Interface Formation and Phase Distribution Induced by Co/SiC Solid State Reactions

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Interface formation and phase distribution by the solid-state reactions between thin sputtered cobalt films and SiC were studied at temperatures between 1023 and 1723 K for various times. The reaction with the formation of silicides and carbon was first observed above 1123 K. At 1323 K, and as the reaction proceeded, the initially formed Co₂Si layer converted to CoSi. The deposited cobalt thin film reacted completely with SiC after annealing at 1323 K for 0.5 h. The thermodynamically stable CoSi is the only observed silicide in the reaction up to 1723 K. A reaction model and a thermodynamic argument are proposed to interpret the interface formation and phase distribution of this system.

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1. Introduction

The study of metal-ceramic interfacial bonding and its reactions is of great interest in materials science because of the technological applications of devices fabricated from both metal and ceramic components.¹⁻⁴⁾ SiC is presently considered as a promising semiconductor for high-power electronic devices, owing to its high thermal and chemical stability. For many applications it is important that the fundamentals of phase distribution and interface chemistry by solid state reactions between metals and ceramics are fully understood. Recently, several studies⁵⁻⁷⁾ have been reported to develop some basic understanding on the physical and chemical interactions at the metal-SiC interfaces. Several transition metals have been evaluated as ohmic contacts for SiC. The contact resistivities have been related to the evolution of related phase formation of the silicides in the metal/SiC interface reaction and the behavior of free carbon remaining after the metal/SiC interface reaction.^{8,9)}

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. A thorough characterization and understanding of metal-SiC interfaces, in terms of reactivity and thermal stability, is 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 silicides-forming tendency at low temperatures. A few detailed studies^{7,9,10)} of the interaction of cobalt with SiC at various temperatures have been reported. However most of the works were phenomenological in nature because of the complex chemistry of interface formations, and the mechanisms proposed by the works were somewhat obscure because of the complicated in-

terface reactions. Therefore, more detailed investigations of the interface formation and phase distribution of the Co/SiC reactions are required for improved understanding of Co/SiC reaction interface.

In this work, we investigated the interface formation and phase distribution of solid state Co/SiC reactions using thin cobalt films sputtered on SiC. The surface morphology, reaction products and interface structure are studied in the temperature range between 773 and 1723 K. Furthermore, a thermodynamic argument and a reaction model are proposed to interpret the interface reaction of Co/SiC system.

2. Experimental Details

The materials used for the experiments were highly dense sintered α -SiC from "Elektroschmelzwerk Kempten", ESK, and thin sputtered cobalt films. 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 a 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 condition used (D.C. potential 400 V, partial pressure of Ar 4.0×10^{-2} mPa). The applied film thickness was fixed at 2.0 μ m for this study. This thickness allows the penetration of the CuK α beam entirely into the reaction zone by X-ray diffraction analysis (XRD). The couples of SiC with thin sputtered cobalt films were annealed at temperatures between 1023 and 1723 K for 0.5–2 h, in a high temperature vacuum furnace. The heating rate was set between 20 and 30 Kmin⁻¹ and the cooling rate between 5 and 10 Kmin⁻¹.

Fig. 1 XRD patterns of the Co/SiC reaction couples after annealing at (a) 1123 K for 4 h, (b) 1323 K for 0.5 h, (c) 1323 K for 2 h and (d) 1723 K for 0.5 h.

For the prediction of all reaction products, the 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 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 thermal 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 Co/SiC 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.

3. Experimental Results

Annealing experiments were performed at temperatures ranging from 1023 to 1723 K. In most cases, thin cobalt films were well coupled with SiC after annealing above 1123 K. Figure 1 shows XRD patterns of the Co/SiC reaction couples after annealing at (a) 1123 K for 4 h, (b) 1323 K for 0.5 h, (c) 1323 K for 2 h and (d) 1723 K for 0.5 h. The identification of reaction products was confirmed by determining the relative XRD peak intensities. Below 1123 K, no reaction was observed. At 1123 K, most of the cobalt-layer reacted and formed the silicide Co_2Si (Fig. 1(a)). No carbide formation, neither Co_2C nor Co_3C was detected by XRD. At 1323 K the entire cobalt film was consumed after 0.5 h (Fig. 1(b)). 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 (*cf.*, Figs. 1(b) and (c)). The same reaction stage was reached at 1523 K after 0.5 h. After 2 h at 1523 K small quantities of graphite could be detected, presumably developing 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 1523 K. At 1723 K, graphite was detected by XRD as the predominant reaction product and had a (001) preferred orientation with respect to the surface of substrate (Fig. 1(d)).

Figure 2 shows the surface morphology of the reaction couple of Co/SiC after annealing at (a) 1323 K, 2 h and (b) 1723 K, 0.5 h. The thickness of the cobalt film on the SiC substrate was fixed at 2 μm . At 1323 K for 2 h, the surface morphology showed shadow contrasts with pores and cracks (Fig. 2(a)). At 1723 K 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(d). Therefore, at this temperature of 1723 K graphites were predominantly precipitated out of the surface of CoSi .

Figure 3 shows the EPMA line scan for cobalt, carbon and silicon over the cross-sectional Co/SiC reaction zone after annealing at 1123 K, 4 h, showing the distinguishable boundary between Co and $\text{Co}_2\text{Si} + \text{C}$ regions. The corresponding phase distribution is also noted on this diagram. On the surface, a Co region was identified. In the areas adjacent to the SiC interface, a mixture of Co_2Si with carbon was formed. The phase distribution of the reaction zone at 1123 K, 4 h can be

(a)

(b)

Fig. 2 Surface morphology of the reaction couples of Co/SiC after annealing at (a) 1323 K, 2 h and (b) 1723 K, 0.5 h. The thickness of the cobalt film on the SiC substrate was fixed at 2 μm.

expressed by the structure: $\text{Co}/\text{Co}_2\text{Si} + \text{C}/\text{SiC}$. This phase distribution will be confirmed later as shown in Fig. 4.

Figure 4 shows cross-sectional scanning electron micrographs of the Co/SiC reaction zone after annealing at (a) 1323 K, 0.5 h and (b) 1323 K, 2 h. At this annealing temperature cobalt-silicide layers extend to 5 μm below the surface, and deposited Co thin film is completely exhausted as described above. In Fig. 4(a) a wide layer of $\text{CoSi} + \text{C}$ was observed with the carbon precipitates in the lower region neighboring the SiC, while a relatively thin layer of Co_2Si was observed without carbon in the upper region. The phase distribution of the reaction zone at 1323 K, 0.5 h can be described by the structure: $\text{Co}_2\text{Si}/\text{CoSi} + \text{C}/\text{SiC}$, which was identified by EPMA. In Fig. 4(b) a wide layer of $\text{CoSi} + \text{C}$ was observed with the precipitations 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 1323 K, 2 h can be described by the structure: $\text{CoSi}/\text{CoSi} + \text{C}/\text{SiC}$. Depending on the annealing time at this temperature, the relative quantities of CoSi increased simultaneously, while Co_2Si decreased. It seems that Co_2Si is

Fig. 3 EPMA line scan for cobalt, carbon and silicon over the cross-sectional Co/SiC reaction zone after annealing at (a) 1123 K, 4 h showing the distinguishable boundary between Co and $\text{Co}_2\text{Si} + \text{C}$ regions.

Fig. 4 Scanning electron micrograph showing the cross-sectional views of the Co/SiC reaction zone after annealing at (a) 1323 K, 0.5 h and (b) 1323 K, 2 h. The arrows indicate the top of the reaction layers.

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 $\text{Co}_2\text{Si}/\text{SiC}$ interface. On increasing the amount of silicon Co_2Si forms CoSi , which probably dissolves carbon which is deposited randomly in this phase region during the cooling process.

To obtain more information on microstructures, the specimens were examined by TEM. Figure 5 shows selected-area

Fig. 5 (a), (b) SAED patterns and (a'), (b') simulated electron diffraction patterns corresponding to (a), (b).

electron diffraction (SAED) patterns of Co/SiC sample annealed at 1323 K for 2 h. SAED patterns obtained from the reacted layer are displayed in Figs. 5(a) and (b). These patterns were obtained from the different positions of 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 ($P2_13$: $a = 0.4446$ nm), Co_2Si ($Pnma$: $a = 0.4918$ nm, $b = 0.3738$ nm, $c = 0.7109$ nm), and CoSi_2 ($Fm\bar{3}m$: $a = 0.5365$ nm). Based on the calculations of F_{hkl} , we have found that the SAED patterns in Figs. 5(a) and (b) are consistent with the (201) and (101) reciprocal lattice planes of CoSi, respectively [Figs. 5(a') and (b')]. That is, the topmost layer consists of CoSi. The results of electron diffraction experiments are consistent with those of X-ray diffraction experiments [Fig. 1(c)]. The mottled layer, as indicated by $\text{CoSi} + \text{C}$ in Fig. 4(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.

4. Discussion

The reaction between cobalt thin film and SiC leads to the formation of cobalt silicides accompanied by carbon precipitates. It is worthwhile discussing the interface formation, phase distribution and thermodynamic stability in the reac-

Fig. 6 Reaction model of the Co/SiC interface formation and phase distribution.

tion zone. A reaction model of the Co/SiC interface formation and phase distribution is proposed in Fig. 6. At 1123 K, 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, which identified near 52° in 2θ by XRD in Fig. 1(a) after heat treatment above 1123 K. Fujimura and Tanaka¹⁰ also examined the formation process of cobalt silicide during annealing using *in situ* X-ray diffraction, and reported the hexagonal Co transforms into the cubic Co. The

Table 1 Gibb's free energy of possible reactions for Co/SiC system at 1323 K.

Possible reaction	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

deposited cobalt thin film reacted completely with SiC after annealing at 1323 K for 0.5 h. At 1323 K, as the reaction proceeded, the initially formed Co_2Si layer converted to CoSi. The interfacial sequence for the phase distribution at 1323 K, 0.5 h can be described by the structure: $\text{Co}_2\text{Si}/\text{CoSi} + \text{C}/\text{SiC}$. Above 1323 K, 2 h the thermodynamically stable CoSi is the only observed silicide in the reaction up to 1723 K. The interfacial sequence for the phase distribution between 1323 K, 2 h and 1523 K, 2 h can be described by the structure: $\text{CoSi}/\text{CoSi} + \text{C}/\text{SiC}$. Above 1723 K graphite were predominantly precipitated out of the surface of CoSi with the following sequence: $\text{C}_G/\text{CoSi}/\text{SiC}$. Fujimura and Tanaka¹⁰⁾ suggested a model of Co/SiC interface reaction under experimental conditions between 921 and 1573 K. They described that the reaction sequence at high temperatures were $\text{Co}/\text{Co}_2\text{Si} + \text{C}/\text{SiC}$, $\text{Co}/\text{Co}_2\text{Si} + \text{CoSi} + \text{C}/\text{SiC}$, $\text{Co}/\text{CoSi} + \text{C}/\text{SiC}$ and $\text{CoSi} + \text{C}/\text{SiC}$. However, in this work, after consuming the cobalt-layer the reaction layer sequences were suggested by the structure: $\text{Co}_2\text{Si}/\text{CoSi} + \text{C}/\text{SiC}$, $\text{CoSi}/\text{CoSi} + \text{C}/\text{SiC}$ and $\text{C}_G/\text{CoSi}/\text{SiC}$.

Considering the Gibb's free energy, ΔG , for various reactions, the reaction products between cobalt and SiC could be correlated within this system. Table 1 shows Gibb's free energy of the possible reactions for Co/SiC system at 1323 K. The result predicts which phases are stable at the thermodynamic equilibrium. At temperatures of 1323 K, 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 reaction 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 value 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 1323 K the Co_2Si layer converted to CoSi and additional carbon precipitates were formed within the CoSi zone. The reason why the Co_2Si layer con-

verted 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,^{11–14)} cobalt is the dominant diffuser in the Co_2Si phase. It also diffuses through Co_2Si and CoSi, and arrives 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 1323 K for 0.5 h only carbon precipitation was observed in the CoSi phase, because ΔG 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.

5. Summary

Interface formation and phase distribution of solid state Co/SiC reactions using thin cobalt films sputtered on SiC were investigated at temperatures between 1023 and 1723 K. At 1123 K, most of the cobalt-layer reacted and initially formed Co_2Si . The interfacial sequence for the phase distribution at this temperature was described by the structure of $\text{Co}/\text{Co}_2\text{Si} + \text{C}/\text{SiC}$. The deposited cobalt thin film reacted completely with SiC after annealing at 1323 K for 0.5 h. At 1323 K, as the reaction proceeded, the initially formed Co_2Si layer converted to CoSi. The interfacial sequence for the phase distribution at 1323 K, 0.5 h was described by the structure of $\text{Co}_2\text{Si}/\text{CoSi} + \text{C}/\text{SiC}$. Above 1323 K for 2 h, the thermodynamically stable CoSi is the only observed silicide in the reaction up to 1723 K. The interfacial sequence for the phase distribution between 1323 K, 2 h and 1523 K, 2 h was described by the structure: $\text{CoSi}/\text{CoSi} + \text{C}/\text{SiC}$. Above 1723 K graphite were predominantly precipitated out of the surface of CoSi with the sequence of $\text{C}_G/\text{CoSi}/\text{SiC}$. The interfacial reaction model of this system has been proposed and discussed in terms of the thermodynamic argument.

REFERENCES

- 1) A. Nishimoto, M. Ando, M. Takahashi, M. Aritoshi and K. Ikeuchi: Mater. Trans., JIM **40** (1999) 953–956.
- 2) T. Ishikawa, M. E. Brito, Y. Inoue, Y. Hirotsu and A. Miyamoto: ISIJ Int. **30** (1990) 1071–1077.
- 3) M. E. Brito, H. Yokoyama, Y. Hirotsu and Y. Mutoh: ISIJ Int. **29** (1989) 253–258.
- 4) M. E. Brito, H. Yokoyama, Y. Hirotsu and Y. Mutoh: MRS Int'l. Mtg. on Adv. Mats. **8** (1989) 23–28.
- 5) T. C. Chou, A. Joshi and J. Wadsworth: J. Mater. Res. **6** (1991) 796–809.
- 6) W. F. J. Slijberman, J. Fisher, J. F. van der Veen, I. Ohdomari, S. Yoshida and S. Misawa: J. Appl. Phys. **66** (1989) 666–673.
- 7) S. W. Park, Y. I. Kim, J. S. Kwak and H. K. Baik: J. Electro. Mat. **26** (1997) 172–177.
- 8) C. S. Lim, H. Nickel, A. Naoumidis and Gyarmati: J. Mater. Sci. **32** (1997) 6567–6572.
- 9) C. S. Lim, H. Nickel, A. Naoumidis and Gyarmati: J. Mater. Sci. **31** (1996) 4241–4247.
- 10) T. Fujimura and S. I. Tanaka: J. Mater. Sci. **34** (1999) 5743–5747.
- 11) S. S. Lau and J. W. Mayer: J. Appl. Phys. **49** (1978) 4005–4010.
- 12) G. J. Van Gurp, W. F. Van der Weg and D. Sigurd: J. Appl. Phys. **49** (1978) 4011–4020.
- 13) F. M. D'Heurle and C. S. Petersson: Thin Solid Films **128** (1985) 283–297.
- 14) A. P. Bitha and R. Pretorius: Thin Solid Films **93** (1982) 127–133.