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Interfacial reactions in Ti/Si₃N₄ and TiN/Si diffusion couples

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Stability and formation kinetics of TiN and silicides in Ti/Si₃N₄ and TiN/Si diffusion joints have been investigated. Reactions in the diffusion couples were studied experimentally in the temperature range between 950 and 1100 °C. Isothermal sections and activity diagrams of the Ti-Si-N system were calculated using the recent thermodynamic data. Both the thermodynamic calculations and experimental results indicate that TiN and Si react with each other and form TiSi₂ and even Si₃N₄ if the activity of nitrogen is high enough. Similarly, results from the Ti/Si₃N₄ couple were in good accordance with calculated phase equilibria. The experiments carried out in vacuum ampoules and in a vacuum furnace showed that the gas phase has a strong effect on the reactions. © *1995 American Institute of Physics.*

I. INTRODUCTION

Silicon nitride is one of the most promising materials among technical ceramics, used in structural components for high temperature applications as well as in electronics industry. Most of these applications require some type of ceramic-ceramic or ceramic-metal joining. Due to its ability to dissociate also chemically very stable compounds, titanium is a common additive in filler metals used for inducing them to wet Si₃N₄ and other ceramics. The ternary Ti-Si-N system is also interesting since several compounds of it, like TiN and TiSi₂ are used in the construction of electrical interconnections in electronic devices. TiN is used as a diffusion barrier in the metallization of silicon integrated circuits and TiSi₂ as a contact material. Thus the chemical reactions between Ti and the ceramic and on the other hand between TiN and Si are important and a better understanding of the Ti-Si-N system is needed. This requires a consistent thermodynamic description of this system.

Beyers *et al.*[1] and Schuster *et al.*[2] have published calculated ternary isotherms of the Ti-Si-N system at 1000 and 1300 °C, respectively. In these papers Ti₅Si₃ is presented as a line compound and all silicides are in equilibrium with TiN$_x$. The notable difference between the diagrams is the equilibrium between TiN and Si, which is present in Beyers's diagram but not in the one of Schuster. Wakelkamp[3] has studied the system experimentally at 1100 °C and observed the solubility of nitrogen in Ti₅Si₃ to be about 11 at. %. There is an equilibrium between TiN$_x$ and Si in Wakelkamp's diagram, which was determined on the basis of the diffusion couple experiments.

The work reported here was conducted as part of a program attempting to gain a better understanding of the role of titanium in activated brazing of ceramics. The present paper concentrates on studying the Ti-Si-N system in more detail. In order to clarify the above mentioned omissions and inconsistencies, Ti/Si₃N₄ and TiN/Si diffusion couple experiments were carried out and the diffusion couples were examined in detail with the SEM/EPMA technique. Since more recent thermodynamic data are available, ternary isothermal sections of the Ti-Si-N system were assessed in this work.

II. MULTIPHASE DIFFUSION

The phase sequence in a binary diffusion couple can be predicted directly from the relevant phase diagrams provided, that mass transport is kinetically favorable. After long annealing all the thermodynamically stable phases will exist as single phase regions between the end members—in accordance with the phase rule. Thicknesses of the layers are determined either by linear or parabolic growth kinetics. However, the metal-ceramic systems contain more than two elements, which makes the prediction of the reaction layers much more difficult.

In ternary diffusion couples two-phase regions can also exist and therefore, theoretically, many phase sequences are possible. Diffusion paths in a ternary phase diagram must fulfill the most important condition: the conservation of mass. When no material is lost or created, the diffusion path is forced to cross the straight line between the end members at least once. Using a model developed by van Loo[4] the actual phase sequence can often be predicted. The central idea in this model is the occurrence of the intrinsic diffusion only in the direction of decreasing activity of the component.

III. THERMODYNAMIC DATA AND MODELS

The Ti-Si-N phase diagram was calculated using data from previous descriptions of the binary Ti-N, Ti-Si, and Si-N systems. The Ti-N system used in this study was taken from Ohtani and Hillert,[5] although it has been successfully re-evaluated by Jonsson.[6] In the temperature range studied the two descriptions do not differ essentially from each other. The Ti-Si system used in this study was assessed by Pajunen and Kivilahti.[7] The description of Si₃N₄ is given by Hillert *et al.*[8]

The interstitial Ti solutions as well as the nonstoichiometric fcc-TiN and Ti₅Si₃[N] phases are described here with

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the sublattice model developed initially by Hillert and Staffanson.[9] According to this model it is convenient for many crystalline phases to divide the lattice into sublattices, since the elements typically have a preference for a specific lattice site. Similarly, it can be supposed that the solutions of metals and gases consist of several sublattices, among which the constituent atoms are assumed to be distributed randomly.

The γ-TiN$_x$ solution phase has the NaCl type of structure, where Ti atoms are arranged in an fcc lattice and all the interstitial octahedral sites are filled with N. The two-sublattice model is used and it can be expressed by the formula Ti$_a$(N,Va)$_c$. For fcc structure $(c/a) = 1$ as there is one octahedral site per solvent atom. The molar Gibbs energy of the γ phase is given by

$$G_m^\gamma = y_N {}^\circ G_{\text{Ti:N}}^\gamma + y_{Va} {}^\circ G_{\text{Ti:Va}}^\gamma + cRt(y_N \ln y_N + y_{Va} \ln y_{Va})$$

$$+ y_N y_{Va} L_{\text{Ti:N},Va}^\gamma, \tag{1}$$

where Va stands for vacancies and y is the site fraction of a component in the sublattice. The parameter $^\circ G_{\text{Ti:N}}$ is the Gibbs energy of stoichiometric TiN, $^\circ G_{\text{Ti:}Va}$ is identical with the Gibbs energy of the Ti (hcp) and $L_{\text{Ti:N},Va}$ represents an interaction energy between nitrogen atoms and vacancies.

The α (hcp) and β (bcc) phases are represented by the two-sublattice model as well. The Ti and Si atoms occupy the first sublattice and N and Va the second sublattice, and the appropriate formula is (Ti,Si)$_a$(N,Va)$_c$. For the hcp structure $a = 1$ and $c = 0.5$. The value 0.5 is chosen, since it is assumed that along the c-axis two neighboring interstitial sites are never occupied by nitrogen atoms at the same time. In the bcc lattice there are three octahedral sites for each solvent atom and thus $(c/a) = 3$.

The Ti$_5$Si$_3$[N] phase has the hexagonal structure and it was modelled with three sublattices. It is assumed that the first sublattice is occupied solely by titanium, the second one can be filled with all three kinds of atoms and the third sublattice is occupied with silicon and nitrogen.

IV. EXPERIMENT

Two different kinds of diffusion couples were made: Ti/Si$_3$N$_4$ and TiN/Si. The Ti/Si$_3$N$_4$ couples were prepared as disks, 10 mm in diameter and 2.0 mm thick. The high purity titanium (>99.99%, Goodfellow) samples were polished electrolytically at -35 °C and etched subsequently in a 10% HF solution. Hot-pressed silicon nitride, 95% in purity, contained Al$_2$O$_3$, Y$_2$O$_3$, and MgO as sintering aids. The samples were cut from a rod of base material and mechanically polished. Titanium and silicon nitride samples were then cleaned ultrasonically in ethanol. The silicon specimens of 1 cm^2 in area were cut from (100) single-crystal wafers. The titanium nitride films were deposited by reactive ion plating (PVD) on the Si substrates in Ar:N$_2$ atmosphere. Before the evaporation of titanium the Si substrates were sputter cleaned. The golden color of the TiN$_x$ film obtained indicates a composition close to the stoichiometric TiN.

The Ti/Si$_3$N$_4$ diffusion couples were annealed in a vacuum furnace ($p < 10^{-5}$ mbar) at 950 and 1100 °C for different periods of time. The pressure at the couple's interface
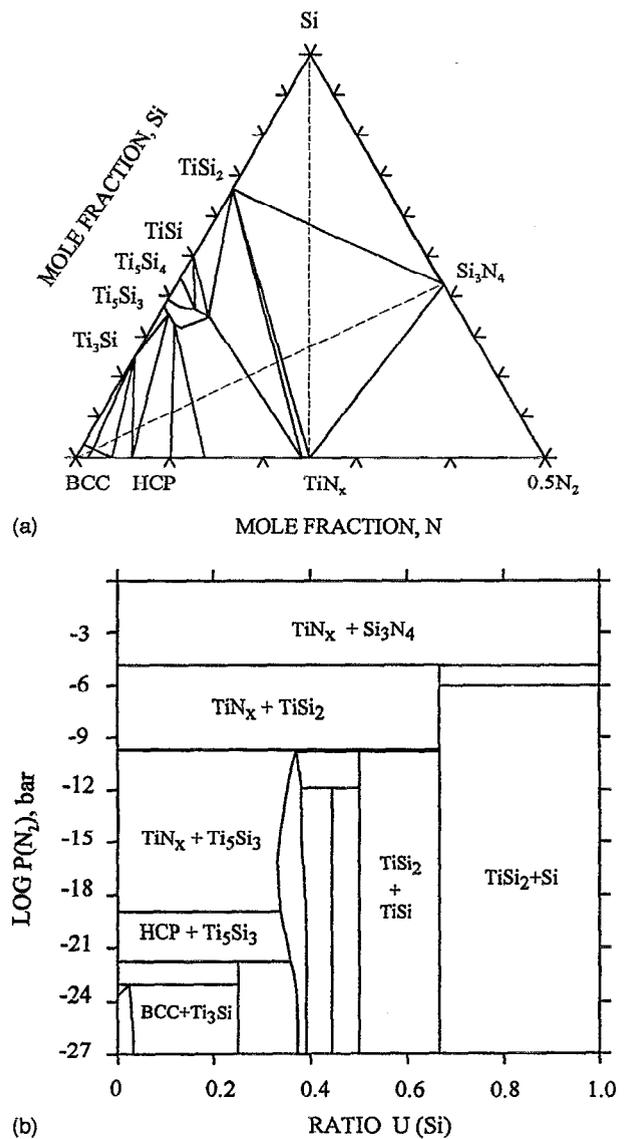

(a) MOLE FRACTION, N

(b) RATIO U (Si)

FIG. 1. (a) Phase diagram of the Ti-Si-N system at 1100 °C with the end-members of the diffusion couple. (b) Nitrogen pressure as a function of the atom ratio $u_{\text{Si}}(=x_{\text{Si}}/x_{\text{Si}}+x_{\text{Ti}})$ at 1100 °C. Note that the two-phase region Ti$_5$Si$_3$+TiSi$_2$ exists in a very narrow pressure region.

was about 200 N/cm^2. The TiN/Si couples were annealed both in the vacuum furnace and in vacuum ampoules at temperatures between 950–1200 °C up to 240 h. The samples were examined with a scanning electron microscope (SEM), and electron microprobe microanalysis (EPMA) and a secondary ion mass spectrometer (SIMS).

V. RESULTS AND DISCUSSION

Figures 1(a) and (b) show the isothermal section of the Ti-Si-N system and the activity of nitrogen as a function of the atom ratio $u_{\text{Si}}(=x_{\text{Si}}/x_{\text{Si}}+x_{\text{Ti}})$ both calculated at 1100 °C. The isotherm is in close agreement with the one determined experimentally by Wakelkamp.[3] Due to the stabilizing effect of dissolved nitrogen, Ti$_5$Si$_3$ is in equilibrium with all other
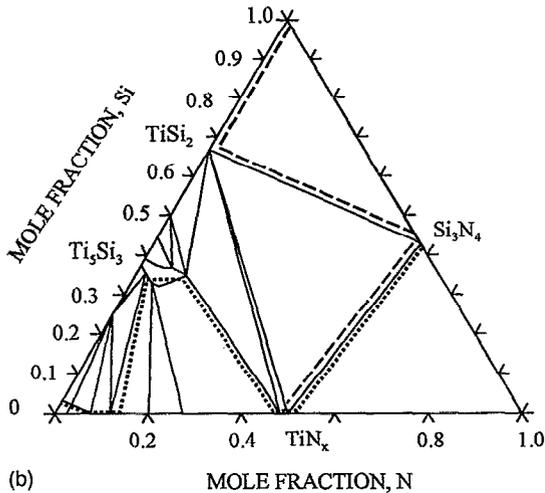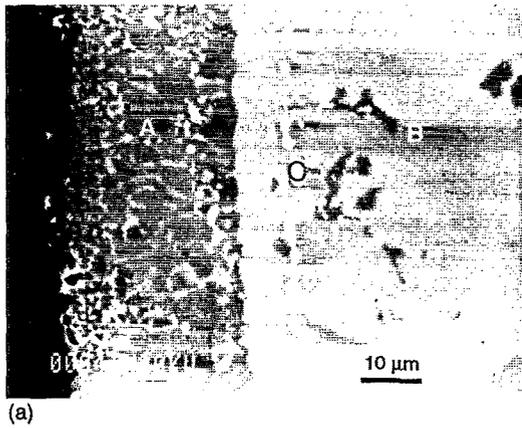
(a)

(b)   MOLE FRACTION, N

FIG. 2. (a) SEM micrograph of the Ti/Si$_3$N$_4$ diffusion couple annealed at 1100 °C for 40 h (A: Ti$_5$Si$_3$[N]+α-Ti[N,Si],B: α-Ti[Si,N], C: Y$_2$O$_3$). (b) Diffusion paths between Ti and Si$_3$N$_4$ (dotted line) and between TiN and Si (dashed line) at 1100 °C.

silicides. Contrary to Wakelkamp's results the thermodynamic calculations show the equilibrium between Si$_3$N$_4$ and TiSi$_2$ instead of the Si-TiN equilibrium.

A. Ti/Si$_3$N$_4$ diffusion couples

Figure 2(a) shows the SEM micrograph taken from the interfacial region of the Ti/Si$_3$N$_4$ diffusion couple after annealing at 1100 °C for 40 h. The joints were invariably fractured along the interface next to the Si$_3$N$_4$. The formation of TiN$_x$ adjacent to the Si$_3$N$_4$ in the Ti/Si$_3$N$_4$ couple has been suggested earlier in similar studies.[3,10] Due to the fractured interface, the TiN$_x$ could not be detected unambiguously but it is likely that the joint has fractured between the TiN$_x$ layer and the two-phase layer consisting of Ti$_5$Si$_3$[N] and α-Ti[N,Si] solid solution [A in Fig. 2(a)]. The qualitative analysis revealed nitrogen in both of these phases. From integral measurements of nitrogen content in Ti$_5$Si$_3$ with EPMA, the solubility of nitrogen in this phase was found to be about 11 at. %.[3] After 40 h annealing the reaction layer (Ti$_5$Si$_3$[N]+α-Ti[Si,N] is about 30 μm thick. The overall reaction zone extends up to 500 μm with a wide layer consisting of α-Ti solution and particles of Ti$_5$Si$_3$[N] [B in Fig.
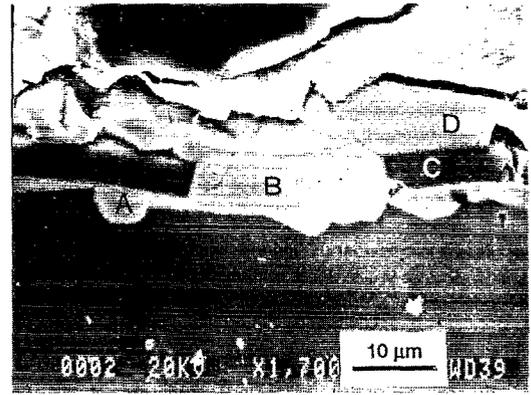

FIG. 3. SEM micrograph of the TiN/Si diffusion couple annealed at 1050 °C for 80 h (A and D: TiSi$_2$, B: TiN$_x$, C: Si$_3$N$_4$).

2(a)], which have precipitated during cooling. There are also two rows of light colored Y$_2$O$_3$ particles [C in Fig. 2(a)]. On the basis of the above observations the layer sequence at 1100 °C is Si$_3$N$_4$/TiN$_x$/Ti$_5$Si$_3$[N]+α-Ti(prec.)/α-Ti/β-Ti. The diffusion path is shown as a dotted line in Fig. 2(b).

In principle, there are two other possible diffusion paths: Si$_3$N$_4$/TiSi$_2$/Ti$_5$Si$_3$[N]/α-Ti/β-Ti and Si$_3$N$_4$/TiN$_x$/TiSi$_2$/Ti$_5$Si$_3$[N]/α-Ti/β-Ti. The former would require notable amounts of nitrogen to be released in the gas phase, because the dissolved nitrogen in the Ti$_5$Si$_3$ is not enough to maintain the mass balance in the system. The latter is very unlikely since the activity of nitrogen decreases only slightly from TiN$_x$ to TiSi$_2$ [Fig. 1(b)] and therefore the driving force for diffusion is small.

In the joint annealed for 240 h at the temperature of 950 °C the diffusion path becomes same as at 1100 °C: Si$_3$N$_4$/TiN$_x$/Ti$_5$Si$_3$[N]+α-Ti(prec.)/α-Ti/β-Ti. Despite of the high pressure at the couple's interface, which makes titanium to yield, the joint was fractured again along the interface next to the Si$_3$N$_4$. The fracture surfaces were both dark grey colored, but as the surface of the Si$_3$N$_4$ was carefully grinded a golden-brown color was revealed. It is likely that this is TiN and that the joint is fractured along the silicide Ti$_5$Si$_3$[N].

Similarly, the calculated phase equilibria at 950 °C did not change essentially from those at 1100 °C. According to the calculations there is an equilibrium between Si$_3$N$_4$ and TiSi$_2$. The solubility of nitrogen in Ti$_5$Si$_3$ is somewhat less at a lower temperature.

B. TiN/Si diffusion couples

After 70 h annealing of the TiN/Si couple in a vacuum ampoule at 1100 °C, a thin layer of TiSi$_2$ with varying thickness (0.5–1 μm) was found to form between TiN and Si. It is likely that the nitrogen released in the reaction dissolves in the TiN solid solution, which might not be fully saturated with N.

The diffusion couples annealed in the vacuum furnace at the temperatures of 1050 and 1100 °C show more pronounced reaction layers. After annealing at 1050 °C for 80 h a TiSi$_2$ layer (A in Fig. 3) is formed next to silicon. The TiN$_x$ layer (B in Fig. 3), originally about 4 μm thick, is largely
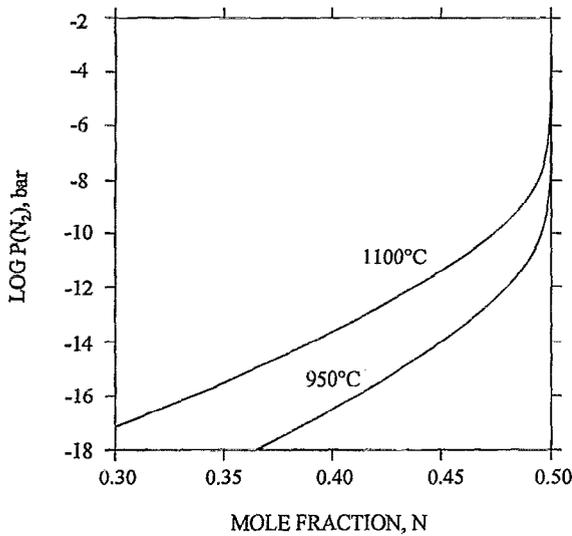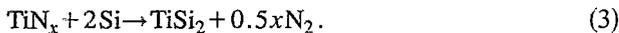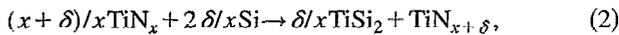
FIG. 4. Partial pressure of N_2 over the TiN_x phase at 1100 and 950 °C.

(a)

FIG. 5. (a) SEM micrograph of the TiN/Si diffusion couple annealed at 950 °C for 240 h. (b) SIMS depth profiles for Ti, Si, and O.

transformed to Si_3N_4 (C in Fig. 3). On the top of the specimen there is another layer of $TiSi_2$ (D in Fig. 3), which is most likely formed in the reaction between TiN and Si in the gas phase. These experiments point out that a phase equilibrium can exist between $TiSi_2$ and Si_3N_4 [dashed line in Fig. 2(b)].

The difference between the reactions taking place in the vacuum furnace and in the ampoules shows the importance of the gas phase. The nitrogen released from the TiN_x in the reaction with silicon has to either dissolve in the TiN_x solid solution (2) or create N_2 atmosphere (3):

$$(x + \delta)/x TiN_x + 2\,\delta/x Si \rightarrow \delta/x TiSi_2 + TiN_{x+\delta}, \qquad (2)$$

$$TiN_x + 2Si \rightarrow TiSi_2 + 0.5x N_2. \qquad (3)$$

In the vacuum ampoules the reaction proceeds from left to right until the activity of nitrogen reaches a value, where the gas phase becomes in equilibrium with the nitrogen rich $TiN_{x+\delta}$ and the reaction will be suppressed. As can be seen from Fig. 4 showing the calculated equilibrium N_2 pressure over the TiN_x solid solution at 1100 and at 950 °C, the maximum solubility of nitrogen in TiN_x depends strongly on the external nitrogen pressure. (Due to the thermodynamic model of the TiN_x phase, which gives TiN as the upper limit for nitrogen, equilibria of N_2 gas with nitrogen rich TiN_x phase could not be calculated.) Assuming the reaction between stoichiometric TiN and Si, a 0.2 μm thick $TiSi_2$ layer can give rise to a nitrogen pressure of about 0.01 bar at 1100 °C in an ampoule having a volume of 25 cm³. According to Fig. 4 the N_2 gas is in equilibrium with stoichiometric TiN at a partial pressure of about 10^{-5} bar. It is likely that the deposited TiN_x is not fully saturated and it dissolves part of the nitrogen released. As can be seen also in Fig. 1(b) the conditions mentioned above should stabilize TiN_x and $TiSi_2$.

By contrast, a vacuum furnace is continuously evacuated and the nitrogen pressure will be about 10^{-9} bar, which is according to Fig. 4 in equilibrium with $TiN_{0.95}$ at 1100 °C. Thus, the TiN_x will be dissociated until this equilibrium composition is reached. Moreover, under high vacuum silicon
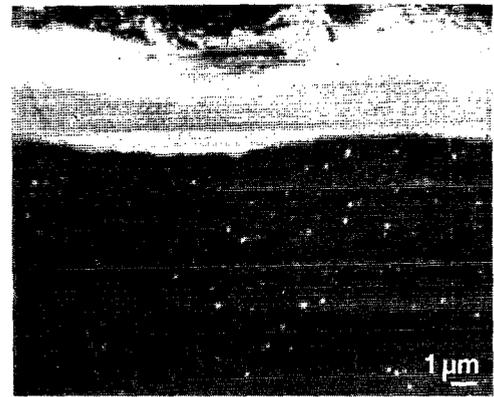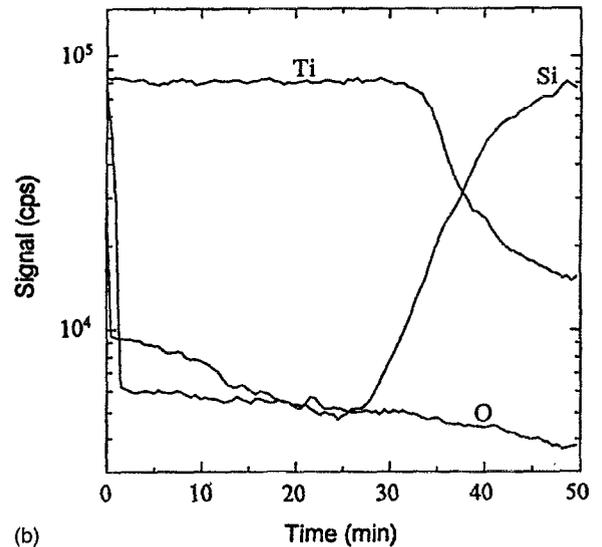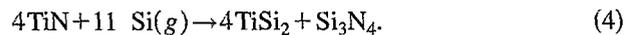
evaporates and part of the gaseous Si reacts with the TiN_x. According to the calculations a partial pressure of silicon of 5×10^{-10} bar is enough for the reaction

$$4TiN + 11\ Si(g) \rightarrow 4TiSi_2 + Si_3N_4. \qquad (4)$$

Due to the $TiSi_2$ layer formed above the TiN_x, nitrogen is not able to vaporize and therefore its activity increases to a level where Si_3N_4 becomes stable.

To summarize, titanium nitride and silicon tend to react according to the reaction (2), but the $TiSi_2$-Si_3N_4 phase equilibrium is possible if Si reacts with the released nitrogen. The thicknesses of the reaction layers depend on the initial composition of the deposited TiN_x layer.

The microstructure of a TiN/Si diffusion couple annealed in the vacuum furnace at 950 °C for 240 h is presented in Fig. 5(a). A layer with varying thickness (0.1–0.3 μm) can be found between the end members. The uneven layer thickness and light-blue color observed optically points to $TiSi_2$, which is according to our calculations in equilibrium with TiN_x at 950 °C. This is in accordance with the SIMS depth profiles [Fig. 5(b)] showing about 0.5 μm-wide diffused region between TiN and Si. There is a thin oxide film on the 2.5 μm thick TiN, but no oxygen contamination is found in

the reaction zone, which contains only titanium and silicon. It seems that the reaction (2) takes place, and it will be suppressed when composition close to the stoichiometric TiN is reached (Fig. 4). At 950 °C silicon is not evaporated under the vacuum of 10^{-9} bar and consequently no Si_3N_4 is formed. Hence, the diffusion path at 950 °C is TiN_x/$TiSi_2$/Si.

VI. SUMMARY

The ternary Ti-Si-N phase diagram was assessed in the present work on the basis of previous thermodynamic evaluations of the binary systems and experimental information on the ternary system. The agreement between thermodynamic calculations and experimental studies is good. Due to the solubility of nitrogen $Ti_5Si_3[N]$ is more stable and will be in equilibrium with other silicides and titanium nitride. Both thermodynamic calculations and direct experiments showed that TiN_x and Si can react with each other and form Si_3N_4 and/or $TiSi_2$. Furthermore, the Ti/Si_3N_4 and TiN_x/Si diffusion couple experiments made in vacuum ampoules and in the vacuum furnace revealed the strong effect of the gas phase on the reactions, where the final thicknesses of the reaction layers depend more on the initial composition of the TiN_x than on the annealing time.

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