ", *J. Electrochem. Soc.*, Vol. 137, No. 2, Feb. 1990, pp 659 - 663.
14. H. Jiang and C. S. Peterson, " Thermal Oxidation of Transition Metal Silicides," *Thin Solid Films*, Vol.140, pp. 115 - 129, 1986.
14. F. d'Heurle, E.A. Irene, and C. Y. Ting, " Oxidation of Silicide Thin Films; TiSi_2 ," *Appl. Phys. Lett.* , Vol.42, No.4, 15 Feb. 1983, pp.361 - 363.

15. B.E. Yoldas, " Formation of Titania-Silica Glasses by Low Temperature Chemical Polymerization," *J. Non-Crys. Solids* 38 & 39, 1980, pp.81 - 86.
16. Manual Ocana et al., " Low-temperature Nucleation of Rutile Observed by Raman Spectroscopy during Crystallization of TiO_2 ," *J. Am. Ceram. Soc.*, Vol.75, No. 7, 1992, pp 2010 - 2012.
17. Young-Joo Kim and Lorraine Falter Francis, " Processing and Characterization of Porous TiO_2 Coatings," *J. Am. Ceram. Soc.*, Vol.76, No.3, 1993, pp.737 - 742.
18. Jee Loon Look and Charles F. Zukoski, " Alkoxide-Derived Titania particles: Use of Electrolytes to Control Size and Agglomeration Levels," *J. Am. Ceram. Soc.*, Vol.75, No.6, 1992, pp.1587 - 1595.
19. Joseph L.Keddie and Emmanuel P. Giannelis, " Effect of Heating Rate on the Sintering of Titanium Dioxide Thin Films: Competition between Densification and Crystallization," *J. Am. Ceram. Soc.*, Vol.74, No.10, 1991, pp.2669 - 2671.
20. G. P. Burns," Titanium Dioxide Dielectric Films Formed by Rapid Thermal Oxidation," *J. Appl. Phys.* , Vol.65, No.5, 1989, pp.2095 - 2097.
21. M. Kamal Akhtar et al., " Dopants in Vapor-Phase Synthesis of Titania Powders," *J. Am. Ceram. Soc.*, Vol.75, No.12, 1992, pp.3408 - 3416.
22. V. A. Zeitler and C. A. Brown, " The Infrared Spectra of Some Ti-O-Si, Ti-O-Ti and Si-O-Si Compounds," *J. Chem. Phys.*, Vol.61, 1957, pp.1174 - 1177.
23. P.C. Schultz and H.T. Smyth, " Ultra-Low-Expansion Glasses and Their Structure in the SiO_2 - TiO_2 System," in *Amorphous Materials*, Edited by R.W. Douglas and B.Ellis, Wiley-Interscience, London, 1972, pp.453 - 461.
24. G.J. Copley et al.," The Influence of Titania upon the Thermal Expansion of Vitreous Silica," *Physics and Chemistry of Glasses*, Vol.14, No.4, August 1973, pp.73 - 76.
25. I.M. Miranda Salvado and J.M. Fernandez Navarro," Phase Separation in Materials of the Systems TiO_2 - SiO_2 and ZrO_2 - SiO_2 Prepared by the Alkoxide Route," *J. Mat. Sci. Lett.*, Vol.9, 1990, pp.173 - 176.
26. Douglas C. Allan and Michael P. Teter, " Local Density Approximation Total Energy Calculations for Silica and Titania Structure and Defects," *J. Am. Ceram. Soc.*, Vol.73, No.11, 1990, pp.3247 - 3250.
27. Y.C. Song et al., "Ceramic Fibres from Polymer Precursor Containing Si-O-Ti Bonds," *J. Mat. Sci.*, 23, (1988), 1911 - 1920.
28. Y. Hasegawa et al., " Ceramic Fibres From Polymer Precursor Containing Si-O-Ti Bonds," *J. Mat. Sci.*, 26, (1991) 3657 - 3664.

29. Atsunori Matsuda et al., " Structural Changes of Sol-Gel Derived TiO_2 - SiO_2 Coatings in an Environment of High Temperature and High Humidity," *J. Am. Ceram. Soc.*, Vol.76, No.11, pp. 2899 - 2903, 1993.
30. T. Kokubu and M. Yamane, " Thermal and Chemical Properties of TiO_2 - SiO_2 Porous Glass-Ceramics," *J. Mat. Sci.*, Vol.22, 1987, pp.2583 - 2588.
31. S.M. Melpolder et al., " Phase Transformations in $\text{TiO}_2/\text{SiO}_2$ Sol-Gel Films as a Function of Composition and Heat-treatment," *J. Mat. Sci.*, Vol.26, 1991, pp.3585 - 3592.
32. Powder Diffraction File, Joint Committee on Powder Diffraction Standards, International Center for Diffraction Data No. 21-1276, 21-1272, 29-1360.
33. R. Beyers and R. Sinclair, " Metastable Phase Formation in Titanium-Silicon Thin Films," *J. Appl. Phys.*, Vol.57, No.12, 15 June 1985, pp.5240 - 5245.
34. T. C. Chou et al., " Lattice Imaging of Metastable TiSi_2 ," *J. Appl. Phys.*, Vol.62, No.6, 15 Sept. 1987, pp.2275 - 2279.
35. W. G. Moffat, in *The Handbook of Binary Phase Diagrams*, General Electric Co.,Schenectady, New York, 1978, (updated 1982).
36. S. P. Murarka, in *Silicides for VLSI Applications* , 1983 Academic Press.
37. H. Bender et al., " AES and XPS Analysis of the Interaction of Ti with Si and SiO_2 During RTA," *Appl. Surf. Sci.*, Vol.38, 1989, pp.37 - 47.
38. R. Beyers et al., " Titanium Disilicide Formation on Heavily Doped Silicon Substrates," *J. Appl. Phys.*, Vol.61, No. 11, 1 June 1987, pp. 5110 - 5117.
39. M. Berti et al., " Titanium Silicide Formation: Effect of Oxygen Distribution in the Metal Film," *J. Appl. Phys.* , Vol. 55, No.10, 15 May 1984, pp. 3558 - 3565.
40. J. F. Jongste et al. , " Modeling of the Formation of TiSi_2 in a Nitrogen Ambient," *Applied Surface Science*, Vol.38, 1989, pp. 57 - 61.
41. M. Tanielian and S. Blackstone, " Physical Properties of Sputter-Deposited Titanium Silicide as a Function of Substrate Temperature," *J. Electrochem. Soc.*, June 1985 Vol. 132, No.6, pp.1487 - 1491.
42. N. de Lanerolle et al., " Titanium Silicide-Silicon Interface Degradation During Heat Treatment," *J. Electronic Mat.*, Vol.19, No.11, 1990, pp. 1185 - 1192.
43. P. Merchant and Jun Amano, " Oxygen Redistribution During Sintering of Ti/Si Structures," *J. Vac. Sci. Technol.*, B2, Vol.4, Oct. - Dec. 1984, pp. 762 - 765.
44. R. R. De Avillez et al., " Quantitative Investigation of Titanium/Amorphous-Silicon Multilayer Thin Film Reactions, " *J. Mater. Res.* Vol. 5, No. 3, Mar. 1990, pp 593 - 600.

45. B.E. Deal and A.S. Grove, " General Relationship for the Thermal Oxidation of Silicon," *J. Appl. Phys.*, Vol. 36, No. 12, Dec. 1965, pp.3770 - 3778.
46. R.D. Frampton et al., " A Study of the Oxidation of Selected Metal Silicides," *J. Appl. Phys.* , Vol.62, No.7, 1 Oct. 1987, pp.2972 - 2980.
47. L.N. Lie et al., " Thermal Oxidation of Silicides," *J. Appl. Phys.*, Vol.56, No.7, 1 October 1984, pp.2127 - 2132.
48. R. Beyers, " Thermodynamic Considerations in Refractory Metal-Silicon-Oxygen Systems," *J. Appl. Phys.* Vol.56, No.1, 1 July 1984, pp.147 - 152.
49. R. Beyers et al., " Phase Equilibria in Thin-Film Metallizations," *J. Vac. Sci. Technol. B* Vol.2, No.4, Oct.-Dec. 1984, pp. 781 - 784.
50. R. Beyers and R. Sinclair, " The Effect of Oxygen in Cosputtering (Titanium + Silicon) Film," *Mat. Res. Soc. Symp. Proc.* , Vol.14, 1983, pp.423 - 427.
51. Marc A. Taubenblatt and C. R. Helms, " Silicide and Schottky Barrier Formation in the Ti-Si and the Ti-SiO_x-Si Systems," *J. Appl. Phys.* 53 (9), Sept. 1982. 6308 - 6315.
52. T. Sandwick and K. Rajan, " The Oxidation of Titanium Silicide, " *J. Electron. Mat.*, Vol.19, No.11, 1990, pp. 1193 - 1199.
53. R. Perez-Casero et al., " Plasma Oxide Growth on Silicon and Titanium Disilicide," *Thin Solid Films*, Vol. 193/194, 1990, pp.627 - 637.
54. J. P. Lu and R. Raj, " Ultra-high Vacuum Chemical Vapor Deposition and in situ Characterization of Titanium Oxide Thin Films," *J. Mater. Res.*, Vol.6, No.9, Sep. 1991, pp.1913 - 1918.
55. N. C. Saha and H. G. Tompkins, " Titanium Nitride Oxidation Chemistry: An X-ray Photoelectron Spectroscopy Study," *J. Appl. Phys.* Vol.72, No.7, 1 October 1992, pp.3072 - 3079.
56. Perkin-Elmer ESCA Manual, Version 3.0 (Perkin-Elmer, Eden Prairie, MN,1991)
57. Handbook of X-ray Photoelectron Spectroscopy, edited by C. D. Wagner, W. M. Riggs, L.E. Davis, J.F. Moulder, and G.E. Muilenberg, Perkin-Elmer, Eden Prairie, 1979.
58. B.D. Cullity, p.102 in Element of X-ray Diffraction. 2nd Edition, Addison-Wesley Publishing Co.
59. G. Socrates, p.143 in Infrared Characteristic Group Frequencies., by John Wiley & Sons, 1980.
60. C.F. Smith Jr., R.A. Condrate Sr., and W.E. Votava, " The Difference Infrared Spectra of Titanium-Containing Vitreous Silica," *Applied Spectroscopy* , Vol.29, No. 1, 1975, 79 - 81.

61. J.B. Lumsden, p.113 in Metals Handbook Vol.10: Materials Characterization , 9th Edition.
62. P.G. Cotter et al., " Physical and X-Ray Study of the Disilicides of Titanium, Zirconium, and Hafnium," *J. Amer. Cer. Soc.*, Vol. 39, No. 1, 1956, 11 - 12.
63. L.S. Hung et al., " Kinetics of TiSi_2 Formation by Thin Ti Films on Si," *J. Appl. Phys.* 54, 1983, pp. 5076 - 5080.
64. P. Gas et al., " Diffusion of Sb, Ga, Ge, and (As) in TiSi_2 ," *J. Appl. Phys.*, Vol. 63, No.11, 1 June 1988, pp 5335 - 5345.
65. I. Barin, O. Knacke and O. Kubaschewski, Thermochemical Properties of Inorganic Substances, Springer-verlag, Berlin, 1977.
66. NBS tables of chemical thermodynamic properties, *J. Phys. Chem. Ref. Data*, Vol.11, Suppl. 2, 1982, pp 111, 209 - 210.
67. D.A. Gulino et al., " Isotopic Study of Oxygen Diffusion in Silicon Dioxide Thin Films ," *Thin Solid Films* , Vol. 188, 1990, pp. 237 - 246.
68. B.E. Deal and A.S. Grove, " General Relationship for the Thermal Oxidation of Silicon," *J. Appl. Phys.*, Vol. 36, No.12, December 1965, pp. 3770 - 3778.
69. Hajimu Wakabayashi and Minoru Tomozawa, " Diffusion of Water into Silica Glass at Low Temperature, " *J. Am. Ceram. Soc.*, Vol 72, No. 10, pp. 1850 -1855, 1989.
70. H. Koster et al., " Comparison of the Properties of TiSi_2 Films Obtained by Silicon and Titanium Co-sputtering and by Composite Target Sputtering," *Thin Solid Films*, Vol. 170, 1989, pp.71 - 80.
71. C.D. Lien and M.A. Nicolet, " Impurity Effects in Transition Metal Silicides," *J. Vac. Sci. Tech.*, B Vol.2, Oct-Dec 1984, pp. 738 - 747.
72. F.M. d'Heurle et al., " Silicides and Rapid Thermal Annealing," *Mat. Res. Soc. Symp. Proc.*, Vol.52, pp.261 - 270.
73. Powder Diffraction File, Joint Committee on Powder Diffraction Standards, International Center for Diffraction Data No. 33-1384.

APPENDIX

- (1) The standard Gibbs free energy of the overall oxidation reactions for titanium silicide:

$$\begin{aligned}\Delta G_{\text{Rx}} &= G_{\text{TiO}_2} + 2G_{\text{SiO}_2} - G_{\text{TiSi}_2} - 3G_{\text{O}_2} \\ &= \Delta H - T \Delta S\end{aligned}$$

$$= H_{\text{TiO}_2} + 2H_{\text{SiO}_2} - H_{\text{TiSi}_2} - T [S_{\text{TiO}_2} + 2S_{\text{SiO}_2} - S_{\text{TiSi}_2} - 3S_{\text{O}_2}] \times 10^{-3}$$

at 298 K

$$\begin{aligned}\Delta G_{\text{Rx}} &= -933 + 2(-904.2) - (-134.3) - 298[49.92 + 2(41.46) - 61.09 - 3(205)] \times 10^{-3} \\ &= -2458.4 \text{ (KJ/mol)}\end{aligned}$$

- (2) The standard Gibbs free energies of sub-reactions in Table 8 are shown below:

	Temp (K)	Rx (A-1)	Rx (B-1)	Rx(C-1)	Rx (D-1)	Rx (E-1)	Rx (F-1)	Rx (A-2)	Rx (B-3)	Rx (C-2)	Rx (E-2)	Overall Rx (3)
1	298	-1580.8	132.2	-853.9	-122.4	-124.7	-745.5	-877.6	-856.5	-726.9	2.3	-2458.4
2	300	-1580.1	132.2	-853.5	-122.8	-124.8	-745.1	-877.3	-856.1	-726.6	2.1	-2457.4
3	400	-1544.3	131.4	-835.9	-141.3	-134.4	-727.3	-858.8	-837.9	-708.3	-6.9	-2403.1
4	500	-1508.4	130.8	-818.3	-159.6	-143.9	-709.7	-840.4	-819.6	-690.1	-15.7	-2348.8
5	600	-1472.7	130.1	-800.8	-177.5	-153.2	-692.1	-822.2	-801.4	-671.9	-24.3	-2294.9
6	700	-1437.2	129.5	-783.4	-195.2	-162.3	-674.8	-804.2	-783.4	-653.9	-32.9	-2241.4
7	800	-1402.1	128.9	-766.1	-212.7	-171.4	-657.5	-786.4	-765.5	-636.0	-41.3	-2188.4
8	900	-1367.3	128.3	-749.0	-229.9	-180.3	-640.3	-768.6	-747.8	-618.3	-49.6	-2135.9
9	1000	-1332.8	127.8	-732.1	-247.0	-189.2	-623.1	-750.9	-730.3	-600.7	-57.8	-2067.0
10	1100	-1298.5	127.3	-715.2	-263.9	-197.9	-606.1	-733.3	-712.9	-583.3	-65.9	-2031.8
11	1200	-1264.5	126.6	-698.5	-280.8	-206.6	-589.0	-715.6	-695.5	-566.0	-74.2	-1980.1
12	1300	-1230.7	125.8	-681.7	-297.7	-215.2	-572.0	-697.8	-678.3	-549.0	-82.5	-1928.5