

Reactive Growth of Tantalum Silicides in Ta–Si Diffusion Couples

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Received: December 31, 2001

The reactive growth of tantalum silicides was studied by means of Ta–Si diffusion couples annealed at 1250–1350 °C for 2–36 h. Two layers, corresponding to Ta₅Si₃ and TaSi₂, were observed in the diffusion zone. The TaSi₂ layer was about 1 order of magnitude thicker than the Ta₅Si₃ layer. Formation of the compounds Ta₃Si and Ta₂Si was not detected, probably because their growth rate is very small. The concept of rate constant of the second kind was used to describe the growth kinetics of the silicides. For Ta₅Si₃, different values of the rate constant of the second kind can be obtained depending on the boundary conditions adopted at the Ta/Ta₅Si₃ interface. The rate constant of the second kind was related to diffusion properties and thermodynamic stability of the given phase. Average values of the interdiffusion coefficient were calculated for the Ta₅Si₃ and TaSi₂ compounds. The corresponding activation energy is ~450 kJ mol⁻¹ for Ta₅Si₃ and ~560 kJ mol⁻¹ for TaSi₂.

1. Introduction

The transition-metal silicides have attracted much attention mainly for their application as thin films in integrated circuit technology because of their high electrical conductivity and their ability to form good contacts to silicon.^{1,2} In particular, MoSi₂, TaSi₂, TiSi₂, and WSi₂ are the compounds used for Schottky barriers and ohmic contacts, gate and interconnectors, and epitaxial conductors in heterostructures. At present, CoSi₂ and NiSi are also very promising for microelectronics. The semiconducting (band gap 0.87–0.89 eV) silicide FeSi₂ has potential application for electroluminescent devices (high-intensity light-emitting diodes, LASERS).³ Silicides are also known for their superconductive properties, in particular V₃Si has a *T_c* of 17 K. Transition-metal silicides show also remarkable mechanical strength and oxidation resistance up to high temperatures, and their use is currently under consideration for structural applications and for coating of alloys sensitive to oxidation.^{4–9} However, only MoSi₂ has been extensively investigated for its high-temperature properties. Many other silicides of the systems Cr–Si, Nb–Si, Ta–Si, Ti–Si, and V–Si might be potential candidates for high-temperature applications. In particular, the compounds of the Ta–Si system are among the most refractory silicides (melting points in the range 2200–2500 °C).

Much attention has been spent on the study of the reactivity of transition-metal silicides, although these studies have been almost totally focused on thin films in view of their application in microelectronics. Many studies were devoted to the growth kinetics, to the identification of the dominant diffusion species, and to the determination of the activation energy for growth. However, despite the huge amount of literature available, the basic aspects of diffusion in silicides are still scarcely known.¹⁰ In particular, most of the investigations on thin films were carried out at relatively low temperature, at which diffusion is

dominated by processes along grain boundaries, surfaces, and extended defects. In addition, the interpretation of interdiffusion in thin films may be complicated by the importance of phase-boundary reactions and nucleation phenomena at the early stage of interaction, by the absence of phases or the formation of nonequilibrium compounds, and by the presence of impurities.¹¹ As a result, there is a lack of diffusion data above ~1000 °C, at which the diffusion process is dominated by lattice diffusion. Only in recent years, reliable diffusion data have been collected for a few systems: Co–Si,^{12,13} Fe–Si,^{14,15} Mo–Si,^{16–18} and Ti–Si.^{19,20} This has contributed to a better understanding of the reactive growth of silicides at high temperature. No reliable diffusion data exist for Cr–Si, Nb–Si, Ta–Si, V–Si, and Zr–Si. For this reason, we undertook a systematic investigation on the diffusional growth of silicides of the aforementioned systems. In a first paper,²¹ we have discussed the growth of vanadium silicides (V₃Si, V₆Si₅, V₅Si₃, VSi₂) in V–Si diffusion couples at 1150–1390 °C and the related diffusion properties. The present study deals with the reactive growth of tantalum silicides in Ta–Si diffusion couples.

2. Generalities

2.1. Growth Kinetics of Stoichiometric Binary Silicides in Metal–Silicon Diffusion Couples and Relation with Diffusion Coefficients. Let us consider a generic M–Si diffusion couple in which *n* binary silicides with narrow homogeneity range grow simultaneously as parallel bands. For the sake of simplicity, the stoichiometry of each silicide is normalized to 1 mol of silicon, M_{*v_i*}Si, and the layer sequence is, accordingly, M/M_{*v₁*}Si/M_{*v₂*}Si/.../M_{*v_n*}Si/Si with *v₁* > *v₂* > ... > *v_n*. For the pure components M and Si, it is *v₀* = ∞ and *v_{n+1}* = 0, respectively. If local thermodynamic equilibrium is established at the phase boundaries and interface processes are all faster than solid-state diffusion, the isothermal growth kinetics of each intermediate silicide (*i* = 1, ..., *n*) will be described by

$$\Delta x_i^2 = 2k_i^1 t \quad (1)$$

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where Δx_i is the layer thickness at time t and k_i^I is the parabolic rate constant of the first kind²² for the formation of phase i . If exclusive formation of compound $M_{\nu_i}\text{Si}$ in a diffusion couple consisting initially of its adjacent phases $M_{\nu_{i-1}}\text{Si}$ and $M_{\nu_{i+1}}\text{Si}$ is considered, eq 1 can be rewritten as

$$\Delta x_i^2 = 2k_i^{\text{II}}t \quad (2)$$

where k_i^{II} is the parabolic rate constant of the second kind²² for formation of phase i . As noted by Wagner,²² the rate constant k_i^I depends on the properties of all phases involved in the reaction, and therefore, it is scarcely useful to understand the reactive growth of compounds. On the contrary, the rate constant k_i^{II} is a fundamental property of the given phase. The rate constant of the second kind can be calculated from the rate constants of the first kind measured on M–Si diffusion couples by means of the equation^{22,23}

$$k_i^{\text{II}} = \frac{(\nu_{i-1} - \nu_{i+1})V_i}{(\nu_{i-1} - \nu_i)(\nu_i - \nu_{i+1})} C_i^2 \left[\nu_i \sum_{j=1}^{i-1} \frac{C_j}{V_j C_i} + \frac{\nu_i}{V_i} + \sum_{j=i+1}^n \frac{\nu_j C_j}{V_j C_i} \right] \quad i = 1, \dots, n \quad (3)$$

where $C_i = \sqrt{k_i^I}$ and V_i is the molar volume of $M_{\nu_i}\text{Si}$, that is, the molar volume of silicide per mole of silicon. The above expression holds if the solubility of the metal in silicon and vice versa is negligible, a condition closely verified for the Ta–Si system.²⁴ The rate constant k_i^{II} can be related to the Darken interdiffusion coefficient of M and Si, \tilde{D} , in the given phase by²³

$$k_i^{\text{II}} = \frac{\nu_i^2(\nu_{i-1} - \nu_{i+1})^2}{(\nu_{i-1} - \nu_i)^2(\nu_i - \nu_{i+1})^2} \frac{1 + \nu_i}{\nu_i} \frac{|\Delta G_i^0|}{\tilde{D}_i RT} \quad (4)$$

where ΔG_i^0 is the Gibbs free energy of formation of 1 mol of $M_{\nu_i}\text{Si}$ from the adjacent phases. The interdiffusion coefficient is defined as

$$\tilde{D} = \frac{1}{1 + \nu_i} \bar{D}_M + \frac{\nu_i}{1 + \nu_i} \bar{D}_{\text{Si}} \quad (5)$$

where \bar{D}_M and \bar{D}_{Si} are the average values of the self-diffusion coefficient of the two elements through the silicide layer. In general, the self-diffusion coefficients depend on the chemical potential of the components, and consequently, they vary moving from the $M_{\nu_{i-1}}\text{Si}/M_{\nu_i}\text{Si}$ interface to the $M_{\nu_i}\text{Si}/M_{\nu_{i+1}}\text{Si}$ interface. When the mobility of the components is very different, as happens in many silicides of the type $M_3\text{Si}$, $M_2\text{Si}$, and MSi_2 (according to the "orderer Cu_3Au " rule²⁵), eq 4 yields directly the diffusion coefficient of the rate-determining element. Hence, the rate constant of the second kind is essentially determined by the product of the diffusion coefficient of the fastest component and of the thermodynamic term $|\Delta G_i^0|/RT$. Expressions similar to eq 4 were also given by Barge et al.¹² and by Gölpen et al.²⁶

2.2. The Ta–Si Phase Diagram and the Thermodynamic Stability of Tantalum Silicides. The available Ta–Si phase diagram²⁴ shows four silicides: TaSi_2 (mp 2200 °C, hexagonal structure, space group $P6_222$), Ta_5Si_3 (mp 2500 °C, tetragonal structure below ~ 1700 °C, space group $I4/mcm$, hexagonal structure at high temperature, space group $P6_3/mcm$), Ta_2Si (mp 2450 °C, tetragonal structure, space group $I4/mcm$), and Ta_3Si (mp 2510 °C, tetragonal structure, space group $P4_2/n$). The compound $\text{Ta}_{4.5}\text{Si}$, reported in previous Ta–Si phase diagrams,

TABLE 1: Thermodynamic Properties of Tantalum Silicides Used in the Present Study, Heat Capacity Parameters ($C_p = a + bT + cT^2$, J mol^{−1} K^{−1}), Standard Entropy (S_{298}^0 , J mol^{−1} K^{−1}), Standard Formation Enthalpy (ΔH_{298}^0 , kJ mol^{−1} of atoms)^a

	Ta ₂ Si	Ta ₅ Si ₃	TaSi ₂
a	72.383	179.703	73.262
$10^3 b$	10.878	39.120	7.699
$10^{-6} c$	−0.586	−0.891	−0.908
S_{298}^0	105.44	280.75	75.312
ΔH_{298}^0	−41.84	−41.84	−39.75

^a From ref 30.

has been rejected in more recent studies. Four eutectics are present in the Ta–Si system; among them, the most Si-rich one (1 atom % Ta) has a melting point of 1385 °C. The solubility of silicon in tantalum is small, approximately 1 atom % between 1300 and 2300 °C, whereas the solubility of tantalum in silicon is negligible.

The thermodynamic properties of Ta silicides were reviewed by Chart^{27–29} and by Schlesinger.²⁴ The data tabulated in ref 30 come from the assessment of Chart, largely based on enthalpy and entropy data reported by Samsonov.³¹ Direct determination of the standard Gibbs free energy of formation of tantalum silicides, ΔG_f^0 , were performed by Levine and Kolodney³² by means of EMF measurements at 900–1100 °C. Comparison between the data of Levine and Kolodney and the assessment of Chart shows a good agreement (within 15%) for Ta_2Si and Ta_5Si_3 , whereas for TaSi_2 there is a large difference. However, the values of ΔG_f^0 reported in ref 32 for TaSi_2 are not consistent with the standard enthalpy of formation of TaSi_2 at 298 K (−39 to −46 kJ/mol) measured by different authors.^{24,33} Therefore, the thermodynamic data of the assessment of Chart³⁰ have been preferred in the following discussion and are summarized in Table 1. According to Schlesinger,²⁴ the thermodynamic properties of the Ta–Si system are not yet completely characterized and additional work is required, in particular to collect improved heat capacity data. Consequently, the data reported in Table 1, although reasonable, should be treated with some caution.

3. Experimental Section

The starting materials were cylindrical slices of tantalum 6.35 mm in diameter and 1–2 mm thick (Aldrich 99.9+ % pure) and silicon substrates (7 mm × 7 mm × 1 mm) cut from a Si(100) wafer. Prior to assembly of the diffusion couple, the mating surfaces of the Ta and Si plates were prepared by grinding with 1200 and 2400 grit silicon carbide metallographic papers, polishing with 1 μm diamond paste, and cleaning with acetone. The cleaned Ta and Si slices were then immediately put in contact; the resulting couple was wrapped in a zirconium foil, which served as an oxygen getter, and pressed between spring-loaded alumina rods inside an alumina sample holder. The Ta–Si couples were annealed in a vertical furnace under a high-purity argon flux. Annealing was carried out at 1250–1350 °C for 2–36 h. After reaction, the samples were mounted in epoxy resin, sectioned perpendicularly to the reaction surface, polished, and examined by optical (OM) and scanning electron (SEM) microscopy. The silicide bands in the diffusion zone can be easily distinguished using the backscatter (BS) electron mode, because of the different composition. Phase identification was also performed by energy-dispersive electron microprobe analysis (EDS-EMPA). The growth kinetics of the silicides was determined by measuring the thickness of the reaction layers at

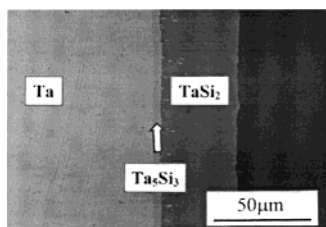


Figure 1. Backscattered SEM image of a Ta–Si diffusion couple. $T = 1350\text{ }^{\circ}\text{C}$; $t = 4\text{ h}$.

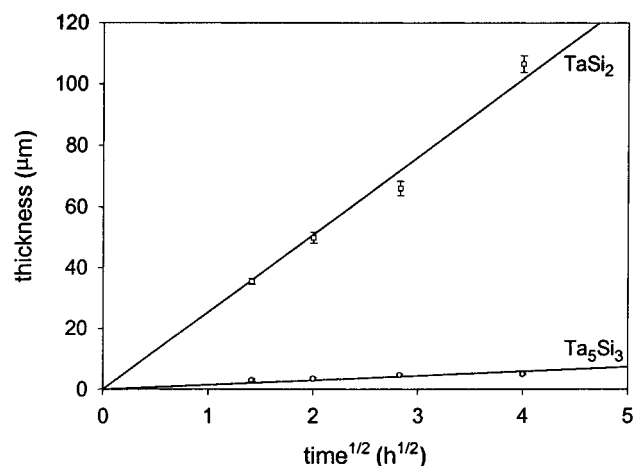


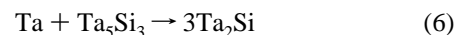
Figure 2. Growth kinetics of Ta₅Si₃ and TaSi₂ in Ta–Si diffusion couples annealed at 1350 °C: (□) TaSi₂; (○) Ta₅Si₃.

different times. The thickness was obtained as the average of ~20 measurements at different locations of the couple.

4. Results and Discussion

The temperature range explored in the present study was limited to 1250–1350 °C. The maximum attainable temperature was imposed by the eutectic (1 atom % Ta) at 1385 °C. Two dense and parallel layers, corresponding to the TaSi₂ and Ta₅Si₃ phases, were observed in the diffusion couples. The composition of the layers was confirmed by EPMA. An example of the microstructure of the reaction zone is shown in Figure 1. According to OM observation, the TaSi₂ layer shows a columnar microstructure with elongated grains of width ~25 μm. The TaSi₂ phase grows much faster than the Ta₅Si₃ phase; the TaSi₂ layer is ~1 order of magnitude thicker than the Ta₅Si₃ layer. The layer growth kinetics conforms well to the parabolic rate law, as shown in Figure 2 for couples reacted at 1350 °C. At temperatures below 1250 °C, the growth rate of Ta₅Si₃ is very small and the development of a band of a few microns in thickness requires very long times. The silicides Ta₃Si and Ta₂Si could not be detected in the diffusion zone, meaning that the corresponding layer thickness is considerably smaller than 1 micron even at 1350 °C after a 16 h reaction. When the silicon component was removed from a couple already treated for 16 h at 1350 °C and the Ta substrate with the Ta₅Si₃ and TaSi₂ layers is further annealed for 16 h at 1450 °C, a uniform but thin (~3 μm) Ta₂Si layer was finally observed. The situation is somewhat similar to that encountered in Mo–Si diffusion couples^{16,17} in which solely the MoSi₂ and Mo₅Si₃ compounds were observed at 900–1350 °C. The Mo₃Si phase could only be detected on Mo–MoSi₂ couples reacted at temperatures ≥ 1400 °C. The nonappearance of one or more phases (like Ta₃Si and Ta₂Si in the present case) during reactive diffusion has been the subject of extended discussions in the literature.^{34–35} Basically, three different explanations can be proposed. The first

and trivial one is that the phase effectively exists in the diffusion zone but it is apparently missing owing to the very small thickness of the corresponding layer. It is worth noting that a compound layer is hardly observable with ordinary microscopy techniques when its thickness is <0.5 micron. Some examples of this situation are provided by the growth of the ζ-V₄C₃ phase in V–C couples, of the ζ-Ta₄C₃ phase in Ta–C couples, and of the η-NbN phase in Nb–N₂ couples.^{36–37} While the above phases were hardly detected in ordinary metal–nonmetal couples for relatively short reaction times, they could be unambiguously identified using very long annealing times (hundreds of hours), in particular by means of wedge-type diffusion couples because these phases thicken considerably toward the tip. A second possibility is related to the possible kinetic instability of thin compound layers. Dybkov,^{38–40} as well as Gösele and Tu,⁴¹ has shown that a phase can appear in the diffusion zone only if the adjacent phases have reached a critical thickness or, equivalently, when the diffusion flux is small enough. A third reason is that a particular phase may not be able to grow due to nucleation difficulties but can form at higher temperatures when the activation energy barrier for nucleation can be easily overcome.³⁵ The Gibbs free energy variation, ΔG_{chem} , corresponding to reaction



is approximately $-12\,000\text{ J mol}^{-1}$ of TaSi₂, that is, -420 J cm^{-3} at 1300 °C. Volume variation accompanying solid-state transformations represents usually the main hindrance to nucleation of the reaction products. The volume change has to be accommodated by the system and the associated elastic strain energy must be taken into account in the calculation of the available free energy. The elastic strain energy per unit volume of the new phase, ΔG_{strain} , can be estimated, as a first approximation, by neglecting the anisotropy effects and assuming that the different phases have the same elastic properties and is given by⁴²

$$\Delta G_{\text{strain}} = \frac{E}{1-p} \left[\left(\frac{V_B}{V_A} \right)^{1/3} - 1 \right]^2 \quad (7)$$

where E is the Young modulus, p is the Poisson ratio, and V_A and V_B are the volume of the matrix and the volume of the inclusion in the unstrained state, respectively. In the case of reaction 6, the volume variation computed from the available crystallographic data⁴³ results well below 1%. The elastic modulus of transition-metal silicides is generally in the range 200–300 GPa and that of Ta is ~200 GPa. The Poisson ratio is 0.15–0.30 for transition-metal silicides and 0.35 for Ta. Therefore, for a volume variation of 1%, the upper limit of the elastic strain energy is ~5 J cm⁻³. This value is negligible in comparison to the chemical Gibbs free energy, -420 J cm^{-3} . Even though the approximations adopted are very crude, eq 7 gives the correct order of magnitude of the strain energy, and the use of more sophisticated theories does not introduce significant variations. In conclusion, the foregoing discussion shows that nucleation difficulty can be reasonably rejected as the reason for the nonappearance of, at least, the Ta₂Si phase. More likely, the Ta-rich silicides are not observed due to their very low growth rate in the present temperature range. However, it is unclear whether the missing phases effectively exist in the couples but are not detected because of the very small thickness or whether the phases are completely absent. This uncertainty is not secondary in the treatment of the multilayer growth kinetics. Two limit cases can be taken into account. If all binary

silicides are considered, it will be $n = 4$ ($i = 1$, Ta₃Si; $i = 2$, Ta₂Si; $i = 3$, Ta₅Si₃; $i = 4$, TaSi₂) in eq 3, with the implicit assumption that the growth of both Ta₃Si and Ta₂Si is diffusion-controlled. In the limit $\Delta x_3, \Delta x_4 \gg \Delta x_1, \Delta x_2$, the expression of the rate constants of the second kind for Ta₅Si₃ and TaSi₂ are

$$k_{3,n=4}^{\text{II}} = \frac{(\nu_2 - \nu_4)}{(\nu_2 - \nu_3)(\nu_3 - \nu_4)} V_3 C_3^2 \left(\frac{\nu_3}{V_3} + \frac{\nu_4}{V_4} \frac{C_4}{C_3} \right) \quad (8)$$

$$k_4^{\text{II}} = \frac{\nu_3}{\nu_3 - \nu_4} V_4 C_4^2 \left(\frac{C_3}{V_3 C_4} + \frac{1}{V_4} \right) \quad (9)$$

where $\nu_3 = 5/3$, $\nu_4 = 1/2$, $V_3 = 25.3$ cm³/mol of Si, $V_4 = 13.1$ cm³/mol of Si. If the compounds Ta₃Si and Ta₂Si are absent, the layer sequence will be Ta/Ta₅Si₃/TaSi₂/Si. Metastable equilibrium can be assumed at the Ta/Ta₅Si₃ phase boundary, while local thermodynamic equilibrium is again appropriate at the Ta₅Si₃/TaSi₂ and TaSi₂/Si interfaces. In such a case, the solution of the kinetic problem is again given by eq 3 considering only two reaction layers. For TaSi₂, the expression of k_4^{II} is equivalent to eq 9, because the boundary conditions for the growth of this phase are unchanged. In contrast, for Ta₅Si₃, it is

$$k_{3,n=2}^{\text{II}} = \frac{1}{\nu_3 - \nu_4} V_3 C_3^2 \left(\frac{\nu_3}{V_3} + \frac{\nu_4}{V_4} \frac{C_4}{C_3} \right) \quad (10)$$

where the difference with respect to eq 8 lies in the term containing the stoichiometric coefficients. The rate constant k_3^{II} is thus dependent on the number of reaction layers in the diffusion couple because different thermodynamic conditions apply at the phase boundaries of the Ta₅Si₃ layer in the two cases. The additional subscript in eqs 8 and 10 denotes the number of silicides considered in the diffusion couple. Figure 3 shows the Arrhenius plot of the parabolic rate constant of the second order for Ta₅Si₃ and TaSi₂ computed according to eqs 8–10. The expressions of the rate constants resulting from regression analysis are (solid lines in Figure 3)

$$k_{3,n=2}^{\text{II}}(\text{Ta}_5\text{Si}_3) = 1.105 \times 10^4 \exp(-4.450 \times 10^5/(RT)) \quad (11a)$$

$$k_{3,n=4}^{\text{II}}(\text{Ta}_5\text{Si}_3) = 4.974 \times 10^4 \exp(-4.450 \times 10^5/(RT)) \quad (11b)$$

$$k_4^{\text{II}}(\text{TaSi}_2) = 4.050 \times 10^8 \exp(-5.437 \times 10^5/(RT)) \quad (11c)$$

The two expressions for Ta₅Si₃ differ in the preexponential factor and the rate constant for the case $n = 4$ is ~ 5 times larger than that corresponding to the case $n = 2$. The average interdiffusion coefficient in Ta₅Si₃ and TaSi₂, calculated by means of eq 4 using the rate constants of the second kind obtained from eqs 8–10 and the Gibbs free energy corresponding to the thermodynamic data of Table 1, is shown in Figure 4. For diffusion in TaSi₂, the activation energy is 559 kJ mol⁻¹ and the expression of the diffusion coefficient results in

$$\tilde{D}(\text{TaSi}_2) = 1.50 \times 10^9 \exp(-5.60 \times 10^5/(RT)) \quad (12)$$

As in the previous discussion, different values of the diffusion coefficients are obtained for Ta₅Si₃ depending on the number of reaction layers taken into account. Namely, the representative lines drawn in Figure 4 may be expressed by the following

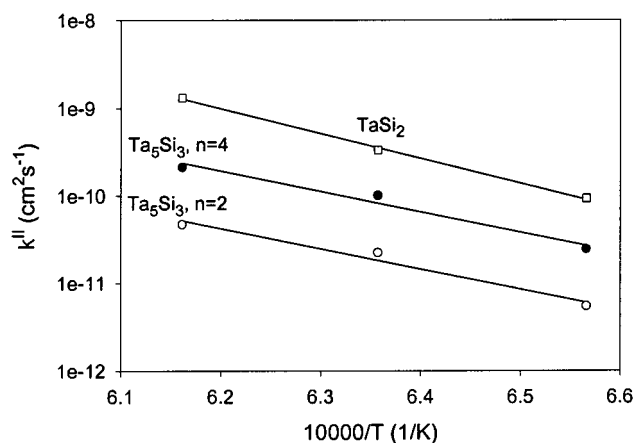


Figure 3. Arrhenius plot of the rate constant of the second kind for the growth of tantalum silicides: (□) TaSi₂; (●) Ta₅Si₃, rate constant calculated according to the layer sequence Ta/Ta₃Si/Ta₂Si/Ta₅Si₃/TaSi₂/Si ($n = 4$); (○) Ta₅Si₃, rate constant calculated according to the layer sequence Ta/Ta₅Si₃/TaSi₂/Si ($n = 2$).

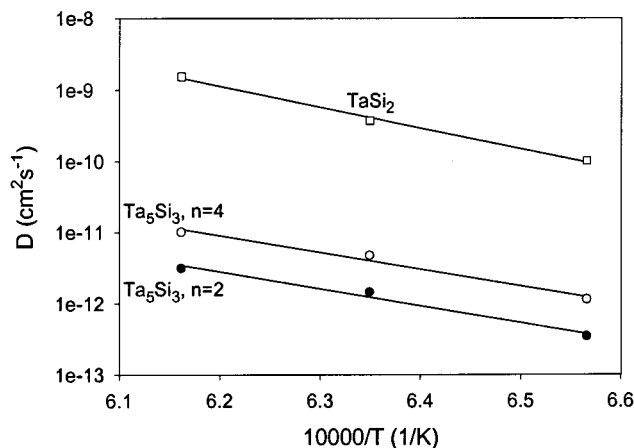


Figure 4. Arrhenius plot of the average interdiffusion coefficient in tantalum silicides: (□) TaSi₂; (○) Ta₅Si₃, interdiffusion coefficient calculated according to the layer sequence Ta/Ta₃Si/Ta₂Si/Ta₅Si₃/TaSi₂/Si ($n = 4$); (●) Ta₅Si₃, interdiffusion coefficient calculated according to the layer sequence Ta/Ta₅Si₃/TaSi₂/Si ($n = 2$).

equations:

$$\tilde{D}_{n=2}(\text{Ta}_5\text{Si}_3) = 1.80 \times 10^3 \exp(-4.57 \times 10^5/(RT)) \quad (13a)$$

$$\tilde{D}_{n=4}(\text{Ta}_5\text{Si}_3) = 3.49 \times 10^3 \exp(-4.50 \times 10^5/(RT)) \quad (13b)$$

The activation energy results are 457 kJ mol⁻¹ in the case $n = 2$ and 450 kJ mol⁻¹ in the case $n = 4$ because the temperature dependence of the term ΔG° in eq 4 is different in the two cases. The previous values should be considered to be affected by some uncertainty, because they were obtained on a restricted temperature range. Nevertheless, they indicate that the activation energy for diffusion in tantalum silicides is quite high, if compared to the behavior of many transition-metal silicides. In general, the activation energies (in eV) for growth of silicides in diffusion couples scale approximately as $T_m(K)/1000$, where T_m is the melting point of the silicide.^{12,23} Considering the melting points of Ta₅Si₃ (2773 K) and TaSi₂ (2473 K), the activation energies (in eV) found in present work are on the order of $2T_m(K)/1000$. Rather high values of activation energy for diffusion were found also for CoSi₂.^{12–13} In the case of lattice self diffusion of Co, the activation energy (in eV) is $1.75T_m(K)/1000$ in the range 700–1200 °C. For Si self diffusion, the

activation energy is $2T_m(K)/1000$ according to Barge et al.,¹² but a much lower value is reported by van Dal et al.¹³ Further discussion on the characteristic of the diffusion process in the tantalum silicides, however, would require the knowledge of the relative mobilities of the two elements, a kind of information not accessible through reactive diffusion experiments such as the ones we presented here. Grain boundary diffusion in silicides is known to give a significant contribution up to temperatures of $T/T_m \approx 0.7$.^{12,26} In the present case, the experiments were carried out at temperatures on the order of $0.6T_m(K)$ and a contribution from short-circuit diffusion cannot be completely excluded. The columnar microstructure observed for TaSi₂ is more likely related to the strong texture developed by disilicide layers grown by diffusion, as described by Tortorici and Dayananda¹⁶ for MoSi₂ and by Maas et al.⁴⁴ for MoSi₂, NbSi₂, VSi₂, and TaSi₂. The grains of the reaction layer can grow with their "fast growth direction" parallel to the direction of diffusion, giving origin to a "diffusion texture".

5. Summary and Conclusions

The rate constants of the second kind are useful parameters to describe the diffusion-controlled growth of compounds in binary metal–silicon diffusion couples. The rate constant of the second kind is directly related to the diffusion properties and to the thermodynamic stability of the given phase. The interdiffusion coefficients in Ta₅Si₃ and TaSi₂ were obtained from the layer growth kinetics measured on Ta–Si diffusion couples at 1250–1350 °C. The activation energies for diffusion, ~ 450 kJ mol⁻¹ for Ta₅Si₃ and ~ 560 kJ mol⁻¹ for TaSi₂, are quite high if compared to those usually found for transition-metal silicides. Considering the melting point of the two compounds, the activation energy (in eV) is on the order of $2T_m(K)/1000$, whereas for many silicides the activation energy (in eV) scales as $T_m(K)/1000$.

The interdiffusion coefficients as obtained above represent average values through the given compound layer because of the existence of a chemical potential gradient. In the case of nonisotropic crystals, like Ta₅Si₃ and TaSi₂, the diffusion coefficient also depends on the crystallographic direction. If the grains have a random orientation, the diffusion coefficient obtained for a polycrystalline layer represents an average value. However, in the case of TaSi₂, the development of elongated columnar grains can reflect a strong texture of the layer and, therefore, the tendency to grow in the direction in which diffusion is faster. This may lead to differences between the interdiffusion coefficient obtained from growth kinetics and the tracer diffusion coefficient measured on polycrystalline materials. In turn, these differences can result in different values of the activation energy.

Attention must be paid when extrapolating the value of the rate constants of the second kind (eq 11) or of the interdiffusion coefficients (eqs 12–13) outside the present temperature range. This is because the explored temperature range is quite limited and the uncertainty on the activation energy and preexponential factor can be significant. In addition, at lower temperatures, grain-boundary diffusion can become important and the activation energies are likely to decrease. The compounds Ta₃Si and Ta₂Si, although reported in the phase diagrams, were not detected in the diffusion couples. A very low growth rate of these silicides is the most likely reason for this behavior.

Finally, it should be stressed that the analysis of the growth kinetics as presented in the foregoing sections cannot be generalized to any system. In particular, eqs 3 and 4 can be applied to the growth of binary compounds with narrow

homogeneity range and when the diffusion in the end components can be neglected. These conditions are usually well-met in the case of transition metal–silicon diffusion couples because of the small deviation from stoichiometry of the silicides and the generally low reciprocal solubility of the elements. For other systems, like transition metal–carbon and transition metal–nitrogen, the homogeneity range can be very broad and other theoretical treatments are more suitable.

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