

Thermodynamic Evaluation of Solid-State Reactions in which a Volatile Product is Formed

Alexander A. Kodentsov^{1,*}, Jorma K. Kivilahti²,
and Frans J. J. van Loo¹

¹ Laboratory of Solid State and Materials Chemistry, Eindhoven University of Technology,
P.O. Box 513, 5600 MB, Eindhoven, The Netherlands

² Laboratory of Electronics Production Technology, Helsinki University of Technology,
FIN-02150 Espoo, Finland

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Summary. The use of equilibrium thermodynamics in describing interfacial reactions between non-ionic inorganic solids is demonstrated using examples of high-temperature interactions in the Ti–Si–N and Mo–Si–N systems. In the case of a diffusion-controlled process, solid-state reactions can be interpreted with chemical potential (activity) diagrams. The role of volatile reaction products formed during interaction in developing the diffusion zone morphology is analysed. The interfacial phenomena in systems based on dense Si₃N₄ and non-nitride forming metals can be explained by assuming a nitrogen pressure build-up at the contact surface. This pressure determines the chemical potential of Si at the interface and, hence, the reaction products in the diffusion zone.

Keywords. Ceramics; Phase diagrams; Thermodynamics; Transition metals compounds.

Introduction

In a diffusion-controlled interaction between solids when local equilibria are supposed to exist within the reaction zone, the chemical potential (thermodynamic activity) of the species varies continuously through the product layers and has the same value at both sides of an interphase interface. The concentration of each component, on the other hand, will change discontinuously across phase boundaries from one end-member of the reaction couple to the other. The resulting microstructure of the reaction zone can be visualized by a diffusion (reaction) path. Under conditions of local equilibria in the diffusion zone of a semi-infinite couple, the reaction path involves a time-independent sequence of intermediate layers, and

* Corresponding author. E-mail: A.Kodentsov@tue.nl

it should obey the rules extensively discussed in earlier papers [1, 2]. *Intrinsic fluxes* of atoms in the reaction zone (measured in the *Kirkendall* frame of reference) are controlled by the direction and magnitude of their chemical potential gradients. Therefore, the nature of the diffusion phenomena can be better interpreted by superimposing the diffusion (reaction) path on the potential (activity) diagram rather than on the *Gibbs* compositional triangle. *Intrinsic diffusion* of an element takes place only in a direction in which it decreases its own chemical potential [3–6].

The main goal of the present paper is to reveal some intrinsic problems, which are encountered when equilibrium thermodynamics is used to evaluate reaction phenomena in material systems, in which a volatile species is produced during the interaction. The ensuing discussion is based upon typical examples of metal-ceramic interactions. One involves a non-nitride forming metal Mo and S_3N_4 , the other deals with reactions in the Ti–Si–N system.

Results and Discussion

Reaction Phenomena in the Ti–Si–N System

At first sight, the interpretation of the interfacial reactions in the ternary Ti–Si–N system looks rather simple. The resulting microstructure of the reaction zone between end-members of the couple can be visualized by the diffusion path and reaction phenomena can be rationalized using the isothermal cross-section and the potential diagrams of the Ti–Si–N system. However, in applying the diffusion-activity model to the reactions in this system considerable caution must be exerted.

There is no agreement in the literature with respect to the Ti–Si–N phase diagram, especially where equilibria involving silicon are concerned. The discrepancies relate to apparently contradictory experimental results and to different interpretations chosen to describe the thermodynamics of the system.

Because it is impossible to prepare the ternary alloys by traditional weighing the pure elements in the appropriate ratio and subsequent melting, the Ti–Si–N isotherms have been constructed using bulk diffusion couples [7, 8] or by investigating equilibrated powder compacts of various composition [9]. Some authors made ternary alloys by gas nitriding the Ti-silicides [10]. Others attempted to derive information about phase relations in this ternary system from thin-film experiments [11].

Beyers et al. [11], *Schuster et al.* [9], and *Sambasivan et al.* [8] have published calculated as well as experimentally determined ternary isotherms of the Ti–Si–N system at 1000 and 1300°C. The authors treated the Ti_5Si_3 -intermetallic as a line compound and all silicides are in equilibrium with titanium nitride. The notable difference between the diagrams is the equilibrium between titanium nitride and Si, which is present at 1000°C in *Beyers' and Sambasivan's* but not in *Schuster's* isotherm. *Wakelkamp* [7] has studied this system also experimentally at 1100°C. He was able to determine the solubility of nitrogen (in terms of very dedicated EPMA) in the Ti_5Si_3 -phase as about 11 at.%, and no nitrogen was detected in other silicides. The relatively high solubility of nitrogen in the Ti_5Si_3 (D8₈) could be

expected when using the considerations of *Nowotny* [12] and our experimental results on the analogous systems Ti–Si–O [13] and Ti–Si–C [14].

No evidence was found for the existence of ternary phases at 1100°C. The topology of the Ti–Si–N isotherm is dominated by the presence of the phase TiN_{1-x} and the solid solution of nitrogen in Ti_5Si_3 in equilibrium with all the binary silicide phases.

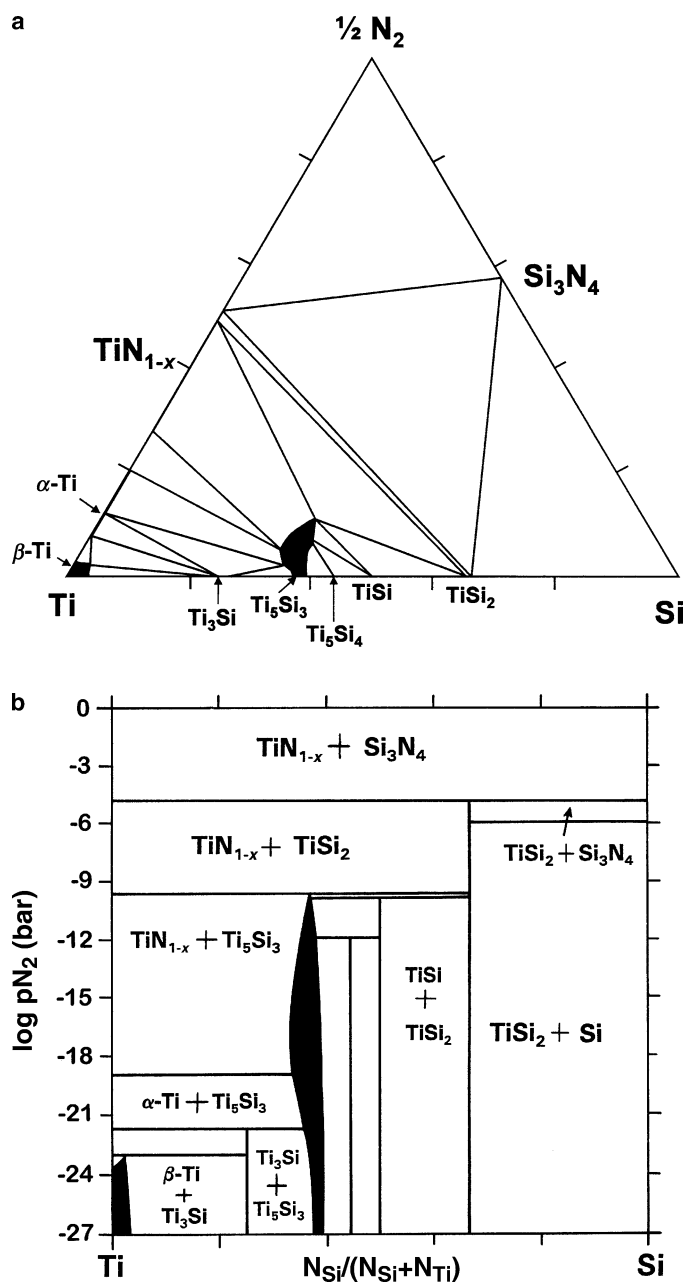


Fig. 1. a) Calculated isothermal cross-section through the Ti–Si–N phase diagram at 1100°C; b) the corresponding chemical potential (activity) diagram for nitrogen

Thermodynamic assessments show that, contrary to the results reported in Refs. [7, 8, 11], the equilibrium between Si_3N_4 and TiSi_2 instead of the Si-TiN_{1-x} tie-line should exist in this ternary system at 1100°C (Fig. 1).

In the case of the interaction between titanium nitride and silicon at 1100°C the formation of only two layer sequences within the diffusion zone might be expected. These are: $\text{TiN}_{1-x}|\text{TiSi}_2|\text{Si}_3\text{N}_4|\text{Si}$ and $\text{TiN}_{1-x}|\text{Si}_3\text{N}_4|\text{TiSi}_2|\text{Si}$ or product phases form a mixed layer of $\text{TiSi}_2 + \text{Si}_3\text{N}_4$. A reaction zone, containing $\text{Ti}_5\text{Si}_3(\text{N})$ or other Ti-silicides, for example, $\text{TiN}_{1-x}|\text{Ti}_5\text{Si}_3(\text{N})|\text{TiSi}_2|\text{Si}_3\text{N}_4|\text{Si}$ must be excluded based on the diffusion-activity model. It can be seen from the potential diagram shown in Fig. 1b that silicon nitride cannot be formed in this hypothetical reaction zone at the position given above, since the intrinsic diffusion of nitrogen should then take place through the product TiSi_2 -layer against the gradient of its chemical potential.

However, a striking pattern was observed in the titanium nitride/silicon diffusion couple after interaction at 1100°C . A representative microstructure of the reaction zone between the “golden coloured” PVD-titanium nitride film and a (100) Si-wafer is given in Fig. 2. The formation of the TiSi_2 -layer next to the silicon is clearly visible. In some part of the transition zone the titanium nitride is transformed to Si_3N_4 . Also a very thin layer of TiSi_2 is present on the “outer surface” of the originally deposited titanium nitride. This phenomenon was observed mainly in the areas adjacent to the newly formed Si_3N_4 . Likely, this is a result of interaction between TiN_{1-x} and Si through the gas phase. A partial pressure of Si of about $5 \cdot 10^{-10}$ bar is enough for the reaction shown in Eq. (1) to proceed at 1100°C .



It was reported that the equilibrium pressure of nitrogen over the TiN_{1-x} increases sharply on approaching the stoichiometric composition [15]. One might

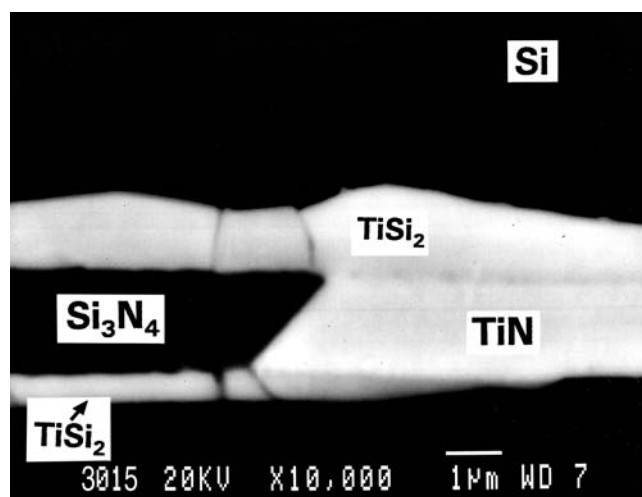
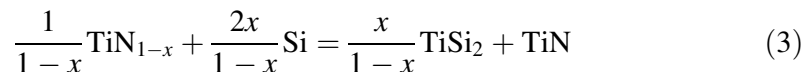
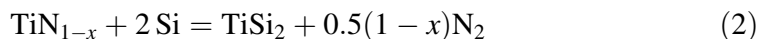


Fig. 2. Back-scattered electron image (BEI) of the diffusion couple Si/TiN_{1-x} after interaction at 1100°C for 25 h in vacuum (10^{-9} bar) (Titanium nitride is denoted by its binary formula)

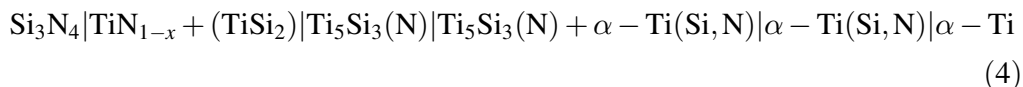
expect that the nitrogen will be released from the titanium nitride in the interfacial reaction with Si. Another possibility is that nitrogen will be dissolved in the TiN_{1-x} solid solution because the PVD-titanium nitride is likely not fully saturated. These possibilities refer to the Eqs. (2) and (3).



The first implies that nitrogen evolved during reaction may build-up (probably locally) a N_2 -pressure (activity) at the contact surface.

In general, the equilibria on the Ti–Si–N isotherm involving only condensed phases are virtually unaffected by changes of the external pressure (activity) of nitrogen. However, when the partial pressure of nitrogen is lower than the dissociation pressure of Si_3N_4 but higher than that for titanium nitride, the topology of the phase diagram will be different. In this situation a three-phase equilibrium $\text{TiSi}_2 + \text{Si} + \text{TiN}_{1-x}$ will occur. Perhaps, the latter conclusion explains the absence of Si_3N_4 in some areas of the titanium nitride/Si diffusion couples observed in our experiments and in the work of *Wakelkamp* [7]. Experimental observations lead to a strong suspicion that in this particular case we are dealing with a reaction zone in which local equilibria might exist at the interfaces, but with variations in the N_2 -pressure (activity) along the contact surfaces. It is, therefore, conceivable that when the TiSi_2 – “outerlayer” is formed on the titanium nitride, nitrogen evolved in the interfacial reaction between the TiN_{1-x} and Si-substrate cannot escape easily and the nitrogen pressure (activity) at the contact surface increases to a level where Si_3N_4 becomes stable, and no Si can be found.

A different situation arises during interaction between Si_3N_4 and Ti. A layer of titanium nitride (probably containing very small amount of TiSi_2 -inclusions) is formed next to the ceramic in the transition zone of the $\text{Si}_3\text{N}_4/\text{Ti}$ couple after interaction at 1100°C in vacuum for 100 h (Fig. 3). Then, the diffusion path enters the single phase region of $\text{Ti}_5\text{Si}_3(\text{N})$. Further, it traverses the two-phase field $\text{Ti}_5\text{Si}_3(\text{N}) + \alpha\text{-Ti}(\text{Si}, \text{N})$. Eventually, the reaction path proceeds in the following phase sequence (Eq. (4)), which is indeed kinetically allowed and thermodynamically possible as may be concluded from the isothermal section and potential diagram.



However, the most conclusive manifestations of the role of volatile products during reactive phase formation in non-ionic solids were found in the case of interaction in $\text{Si}_3\text{N}_4/\text{non-nitride}$ forming metal systems [16]. In contrast to the above picture, in which nitrogen can be incorporated within the product layer, no thermodynamically stable nitrides can be formed. Only nitrogen can be formed as a side product next to the metal silicides or metal-silicon solid solution. This nitrogen gas has to disappear from the interface and it is clear that this poses some problems.

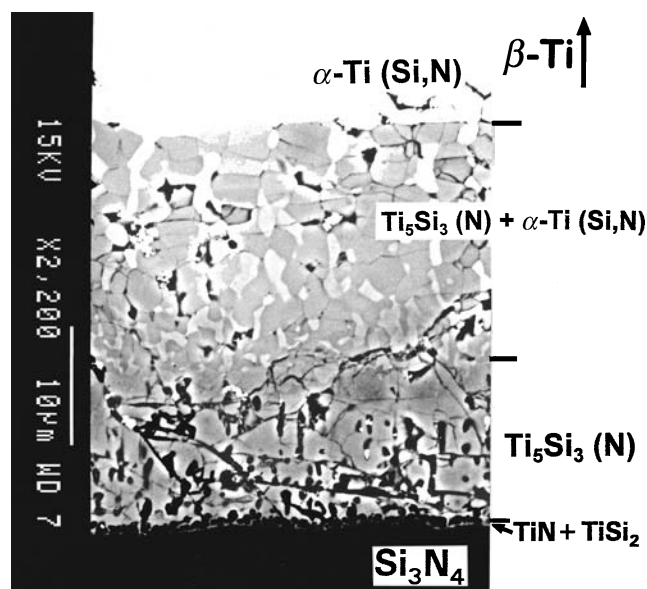


Fig. 3. Morphology of the diffusion zone between dense Si_3N_4 and Ti after reaction in vacuum at 1100°C for 100 h (BEI) (Titanium nitride is denoted by its binary formula); note that the original β -Ti end-member is much further away from the reaction product layer

Interactions of Non-Nitride Forming Metals with Silicon Nitride

The type of reaction products which can be formed at an elevated temperature in the diffusion zone between Si_3N_4 and any metal (or alloy) depends on the chemical potential (activity) of silicon and, hence, on the activity (fugacity) of nitrogen at the contact surface. When using diffusion couples consisting of dense Si_3N_4 ceramics and non-nitride forming metals the interior of the couple is not in direct contact with the surrounding atmosphere. Nitrogen, which formed by the interfacial reaction, cannot escape easily. A nitrogen pressure (fugacity) will be built up at the contact surface. This pressure determines the activity of Si at the metal/ceramic interface. It is clear that in such system the partial pressure of nitrogen (and therefore its chemical activity) can cover a large range of values. The isothermal cross-section through the phase diagram $Me\text{-Si-N}$ and, more specifically, the position of the monovariant equilibrium $\text{N}_2\text{-gas} + \text{Si}_3\text{N}_4 + \text{Me}_x\text{Si}_y$ is dependent on this partial pressure.

The most convincing evidence of a nitrogen pressure build-up at the contact surface was found in the $\text{Si}_3\text{N}_4/\text{Mo}$ system. For a generalization let us turn our attention to Fig. 4 being a representation of the phase equilibria in the Mo-Si-N system at 1300°C and various partial pressures (fugacities) of nitrogen. The important feature here is the dependence of the phase diagram and, more specifically, the position of the monovariant equilibrium involving nitrogen on the partial pressure of nitrogen. This gives an ideal possibility to verify theoretical predictions concerning the phase formation during reaction between Mo and Si_3N_4 .

If now we look at Fig. 4 and try to predict the type and sequence of the reaction products in a $\text{Si}_3\text{N}_4/\text{Mo}$ diffusion couple at one bar partial pressure of N_2 , we would suggest the sequence $\text{Mo}|\text{Mo}_3\text{Si}|\text{Mo}_5\text{Si}_3|(\text{N}_2)|\text{Si}_3\text{N}_4$, according to the

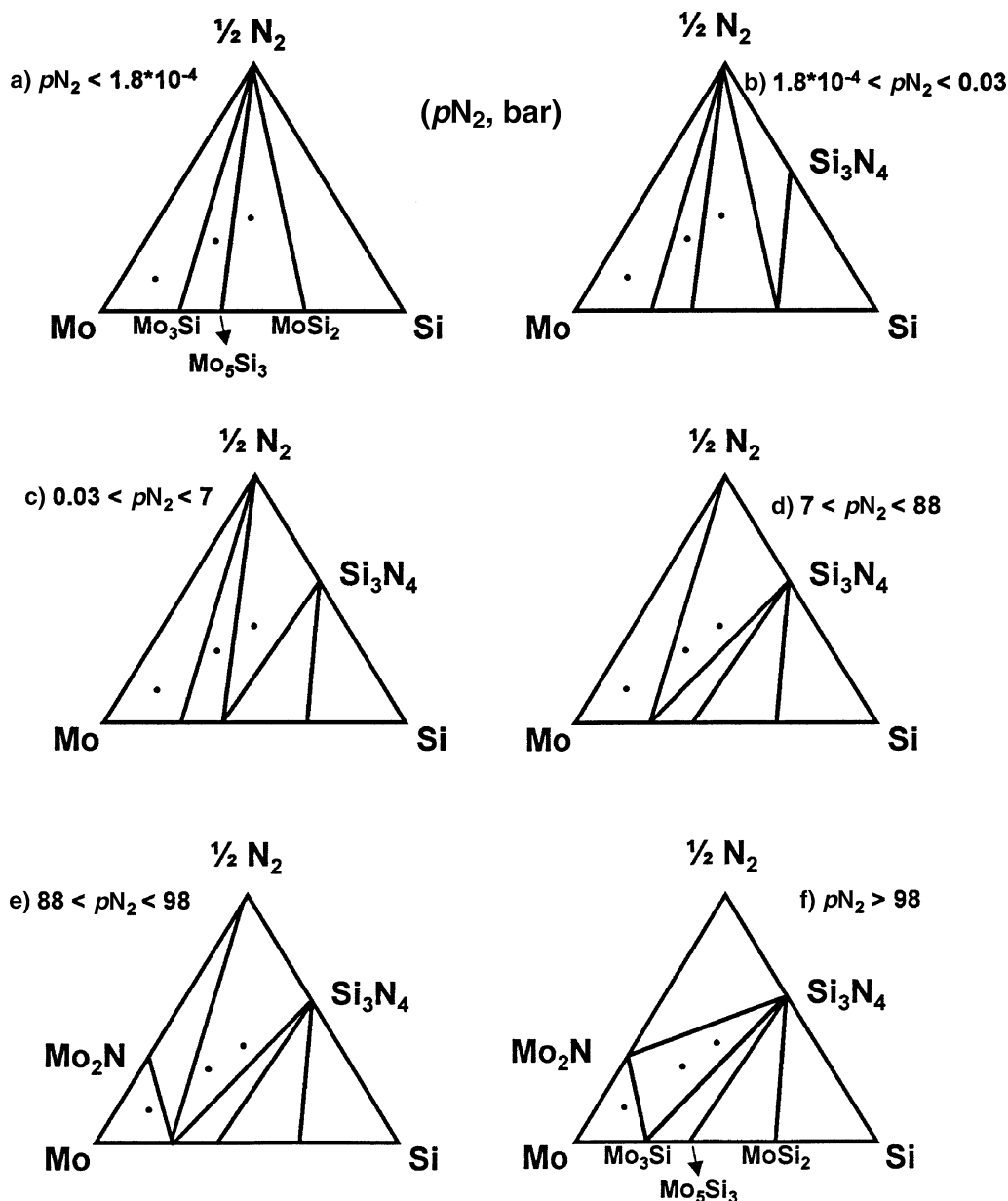


Fig. 4. The isothermal cross-section through the Mo-S-N phase diagram at 1300°C at various partial pressures (bar) of nitrogen; the compositions of the experimentally investigated powder mixtures are depicted as points

reasoning explained in the previous section. However, only Mo_3Si was found in the reaction zone after interaction of dense Si_3N_4 with Mo at 1300°C under 1 bar of nitrogen or argon, or in vacuum ($\sim 10^{-9}$ bar), and no Mo_2N had been formed (Fig. 5a).

These observations indeed suggest that the nitrogen pressure in the gas atmosphere surrounding the couple does not influence the interfacial reaction in the central part of the joint. This becomes quite clear from considering that N_2 -gas

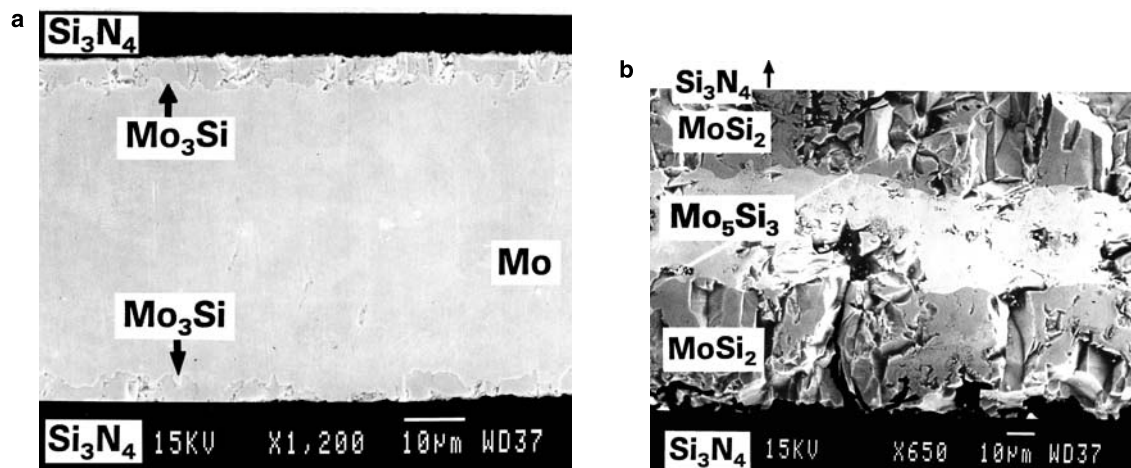


Fig. 5. a) Secondary electron image (SEI) of the transition zone between Mo and dense Si₃N₄ after annealing during 32 h at 1300°C in vacuum; b) SEI of the reaction zone between Mo and 50% porous Si₃N₄ after annealing at 1300°C for 50 h under flowing argon containing of about 500 vpm of nitrogen

has to escape somehow from the interior of the transition zone and this is difficult in fully dense diffusion couple. Therefore, a nitrogen pressure (fugacity) will build up at the contact surface. This pressure determines the activity of Si at the metal/ceramic interface. According to calculations for the Mo–Si–N system at 1300°C this pressure is in between 7 and 88 bar, because Mo₃Si has been found in equilibrium with Si₃N₄ but Mo₂N has not been formed.

So far we have considered interaction between fully dense end-members. When using a diffusion couple consisting of 50% porous Si₃N₄, the layers of MoSi₂ and Mo₅Si₃ are formed in the transition zone after annealing at 1300°C under flowing argon containing of about 500 vpm of N₂ (Fig. 5b). Obviously, the whole Mo part of the couple has been consumed, as well as the Mo₃Si layer that must have been present after shorter annealing times. It is clear that no N₂-pressure can build up at the interface because nitrogen can escape through the open pores in the Si₃N₄. It increases the chemical potential of silicon at the contact surface resulting in the formation of Si-rich silicides. In other words, the reaction products in this couple will entirely depend on the surrounding N₂-partial pressure, because this pressure determines the activity of silicon at Si₃N₄ interface.

Experimental

Throughout the investigation the diffusion couple technique has been used. Plan-parallel slices of the “as supplied” materials were clamped together and annealed in different gas atmospheres for varying times and at various temperatures.

In the case of the Si/TiN couples, the titanium nitride films of about 2 µm thick were deposited onto a (001) oriented silicon wafer by means of reactive PVD in the Ar + N₂ atmosphere. The Si-substrates were sputter-cleaned prior to deposition to ensure a good contact between the end-members.

After standard metallographic preparation, cross-sections of the diffusion couples were examined by polarized light microscopy, scanning electron microscopy (SEM), and the composition was measured by electron probe microanalysis (EPMA).

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