Journal of Korean Association of Crystal Growth
Vol. 5, No. 4 (1995) 358-369

Surface structure and critical load of thin metal films on SiC substrate

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SiC 기판상의 금속박막의 표면구조 및 임계하중

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Abstract Surface structure and adhesion by the reaction between thin metal films and SiC were studied at temperatures between 550 and 1450℃ for various times. The reaction with the formation of various silicides was initially observed above 850℃ for SiC/Co system and 650℃ for SiC/Ni system. The cobalt reacted with SiC and consumed completely at 1050℃ for 0.5 h and the nickel at 950℃ for 2 h. The observed CoSi phase in SiC/Co and Ni_2Si phase in SiC/Ni are thermodynamically stable in the reaction zone up to 1250℃ and 1050℃ respectively. Carbon was crystallized as graphite above 1450℃ for SiC/Co reaction surface and 1250℃ for SiC/Ni. The critical loads of the thin metal films on SiC substrate were qualitatively compared in terms of the scratch test method. At temperatures between 850 and 1050℃, relatively higher values of 20～33 N were observed for SiC/Ni couples.

요 약 SiC와 금속박막의 반응에 의한 표면구조 및 부착력이 550℃에서 1450℃의 온도범위에서 조사되어졌다. SiC/Co계에서는 850℃ 이상에서, SiC/Ni계에서는 650℃ 이상에서 여러가지 규소화물이 형성된 반응이 최초로 나타났다. 코발트는 1050℃, 0.5 h에서 니켈은 950℃, 2 h에서 SiC와 완전히 반응하여 소모되었다. SiC/Co에서는 CoSi상이 SiC/Ni에서는 Ni_2Si상이 1250℃와 1050℃의 반응에서까지 각각 열역학적으로 안정하게 관찰되어졌다. 탄소는 SiC/Co 반응표면에서는 1450℃ 이상에서 그리고 SiC/Ni 반응표면에서는 1250℃ 이상에서의 온도에서 흑연으로 결정화되었다. SiC기판과 금속박막의 임계하중이 scratch test 방법에 의하여 정성적

으로 비교되어져, 850℃에서 1050℃의 온도범위에서 SiC/Ni couple이 20~33 N의 상대적으로 높은 값을 나타내었다.

1. Introduction

The properties of metal-SiC contacts are of increasing technological interest as the result of large band gap of single crystal SiC (2.9 eV). The largy band gap allows SiC to be used in a variety of solid-state electronic devices, e.g., wide spectra range light emitting diodes [1-3]. In the case of silicon-metal contacts, the interaction between the SiC and a metal during thermal annealing determines the properties of the contacts. One area of interest is the use of metals forming silicides on SiC substrates at low temperature, in the attempt to form contacts with thermal annnealing [4-8].

Many metals have a strong tendency to interdiffuse at semiconductor-metal interfaces and most metals readily form carbides or silicides. A thorough characterization and understanding of SiC-metal interfaces, in terms of reactivity and thermal stability, is therfore crucial in the design of SiC devices. Several studies have been reported to develop some basic understanding on the physical and chemical interactions at the SiC-metal interfaces [9-13]. For the reaction of SiC with various types of metals, different silicides, free carbon, metallic alloys and carbides have been observed as reaction products.

Cobalt and nickel could be used to make good high-temperature contacts for utilizing the properties of SiC. They are also of specific interest due to its silicide-forming tendency at low temperature, making a suitable material for metallization. In this paper, the surface structure and adhesion of thin sputtered cobalt and nickel films with 2 μm thickness doposited on SiC were studied at temperatures between 550 and 1450℃ for various times. The adhesion of the formed surface between the polycrystalline SiC and the thin metal layers is discussed on the basis of measurement of the critical load, using the scratch test.

2. Experimental

The materials used for the experiments were sintered and highly dense α-SiC from "Elektroschmelzwerk Kempten", ESK, and thin sputtered cobalt and nickel films. The polycrystalline SiC contained 1.5 wt% total impurities, such as carbon and aluminium (ESK). SiC plates were cut into small pieces with a diameter of 20 mm and a thichness of 3 mm and ground with a BN/C disk. The ground SiC samples were ultrasonically cleaned in ethanol, rinsed with water and dried. After the grinding process, the surface of the samples showed an average roughness of 32.6 nm (measured by surface profilometry). The SiC plates were then polished with a diamond disk using diamond pastes of 30, 15, 3, 1 μm and hyprez liquids (polishing solution).

The cobalt and nickel films were sputter-deposited on to the polished SiC substrates in a commercial sputter equipment (Leybold /Germany, type Z-400). A magntron-type D.C. sputtering source was used to deposit the coatings. Flowing argon was employed as a sputter gas with a partial pressure of $4.0 - 7.0 \times 10^{-2}$ mbar. D.C. potentials were varied between 400 and 500 V depending on the current density and pressure. The temperature of the substrate during deposition was estimated to be between 50 and 250℃. Film thicknesses were measured by the observation of film steps on reference substrates using surface profilometry. Prior to coating, the thickness of nickel films was controlled by covering the substrate holders and by exposing the substrates for predetermined times.

Annealings were conducted in a high-temperature vacuum furnace with a graphite heating element manufactured by Degussa/Germany. The thin sputtered metal films on SiC were placed in a graphite crucible. The specimens were surrounded by titanium to remove the residual oxygen during the annealing time. After positioning the samples, the furnace was evacuated to 6×10^{-6} mbar and subsequently filled with a gas mixture of Ar/4 vol%H_2 for the annealing time. Thermocouples of type EL18(PtRh30/PtRh6) were used for temperature measurement in the range 550 ~ 1450℃ for 0.5 ~ 2 h. The heating rate was set between 20 and 30 $Kmin^{-1}$ and the cooling rate between 5 and 10 $Kmin^{-1}$.

After reaction runs, the samples were characterized at the surface. The macroscopic variation of the surface structure and the progress of the reaction on the surface were examined by optical microscopy, scanning electron microscopy (SEM) and surface profilometry. The qualitative progress of the reaction of the thin metal films on SiC substrate was estimated by determining phase fractions from relative X-ray diffraction (XRD) peak intensities of at least three coincidence-free reflections. The scratch test revealed the adhesive strength of the annealed samples by measurement of the critical load for film debonding.

3. Results and discussion

3.1. Sputter deposition process

Figure 1 shows the polished and etched surfaces of sintered SiC (SSiC) and highly dense SiC (SiC-HD). After polishing, the surface showed an average roughness of 4.7 nm. The polished SiC was eched with Murakami solution prepared from 3 g KOH and 30 g $K_3[Fe(CN)_6]$ in 60 ml H_2O at boiling temperature for 13 min. The etched SiC surface in Fig. 1 shows a typical mixed structure of globular form to long/plate form and the average grain size is 1.78 μm for SSiC and 3.69 μm for SiC-HD.

Figure 2 represents the measurements of the thickness of the sputtered cobalt and nickel thin films as a function of the sputter

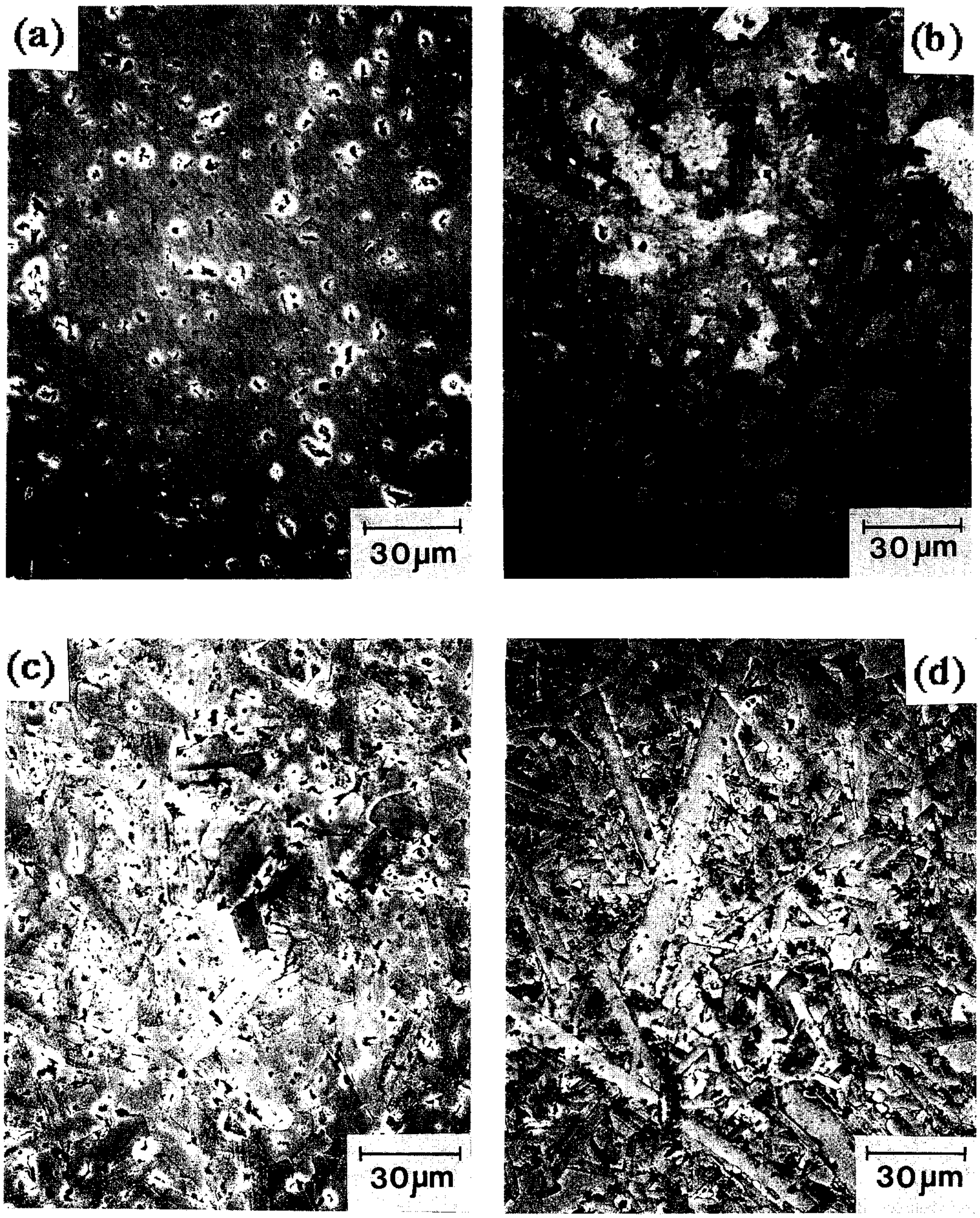

Fig. 1. Scanning electron micrograph surface structure of ; (a) polished SSiC, (b) polished SiC -HD, (c) etched SSiC and (d) SiC-HD.

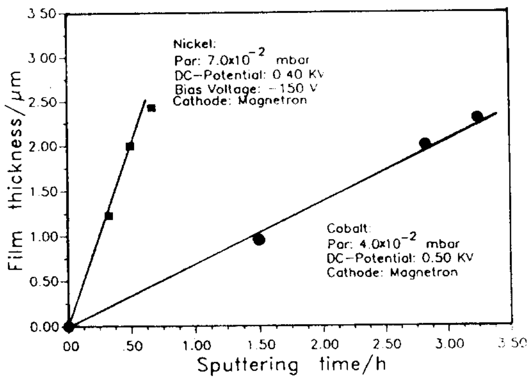

Fig. 2. The thickness of the cobalt and nickel thin film as a function of the sputter times in the range from 0 to 3.5 h. The growth rate of the cobalt and nickel films in a magnetron-type D.C. sputtering source was determined to be 11.7 and 667 nm/min respectively.

times in the range from 0 to 3.5 h. In both cases, a magntron-type D.C. sputtering source was used to deposit the coating. The growth rate of nickel films was calculated to be 667 nm/min under the conditions used (D.C. potential 400 V, partial pressure of Ar 7.0×10^{-2} and bias voltage -150 V), and the growth rate of cobalt films was calculated to be 11.7 nm/min under the conditions used (D.C. potential 500 V and partial pressure of Ar 4.0×10^{-2}). The applied film thickness was fixed at 2.0 μm for this study. This thickness allows the penetration of the CuK_{α} beam entirely into the reaction zone for investigating the reaction products by XRD.

The structure of the typical as-sputtered surface of cobalt and nickel film on a SiC substrate is shown in Fig. 3. The surface is

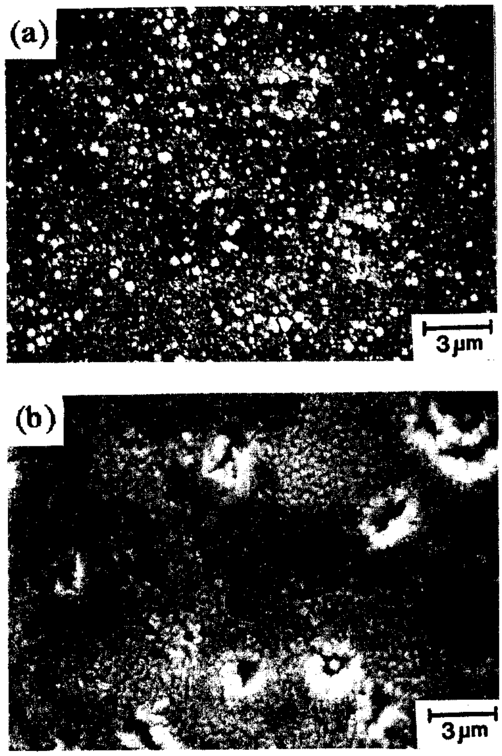

Fig. 3. Scanning electron micrograph surface structure of the metal films (2 μm thick) deposited on the SiC substrate : (a) cobalt and (b) nickel.

composed of many solidified bubble shapes about 0.1 ~ 0.5 μm diameter. According to XRD analysis, the deposited cobalt film was crystallized hexagonally, while the nickel was crystallized as the cubic modification.

3.2. *Surface structure*

Annealing experiments were performed in the temperature ranges between 550 and 1450℃. Surface structures of the thin cobalt films SiC after annealing at 650, 850, 1050 and 1250℃ are shown in Fig. 4. After annealing at 650℃ (Fig. 4 (a)), no distinct changes on the surface were observed. Shadow contrasts and pores were revealed after a heat treatment at 850℃ for 4 h (Fig. 4 (b)). At 1050℃ for 2 h, the surface morphology showed increased pore growth and crack formation (Fig. 4 (c)). After annealing at 1450℃, severe reactions were observed among the randomly distributed precipitations on the surface (Fig. 4 (d)).

The identification of reaction products was confirmed by determining the relative XRD peak intensities. Figure 5 shows the qualitative phase analysis of the thin cobalt

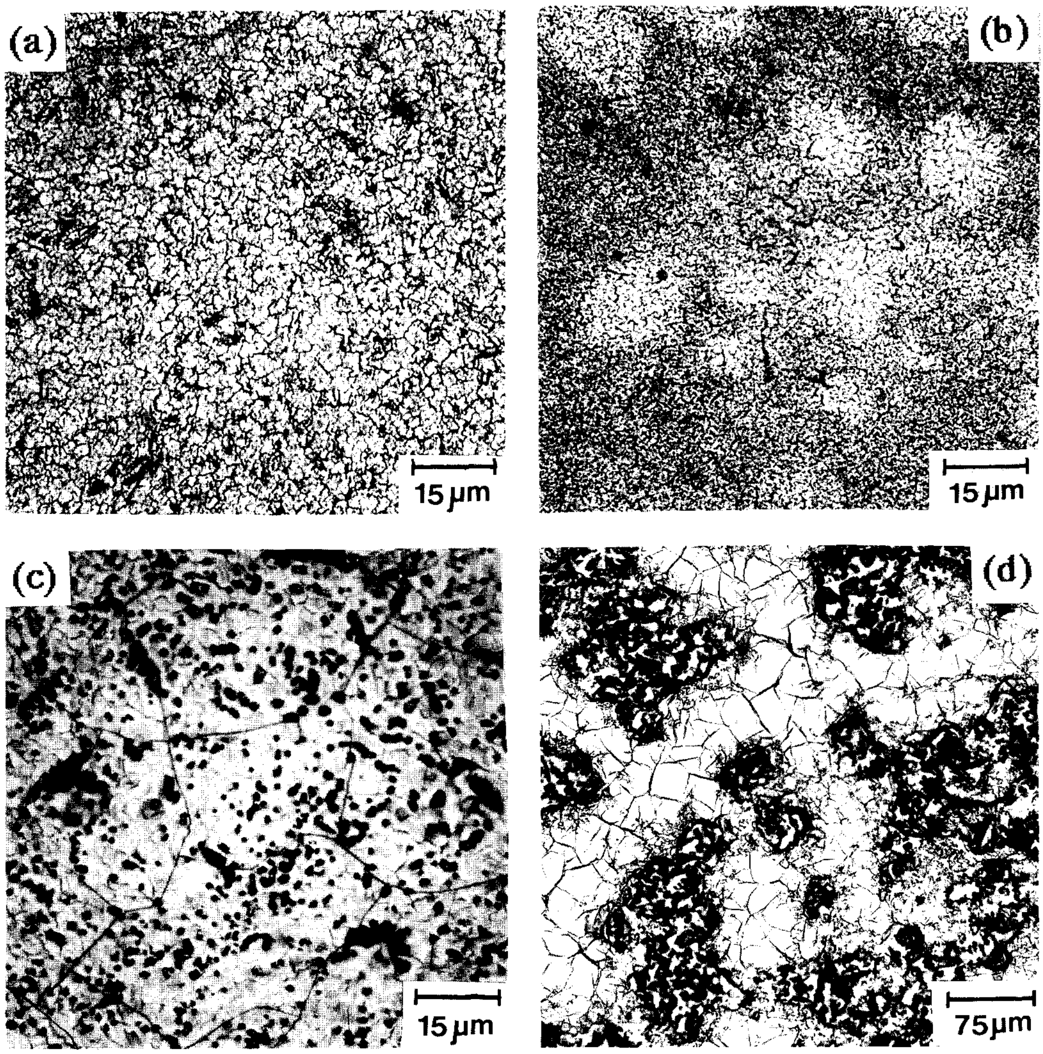

Fig. 4. Surface structures of the thin cobalt films on SiC after annealing at (a) 650℃, 2 h, (b) 850℃, 2 h, (c) 1050℃, 2 h and (d) 1450℃, 2 h. The thickness of the cobalt film on SiC substrate was fixed at 2 μm.

films on SiC based on relative XRD phase estimation for various annealing conditions. Below 750℃, no reaction was observed. At 850℃, most of the cobalt layer reacted and formed the silicide Co_2Si. Unreacted cobalt initially crystallized hexagonally, as identified by XRD, after this heat treatment as the cubic modification. It was distributed predominantly in the film surface. No carbide formation, either Co_2C or Co_3C, was detected by XRD.

At 1050℃ 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 (Fig. 5). The same reaction stage was reached at 1250℃ after 0.5 h. After 2 h at 1250℃ small quantities of graphite could be detected, presumably developing of graphitization of carbon formed through the reaction $Co + SiC = CoSi + C$. The quantity of graphite was detected XRD as the predominate reaction product and was epitaxially deposited on the surface of the sample.

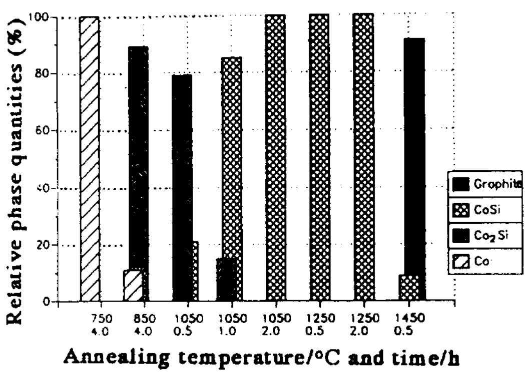

Fig. 5. Qualitative analysis of the thin cobalt films on SiC based on relative XRD phase estimation for various annealing conditions.

A reaction product of the thin nickel films on SiC was initially detected at 650℃ (after 2 h). Photographs of the surface structures after annealing at 650, 950, 1050 and 1250 ℃ are shown in Fig. 6. After annealing at 650℃ (Fig. 6 (a)), shadow contrasts on the surface were observed. A fein agglomation of the reaction products was revelaed at 950 ℃ for 2 h (Fig. 6 (b)). At 1050℃ for 2 h, the surface morphology showed relatively increased agglomations with a partial melting (Fig. 6 (c)). After annealing at 1250℃, severe reactions were observed among the randomly distributed precipitations on the surface (Fig. 6 (d)). On this sample, graphite formation was indentified by XRD analysis.

Fig. 7 shows the qualitative phase analysis of the thin nickel films on SiC based on the XRD analysis for different temperatures and times. Below 650℃, no reaction was observed. At 650℃, most of the nickel layer reacted and formed the silicides Ni_2Si and Ni_3Si_2. Unreacted nickel was crystallized, as identified by XRD, after this heat treatment as the cubic modification. It was distributed predominantly in the film surface. No carbide formation, either Ni_2C or Ni_3C, was detected by XRD. At 750℃, the Ni_3Si_2 phase was transformed to be the Ni_2Si phase after 2 h. At 950℃ the entire nickel film was fully consumed after 2 h. The Ni_2Si is the only observed silicide in the reaction zone up to 1050℃. After 2 h at 1250℃, the Ni_2Si phase with small quantities of Ni_3Si_2 and

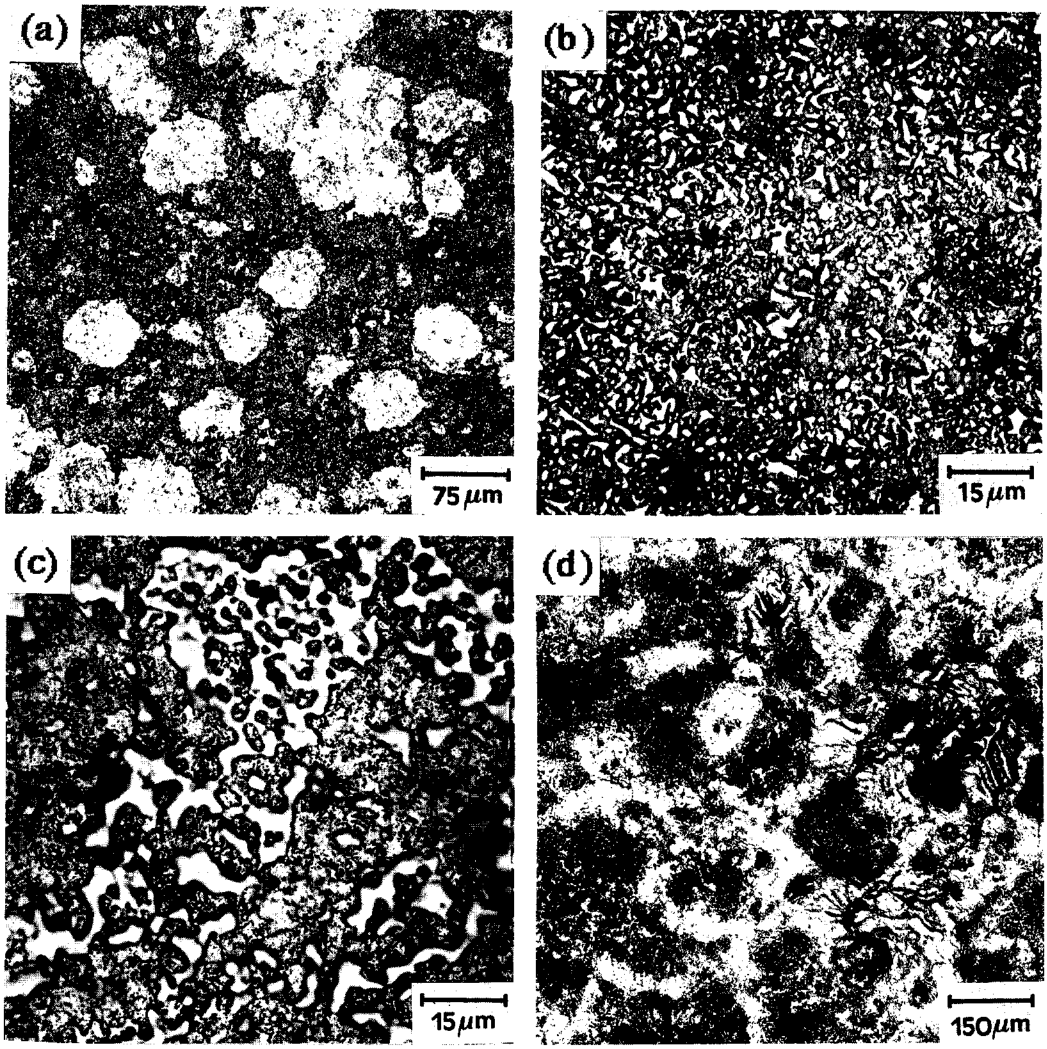

Fig. 6. Surface structures of the thin nickel films on SiC after annealing at (a) 650℃, 2 h, (b) 950℃, 2 h, (c) 1050℃, 2 h and (d) 1250℃, 2 h. The thickness of the nickel film on SiC substrate was fixed at 2 μm.

graphite could be detected, presumably developing by graphitization of carbon formed through the reactions $Ni + \frac{1}{2} SiC = \frac{1}{2} Ni_2Si + \frac{1}{2} C$ and $Ni + \frac{2}{3} SiC = \frac{1}{3} Ni_3Si_2 + \frac{2}{3} C$. An increase in temperature results in an increase in the intensity of the XRD peaks of graphite. While no carbide was detected in reacted couples at 1250℃, nickel silicides and graphite were detected by XRD.

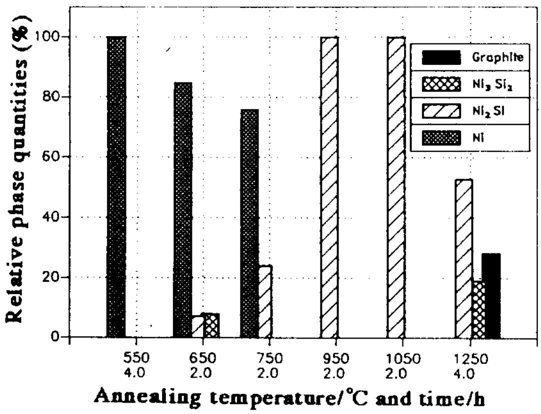

Fig. 7. Qualitative analysis of the thin nickel films on SiC based on relative XRD phase estimation for various annealing conditions.

3.3. Critical load

The adhesive strength is presented in terms of the critical load determined with the scratch test method. A commercially available scratch test apparatus, designed by the Laboratoire Suisse de Recherches Horlogeres (LSRH), was used to study the adhesion of the thin metal films on SiC substrate before and after various annealings. The unit has a diamond stylus in the form of a Rockwell C 120° cone with a spherical tip radius of 0.20 mm. Loads were applied in steps of 100 gf up to a maximum of 20 kgf (1 kgf = 9.8067 N). The typical acoustic emmision signal curve on the cobalt films on SiC after various annealing conditions are il-

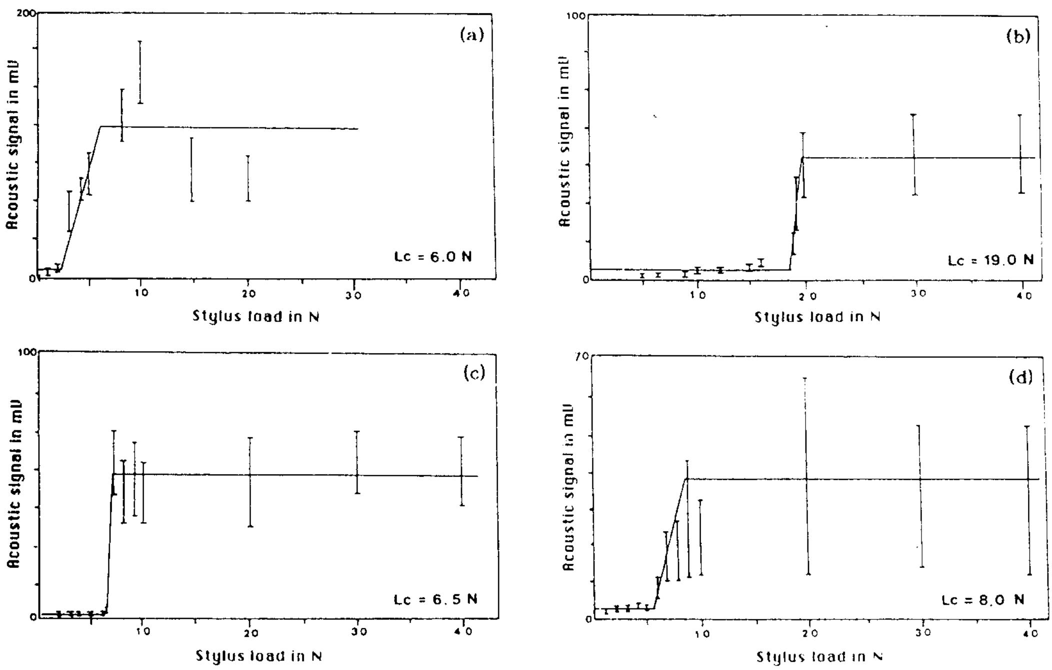

Fig. 8. Acoustic signals as a function of stylus load for various reaction surfaces of cobalt films on SiC after annealing at: (a) 850°C, 2 h, (b) 1050°C, 2 h, (c) 1250°C, 2 h and (d) 1450°C, 2 h.

lustrated in Fig. 8 as a function of stylus. In order to determine the critical load of the metal films on SiC, an acoustic signal was emitted in the range 0-200 mV. At low loads the curves are smooth. When coating loss occures, the signal increases suddenly. In temperature ranges between 850 and 1450℃, the critical loads could be determined to be 6 N in Fig. 8 (a), 19 N in Fig. 8 (b), 6.5 N in Fig. 8 (c) and 8 N in Fig. 8 (d) respectively.

The determined critical loads have been compared with microscopy observations. The critical load increased with increasing coating thickness [14]. In this study the coating thickness was fixed at 2 μm. Fig. 9 shows an optical micrograph of scratch channels on the nickel films on SiC after various annealing conditions under various stylus loads. The load was increased with each traverse until the coating was stripped cleanly from the substrate. The load at which the coating was stripped from the substrate was termed the critical load. From this measurements, the critical load of the nickel films on SiC could be determined to be 33 N in Fig. 9 (a), 21 N in Fig. 9 (b) and 17 N in Fig. 9 (c) respectively.

Figure 10 shows the average critical loads of the metal films on SiC for various annealing temperatures. According to the measurements, the average critical loads varied between 6-19 N for the cobalt films on SiC and between 8-33 N for the nickel films. The average critical loads of the nickel films on SiC was relatively higher than that of the cobalt films. Relatively higher values of 20-

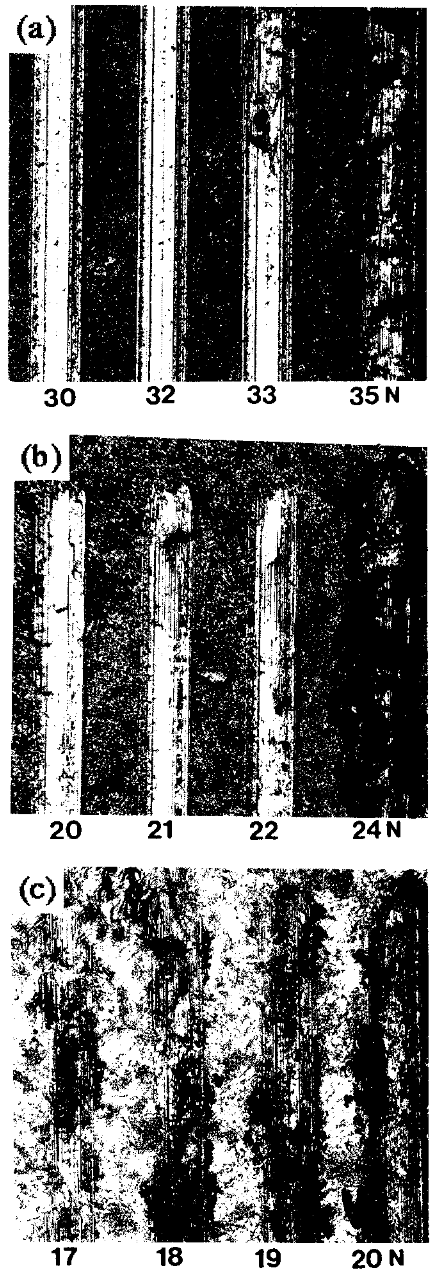

Fig. 9. Optical micrographs of scratch channels for the reaction surface of the nickel films on SiC under various stylus loads after annealing at : (a) 950℃, 2 h, (b) 1050℃, 2 h and (c) 1250℃, 2 h.

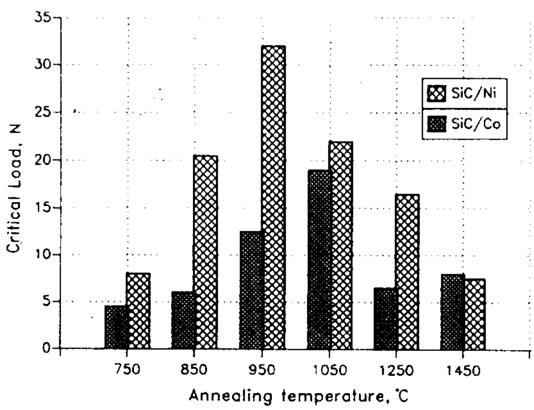

Fig. 10. Average critical loads of the metal films on SiC for various annealing temperatures.

30 N of the nickel films on SiC were observed for couples reacted between 850 and 1050℃.

4. Conclusions

The reaction with the formation of various silicides was initially observed above 850 ℃ for SiC/Co system and 650℃ for SiC/Ni system. The cobalt reacted with SiC and consumed completely at 1050℃ for 0.5 h and the nickel at 950℃ for 2 h. The observed CoSi phase in SiC/Co and Ni_2Si phase in SiC/Ni are thermodynamically stable in the reaction zone up to 1250℃ and 1050℃ respectively. Carbon was crystallized as graphite above 1450℃ for SiC/Co reaction surface and 1250℃ for SiC/Ni.

The average critical loads varied between 6-19 N for the cobalt films on SiC and between 8-33 N for the nickel films. The average critical loads of the nickel films on SiC was relatively higher than that of the cobalt films. Relatively higher values of 20-33 N of the nickel films on SiC were observed for couples reacted between 850 and 1050℃.

References

[1] G.L. Harris, M.G. Spencer and C.Y.W. Yang : Amorphous and Crystalline Silicon Carbide III, (Springer-Verlag Berlin, Heidelberg, New York, 1992).

[2] R.J. Trew, J.B. Yan and P.M Mock, Proc, IEEE 79 (1991) 598.

[3] R.F. Davis, G. Kelner, M. Shur, W. Palmour and J.A. Edmond, Ibid. 80 (1991) 667.

[4] D. Fathy. O.W. Holland, J. Narayan and B.R. Appleton, Nuclear Instruments and Methods in Physics Research B7 (1985) 571.

[5] W.F.J. Slijkerman, A.E.M. Fischer, J. F. van der Veen, I. Ohdomari, S. Yoshida and S. Misawa, J. Appl. Phys. 66 (1989) 666.

[6] I. Ohdomari, S. Sha, H. Aochi, T. Chikyow and S. Suzuke, Ibid. 62 (1987) 3747.

[7] C.S. Pai, C.M. Hanson and S.S. Lau, Ibid. 57 (1985) 618.

[8] J. Narayan, D. Fathy. O.W. Holland, B.R. Appleton and R.F. Davis, Ibid. 56 (1984) 1577.

[9] C.S. Lim, H. Nickel, A. Naoumidis and E. Gyarmati, J. Mat. Sci. 30 (1995)

3874.
[10] C.S Lim and H. Nickel, J. Kor. Assoc. Crystal Growth 5 (1995) 109.
[11] R.C.J. Schiepers, F.J.J. van Loo and G. D. With, J. Am. Ceram. Soc. 71 (1988) C-284.
[12] M. Backhaus-Ricoult, Ber. Bunsenges. Phys. Chem. 93 (1989) 1277.
[13] T.C. Chou. A. Joshi and J. Wadsworth, J. Mater. Res. 6 (1991) 796.
[14] A.J. Perry, Thin Solid Films 78 (1981) 77.