

Interface chemistry and kinetics induced by SiC/Co solid state reactions

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Interfacial chemistry and kinetics induced by SiC/Co solid state reactions were investigated at temperatures between 850 °C and 1450 °C for various times. The reaction mechanisms and the typical layer sequence in the reaction zone are discussed under the consideration of reaction kinetics and thermodynamics. The formation of silicides and carbon was first observed above 850 °C. At 1050 °C, and as the reaction proceeded, the initially formed Co₂Si layer was converted to CoSi. The deposited cobalt thin film reacted completely with SiC after annealing at 1050 °C for 0.5 h. The thermodynamically-stable CoSi was the only observed silicide in the reaction up to 1450 °C. Reaction kinetics are proposed to estimate the effective reaction constant from parabolic growth of the reaction zone. An interfacial model is discussed to interpret the interfacial formation and phase distribution of this system.

Key words: interface chemistry, reaction kinetics, cobalt silicides, SiC/Co, solid state reaction.

Introduction

Solid state reactions between ceramics and metals are of great interest in materials science because of the technological applications for devices fabricated with both metal and ceramic components. Recently, several studies [1-3] have been reported to develop some basic understanding of the physical and chemical interactions at metal-SiC interfaces. For many applications it is important that the fundamentals of the phase distribution and interfacial chemistry by solid state reactions between metals and ceramics are fully understood. Several transition metals have been evaluated as ohmic contacts for SiC. The contact resistivities have been related to the evolution of the related phase formation of the silicides in the metal/SiC interfacial reaction and the behavior of free carbon remaining after the metal/SiC interfacial reaction [4, 5]. Some transition-silicides with semiconducting or semimetallic properties have attracted considerable attention due to their practical applications in electronics and thermoelectric devices [6-8].

In the case of the use of metals forming silicides on SiC substrates at low temperatures, many metals have a strong tendency to interdiffuse through semiconductor-metal interfaces and most metals readily form carbides or silicides [9-12]. A thorough characterization and understanding of metal-SiC interfaces, in terms of reactivity and thermal stability, are therefore crucial in the design of SiC devices. Cobalt could be used to make good high-temperature contacts for utilizing the properties of SiC. Making a suitable material for metallization is also of specific interest because of its silicide-forming tendency at low temperatures. A few

studies [13-16] of the interaction of SiC with cobalt at various temperatures have been reported. However most of these studies were of a phenomenological in nature because of the complex chemistry of interfacial formations, and the mechanisms proposed by these studies were somewhat obscure because of the complicated interfacial reactions. Therefore, more detailed investigations of the interfacial chemistry and kinetics of SiC/Co reactions are required to improve the understanding of the SiC/Co reaction interface.

In this study, the interfacial chemistry and kinetics induced by the solid-state reactions between SiC and cobalt thin films and foils were investigated in detail. The surface morphology, reaction products and interfacial structure are discussed in the temperature range between 850 and 1450 °C. Consequently, the reaction mechanisms and an interfacial model of the typical layer sequence in the reaction zone are discussed under consideration of the reaction kinetics and thermodynamics.

Experimental

The materials used for the experiments were highly dense sintered α -SiC from ESK, and thin sputtered cobalt films and thick foils. The polycrystalline SiC contained 1.5 mass% total impurities, such as carbon and aluminum. The SiC plates were cut into small pieces with a diameter of 20 mm and a thickness of 3 mm and ground with a BN/C disk. The ground SiC samples were then polished using diamond pastes of 30, 15, 3, 1 μ m. Cobalt films were sputter-deposited on to the polished SiC substrates in commercial sputter equipment (Leybold, type Z-400). A magnetron-type D.C. sputtering source was used to deposit the coatings. The growth rate of cobalt films was calculated to be 11.7 nm/min under the conditions used (D.C. potential 400 V, partial pressure of Ar 4.0×10^{-2} mbar). The applied cobalt film

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thickness was fixed at 2.0 μm . The thickness of cobalt foils was 0.5–1 mm from Alfa Prod./Johnson Matthey Company. The thin sputtered cobalt film thickness allows the penetration of the $\text{CuK}\alpha$ beam entirely into the reaction zone by X-ray diffraction analysis (XRD). The couples of SiC with thin sputtered cobalt films and thick foils were annealed at temperatures between 850 and 1450 $^{\circ}\text{C}$ for 0.5–400 h, in a high temperature vacuum furnace. The heating rate was set between 20 and 30 $^{\circ}\text{Cmin}^{-1}$ and the cooling rate between 5 and 10 $^{\circ}\text{Cmin}^{-1}$.

For the prediction of all reaction products, a qualitative process of the reaction in SiC with thin sputtered cobalt films was estimated by determining phase fractions from relative XRD peak intensities of at least three coincidence-free reflections. The polished cross-sections of annealed SiC/Co were investigated using scanning electron microscopy (SEM). Quantitative atomic concentration profiles of silicon, carbon and cobalt were measured using electron probe microanalysis (EPMA). Microstructures of the thermally annealed specimens were also examined using a JEOL JEM-3000F transmission electron microscope (TEM) operating at 300 kV. Cross-sectional TEM samples were prepared by gluing an annealed SiC/Co to the surface of another one, cutting cross-sections of the sample (perpendicular to the film surface), and using a tripod polishing technique to thin the specimens prior to ion milling with 4 keV Ar^+ ions.

Results and Discussion

Annealing experiments were performed at temperatures ranging from 850 to 1450 $^{\circ}\text{C}$. In most cases, thin cobalt films were well coupled with SiC after annealing above 850 $^{\circ}\text{C}$. Fig. 1 shows phase quantities of the SiC/Co solid state reaction couples based on relative XRD estimation for various annealing temperatures and times. The identification of reaction products was confirmed by determining the relative XRD peak intensities. Below 750 $^{\circ}\text{C}$, no reaction

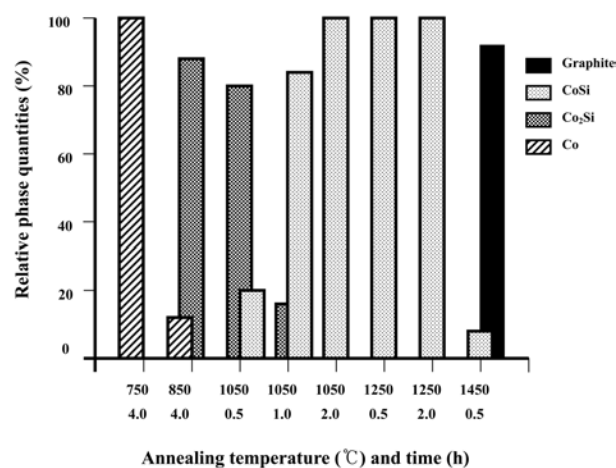


Fig. 1. Phase quantities of the SiC/Co solid state reaction couples based on relative XRD estimation for various annealing temperatures and times.

was observed. At 850 $^{\circ}\text{C}$, most of the cobalt-layer reacted and formed the silicide Co_2Si . No carbide formation, neither Co_2C nor Co_3C was detected by XRD. At 1050 $^{\circ}\text{C}$ the entire cobalt film was consumed after 0.5 h. At this temperature, the amount of CoSi phase increased with annealing time by decreasing the fraction of Co_2Si phase. Co_2Si was fully consumed after 2 h. The relative quantities of both silicides, estimated from the XRD peak intensity ratio as a function of the annealing time at 1050 $^{\circ}\text{C}$, are listed in Table 1. The same reaction stage was reached at 1250 $^{\circ}\text{C}$ after 0.5 h. After 2 h at 1250 $^{\circ}\text{C}$ small quantities of graphite could be detected, presumably developed by the graphitization of carbon formed through the reaction $\text{Co} + \text{SiC} = \text{CoSi} + \text{C}$. The quantity of formed graphite increased with the annealing temperature and time above 1250 $^{\circ}\text{C}$. At 1450 $^{\circ}\text{C}$, graphite was detected by XRD as the predominant reaction product and had a (001) preferred orientation with respect to the surface of the substrate.

Fig. 2 shows the surface morphology of the reaction

Table 1. Relative phase quantities of the silicides from the reaction products after annealing at 1050 $^{\circ}\text{C}$ for various times

Annealing times	Reaction products	
	Co_2Si (wt%)	CoSi (wt%)
0.5	78.5	22.7
1.0	25.6	74.4
2.0	0.0	100.0

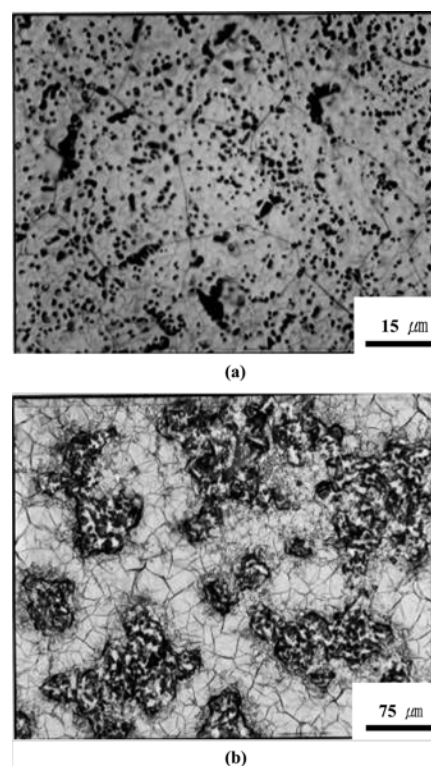


Fig. 2. Surface morphology of the reaction couples of SiC/Co after annealing at (a) 1050 $^{\circ}\text{C}$, 2 h and (b) 1450 $^{\circ}\text{C}$, 0.5 h. The thickness of the cobalt film on the SiC substrate was fixed at 2 μm .

couple of SiC/Co after annealing at (a) 1050 °C for 2 h and (b) 1450 °C for 0.5 h. The thickness of the cobalt film on the SiC substrate was fixed at 2 μm . At 1050 °C for 2 h, the surface morphology showed shadow contrasts with pores and cracks (Fig. 2(a)). At 1450 °C for 0.5 h, severe reactions were observed among the randomly distributed precipitates on the surface (Fig. 2(b)). On this sample, graphite formation was identified by XRD analysis in Fig. 1. Therefore, at this temperature of 1450 °C graphite were predominately precipitated out of the surface of CoSi.

Fig. 3 shows cross-sectional scanning electron micrographs of the SiC/Co reaction zone after annealing at (a) 1050 °C for 0.5 h and (b) 1050 °C for 2 h. At this annealed temperature cobalt-silicide layers extend to 5 μm below the surface, and the deposited Co thin film is completely consumed as described above. In Fig. 3(a) a wide layer of CoSi + C was observed with carbon precipitates in the lower region neighboring the SiC, while a relatively thin layer of Co₂Si was observed without carbon in the upper region. The phase distribution of the reaction zone at 1050 °C for 0.5 h can be described by the structure: Co₂Si/CoSi + C/SiC, which was identified by EPMA. In Fig. 3(b) a wide layer of CoSi + C was observed with precipitates of carbon in the lower region neighboring the SiC, while a relatively thin layer of CoSi was observed without carbon in the upper region. The phase distribution of the reaction zone at 1050 °C,

2 h can be described by the structure: CoSi/CoSi + C/SiC. Depending on the annealing time at this temperature, the relative quantities of CoSi increased simultaneously, while Co₂Si decreased. It seems that Co₂Si is the first reaction product between cobalt and SiC under these conditions. The migration rate of silicon in this phase is assumed to be much higher than that of carbon, indicating the progress of the reaction up to the full consumption of metallic cobalt. The carbon remains along the Co₂Si/SiC interface. On increasing the amount of silicon Co₂Si forms CoSi, which probably dissolves carbon which, during the cooling process is deposited randomly in this phase region.

To obtain more information on microstructures, the specimens were examined by TEM. Fig. 4 shows selected-area electron diffraction (SAED) patterns of SiC/Co sample annealed at 1050 °C for 2 h. SAED patterns obtained from reacted layer are displayed in Fig. 4(a) and 4(b). These patterns were obtained from the different positions in the topmost layer. To identify the crystalline phase of the topmost layer, the structure factor, F_{hkl} , where hkl represents a specific Bragg reflection, was calculated for several cobalt-silicides such as CoSi, Co₂Si, and CoSi₂. Based on the calculations of F_{hkl} , we have found that the SAED patterns in Fig. 4(a) and 4(b) are consistent with the (201) and (101) reciprocal lattice planes of CoSi, respectively [Fig. 4(a) and 4(b)]. That is, the topmost layer consists of CoSi. The mottled layer, as indicated CoSi + C in Fig. 3(b), is also CoSi, but energy-dispersive X-ray spectroscopy measurements indicated that carbon-rich precipitates (black regions in the mottled layer) are formed in this layer. These results are in agreement with those obtained by EPMA.

The reaction kinetics of the reaction between SiC and Co thick foils were studied for temperatures 950 °C and 1250 °C and times between 4 and 400 h. On the assumption

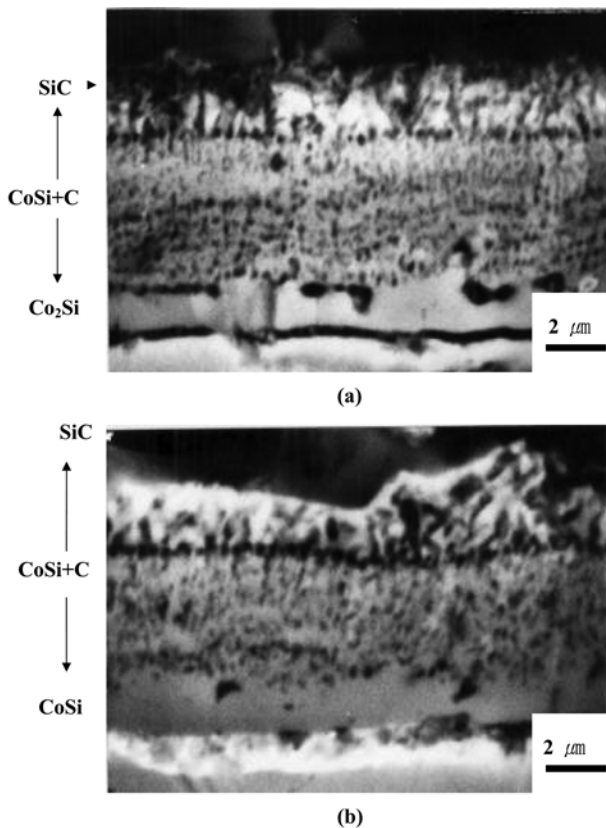


Fig. 3. Scanning electron micrographs showing cross-sectional views of the SiC/Co reaction zone after annealing at (a) 1050 °C, 0.5 h and (b) 1050 °C, 2 h.

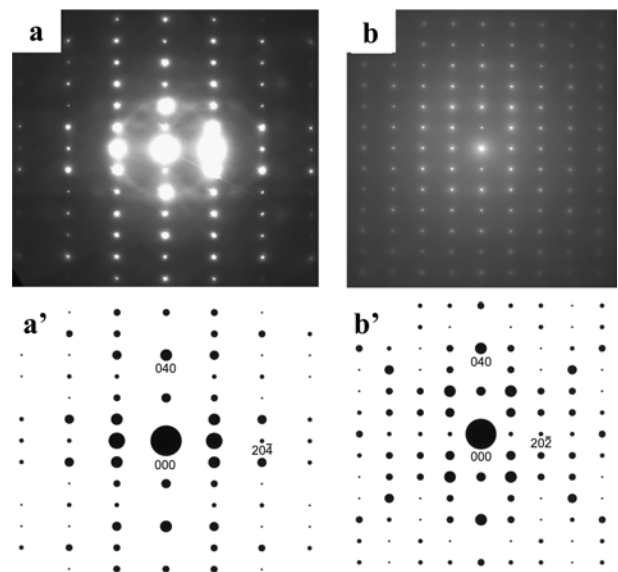


Fig. 4. (a, b) SAED patterns and (a', b') simulated electron diffraction patterns of the SiC/Co reaction zone after annealing at 1050 °C, 2 h.

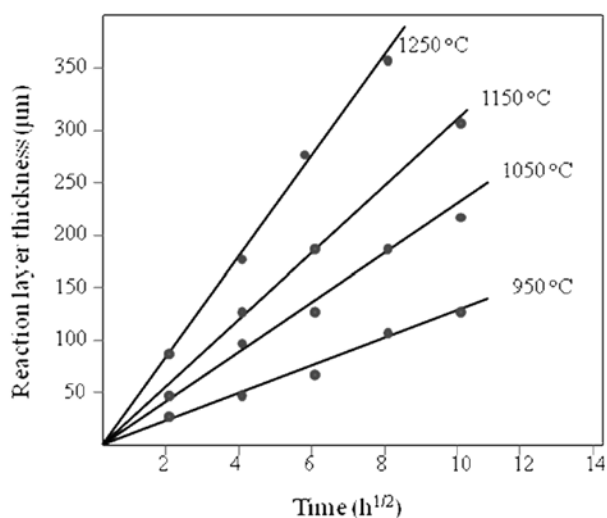


Fig. 5. Growth of the reaction thickness in SiC/Co reaction zone versus square root of time for various times and temperatures.

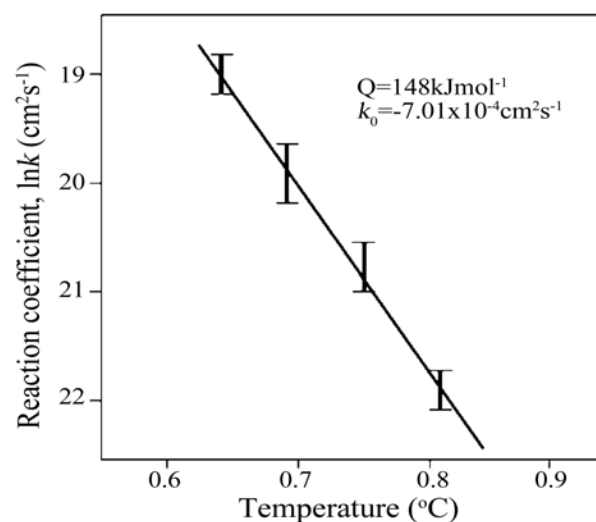


Fig. 6. Reaction coefficients in SiC/Co reaction zone versus reciprocal absolute temperature [$\ln k = f(1/T)$].

that the relation is diffusion-controlled, the thickness of the reaction zone follows a parabolic growth law. Therefore, the thicknesses of the reaction zone are plotted in Fig. 5 for various temperatures as a function of the square root of annealing times. This relation shows a linear relationship indicating that the reaction is diffusion-controlled. The reaction coefficient, k , is equal to x^2/t and is dependent with the temperature according to the equation of $k = k_0 \exp(-Q/RT)$, where k_0 is the frequency factor and Q the activation energy of the chemical process. The relation of the logarithm of the reaction coefficients versus the reciprocal of the absolute temperature is linear, as plotted in Fig. 6. The activation energy and the frequency factor calculated from this relationship are 148 kJ mol^{-1} and $7.01 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$, respectively.

The reaction between a cobalt thin film and SiC leads to the formation of cobalt silicides accompanied by carbon precipitates. It is worthwhile discussing the interfacial formation, phase distribution and thermodynamic stability in the reaction zone. A reaction model of the SiC/Co interfacial formation and phase distribution is proposed in Fig. 7. At 850°C , most of the cobalt-layer reacted and initially formed the silicide Co_2Si . The interfacial sequence for the phase distribution at this temperature can be described by the structure: $\text{Co}/\text{Co}_2\text{Si} + \text{C}/\text{SiC}$. Unreacted cobalt was crystallized as a cubic modification. The deposited cobalt thin film reacted completely with SiC after annealing at 1050°C for 0.5 h. At 1050°C , as the reaction proceeded, the initially formed Co_2Si layer converted to CoSi . The interfacial sequence for the phase distribution at 1050°C ,

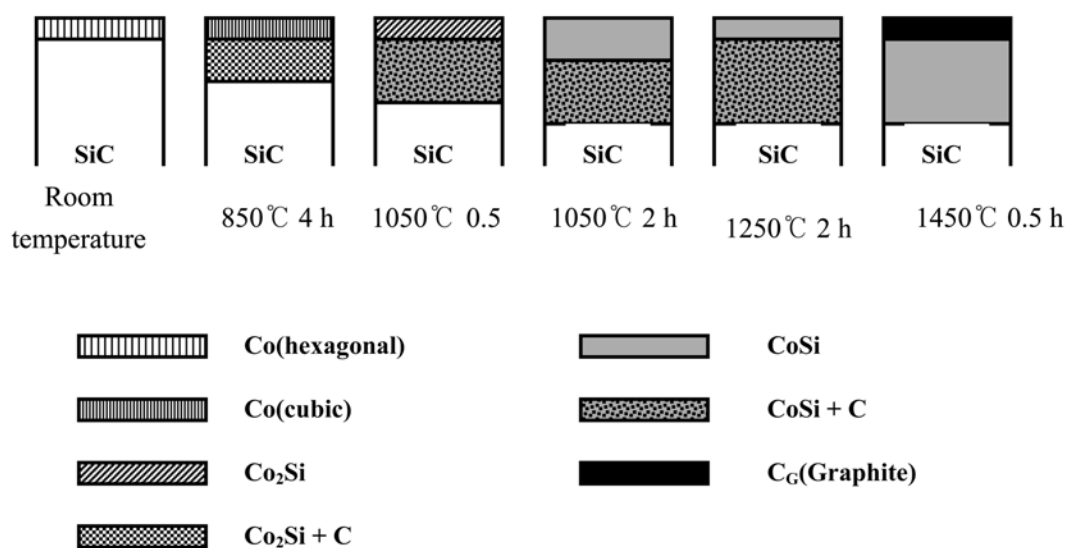


Fig. 7. Interface model and phase distribution of the SiC/Co solid state reaction.

Table 2. Gibb's free energy of possible reactions for SiC/Co system at 1050 °C

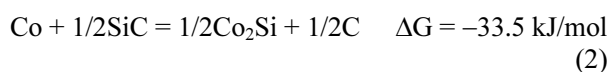
Possible reactions	Gibb's free energy (kJ/mol)
$\text{Co} + 1/2\text{SiC} = 1/2\text{Co}_2\text{C} + 1/2\text{Si}$	27.5
$1/2\text{Co} + \text{SiC} = 1/2\text{CoSi}_2 + \text{C}$	2.4
$\text{Co} + \text{SiC} = \text{CoSi} + \text{C}$	-37.4
$2\text{Co} + \text{SiC} = \text{Co}_2\text{Si} + \text{C}$	-67.0
$1/2\text{Co} + \text{Si} = 1/2\text{CoSi}_2$	-46.9
$\text{Co} + \text{Si} = \text{CoSi}$	-86.7
$2\text{Co} + \text{Si} = \text{Co}_2\text{Si}$	-99.6

0.5 h can be described by the structure: $\text{Co}_2\text{Si}/\text{CoSi} + \text{C}/\text{SiC}$. Above 1050 °C, 2 h the thermodynamically-stable CoSi is the only observed silicide in the reaction up to 1450 °C. The interfacial sequence for the phase distribution between 1050 °C, 2 h and 1250 °C, 2 h can be described by the structure: $\text{CoSi}/\text{CoSi} + \text{C}/\text{SiC}$. Above 1450 °C graphite were predominately precipitated out of the surface of CoSi with the following sequence: $\text{C}_G/\text{CoSi}/\text{SiC}$.

Considering the Gibb's free energy, ΔG , for various reactions, the reaction products between cobalt and SiC could be correlated within this system. Table 2 shows Gibb's free energy of the possible reactions for the Co/SiC system at 1050 °C. The result predicts which phases are stable at thermodynamic equilibrium. At a temperature of 1050 °C, cobalt is known to react with silicon to form various silicides CoSi, Co_2Si and CoSi_2 , because the ΔG values for the formation of these compounds are highly negative. Less negative values are calculated for the corresponding reactions with SiC, i.e.:



and



because of the energy needed for SiC decomposition. The formation of CoSi_2 and Co_2C by the reaction between SiC and Co is not thermodynamically possible at this temperature, because of the positive ΔG values of 2.4 and 27.5 kJ/mol, respectively. Therefore, the solid state reaction between cobalt and SiC could be generally described as the formation of $\text{CoSi} + \text{C}$ and $\text{Co}_2\text{Si} + \text{C}$, which results in the decomposition of SiC and the precipitation of carbon. According to the present experimental results, cobalt reacts with SiC and forms various silicides at the SiC interface. At 1050 °C the Co_2Si layer converted to CoSi and additional carbon precipitates were formed within the CoSi zone. The reason why the Co_2Si layer converted to CoSi is attributed to the availability of more cobalt atoms, as compared to silicon atoms, in the reaction zone because of a faster consumption rate of cobalt. According to reported diffusion data [17, 18],

cobalt is the dominant diffuser in the Co_2Si phase. It also diffuses through Co_2Si and CoSi, and arrives at the SiC interface to react with SiC. After the metallic cobalt layer is completely consumed, cobalt migration takes place from the Co_2Si , resulting in the growth of the CoSi layer. It is possible that CoSi grows at the $\text{Co}_2\text{Si}/\text{CoSi}$ and CoSi/SiC interfaces, resulting in the growth of CoSi with heating time and increasing temperature. At 1050 °C for 0.5 h carbon precipitation was only observed in the CoSi phase, because DG of CoSi (-37.4 kJ/mol) is lower than that of the Co_2Si phase (-33.5 kJ/mol) and could provide the thermodynamic driving force for carbon precipitation.

Conclusions

The interfacial chemistry and kinetics of the SiC/Co solid state reactions were investigated between 850 °C and 1450 °C. At 850 °C, most of the cobalt-layer reacted and initially formed Co_2Si . The formation of silicides and carbon was first observed above 850 °C. At 1050 °C, and as the reaction proceeded, the initially formed Co_2Si layer was converted to CoSi. The deposited cobalt thin film reacted completely with SiC after annealing at 1050 °C for 0.5 h. The thermodynamically-stable CoSi was the only observed silicide in the reaction up to 1450 °C. The reaction kinetics of growth in the thickness of the reaction zone showed parabolic relationship. The activation energy and frequency factors were proposed to be 148 kJmol^{-1} and $7.01 \times 10^{-4} \text{ cm}^2\text{s}^{-1}$. The interfacial reaction model of this system has been proposed and discussed in terms of the thermodynamic argument.

Acknowledgements

The author gratefully thanks Prof. Yoshihiko Hirotsu and Prof. Manabu Ishimaru at ISIR in Japan for helpful discussions and TEM investigation. This study was supported by Basic Science Research Program through the National Research Foundation of Korea(NRF) funded by the Ministry of Education, Science and Technology (2010-0023911).

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