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Deposition and microhardness of SiC from the Si_2Cl_6–C_3H_8–H_2–Ar system

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We obtained SiC coating layers on a graphite substrate using hexachlorodisilane (Si_2Cl_6, boiling point 144° C) as a silicon source and propane as a carbon source. We examined the deposition conditions, contents of carbon, silicon and chlorine in the deposits, and the microhardness. Mirror-like amorphous silicon layers were deposited in the reaction temperature range 500 to 630° C. Well-formed silicon carbide layers with good adherency to the substrate were obtained above 850° C. The lowest deposition temperature of SiC was estimated to be 750 to 800° C. The Vickers microhardness of the SiC layer was about 3800 kg mm^{-2} at room temperature and 2150 kg mm^{-2} at 1000° C.

1. Introduction

Silicon carbide is the candidate with most potential as a high-temperature structural material because of its excellent high-temperature oxidation, corrosion, erosion and/or abrasion resistance, its high degree of elastic modulus and strength, and its high thermal shock resistance. Furthermore, silicon carbide is very promising as a protective coating for materials exposed to harsh oxidative, corrosive, erosive and/or abrasive conditions at elevated temperatures, and is also interesting in electronic applications.

Silicon carbide has been prepared hitherto by various deposition processes using widely varying conditions of source gas and its composition, temperature, pressure, and substrate, in the presence or absence of glow discharge. As a source of silicon, silicon tetrachloride [1–6], trichloromethylsilane [4, 7–10], tetramethylsilane [11, 12] and silane [13–18] are generally used. Among these compounds, silane is in general used in the plasma deposition process for SiC passivation films in silicon device technology. Silicon tetrachloride is most conveniently used for the preparation of SiC protective coatings by the chemical vapour deposition (CVD) process.

In this work we obtained SiC coating layers on a graphite substrate using hexachlorosilane (Si_2Cl_6, b.p. 144° C) as a silicon source and propane as a carbon source. We examined the deposition conditions, contents of carbon, silicon and chlorine in the deposits, and the microhardness.

2. Experimental details

A graphite substrate (10 mm in diameter and 2 mm in thickness) was placed on a support located in the central part of a vertical reaction tube (quartz, 19 mm internal diameter and 400 mm length). The reaction tube was heated from the outside by a nichrome element. Reagent-grade hexachlorodisilane was saturated into the carrier hydrogen gas was introduced into the upper inlet of the reaction tube. SiC deposits obtained were analysed using electron probe microanalysis (EPMA). Contents of carbon and silicon in the deposits were estimated from the peak ratio of $CK\alpha$ and $SiK\alpha$ in the deposits compared with that of the standard graphite and silicon wafer, respectively. The chlorine content in the deposits was estimated from the peak ratio of $ClK\alpha$ to $SiK\alpha$ in the deposits.

3. Results and discussion

3.1. Deposition conditions, identification and morphology

The effect of reaction temperature on the weight gain of the substrate is shown in Fig. 1, in which the reaction time was fixed at 60 min. An appreciable weight gain was observed at reaction temperatures above 450° C. The weight gain increased gradually at low deposition temperatures of below 700° C and rapidly above 800° C, and reached a maximum at 1000° C. The rapid decrease of weight gain at reaction temperatures above 1100° C is caused by the preferential deposition of SiC on to the inner wall of the reaction tube. Mirror-like layers with a silver lustre and yellowish powders were deposited in the temperature ranges 500 to 630° C and 630 to 750° C, respectively. In the reaction temperature range 850 to 1100° C, well-formed greyish layers with good

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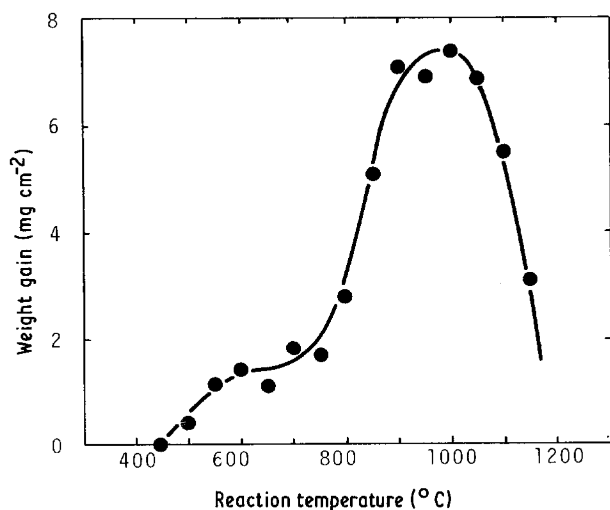

Figure 1 Effect of reaction temperature on the weight gain. H_2 flow rate 3.0 ml sec^{-1}, Si_2Cl_6 flow rate 0.016 ml sec^{-1}, C_3H_8 flow rate 0.05 ml sec^{-1}, reaction time 60 min.

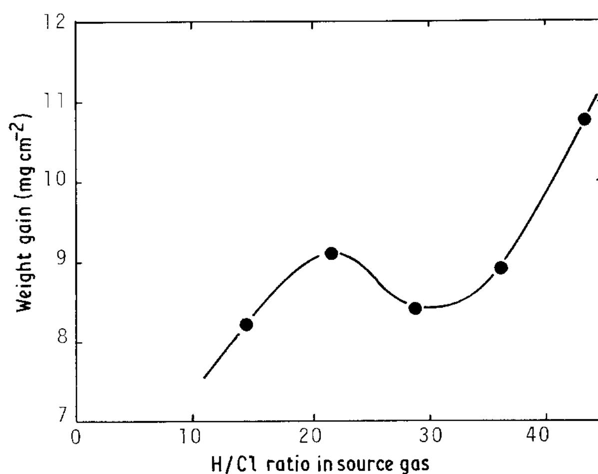

Figure 2 Effect of the flow ratio (H/Cl) in the source gas on the weight gain. Reaction temperature 950° C, reaction time 30 min, Si_2Cl_6 flow rate 0.021 ml sec^{-1}, C_3H_8 flow rate 0.1 ml sec^{-1}.

adherency were deposited. At reaction temperatures above 1100° C, greyish powders were deposited together with coating layers on the substrate.

The weight gain increased rapidly with increasing flow rate of Si_2Cl_6 and attained a constant value above 0.005 ml sec^{-1}. The effect of the flow ratio (H/Cl) in the source gas on the weight gain is shown in Fig. 2 in which the reaction temperature, reaction time and Si_2Cl_6 flow rate were fixed at 950° C, 30 min and 0.021 ml sec^{-1}, respectively. No weight gain was observed at flow ratios below 10. Greyish powders, which included small amounts of yellowish powder, were deposited at flow ratios of 10 to 30. Well-formed adherent layers were obtained at flow ratios above 30, and the weight gain increased rapidly with increasing flow ratio.

The deposition yield of well-formed layers on the substrate was estimated as a function of silicon in the source, and the result is shown in Fig. 3 with respect to the Si_2Cl_6 flow rate; the reaction temperatures was fixed at 1000° C. The maximum deposition yield of about 10 wt % was obtained at an Si_2Cl_6 flow rate of 0.005 ml sec^{-1}, and the yield decreased rapidly with increasing flow rate. This variation of deposition yield is very similar to that of SiC deposition from a gas mixture of CH_3SiCl_3 and H_2 [19].

Micrographs of the surface and a ruptured cross-section of the SiC layers are shown in Fig. 4. Many nodules are observed on the surface of the coating layers. However, the bulk layer is very dense and defects such as cavities are not observed at all, as can be seen in the ruptured cross-section (Fig. 4b).

The results of X-ray diffraction analysis on the surface of layers formed on the graphite substrate are shown in Fig. 5. Peaks marked C in Fig. 5 arise from the graphite substrate. At a reaction temperature of 800° C, no peaks except for those of the graphite substrate are observed, indicating an amorphous phase in the deposits. Apparent peaks of the SiC phase are observed at a reaction temperature of 850° C (Fig. 5b), but distinction of whether the SiC obtained is α-type or β-type cannot be carried out because of the overlap of the respective peaks.

Etching tests were carried out on the deposits using buffered hydrofluoric acid. The mirror-like layers obtained in the deposition temperature range 450 to 630° C were easily etched, and thus were considered to be an amorphous silicon. On the other hand, the greyish coated layers obtained at 850° C were not

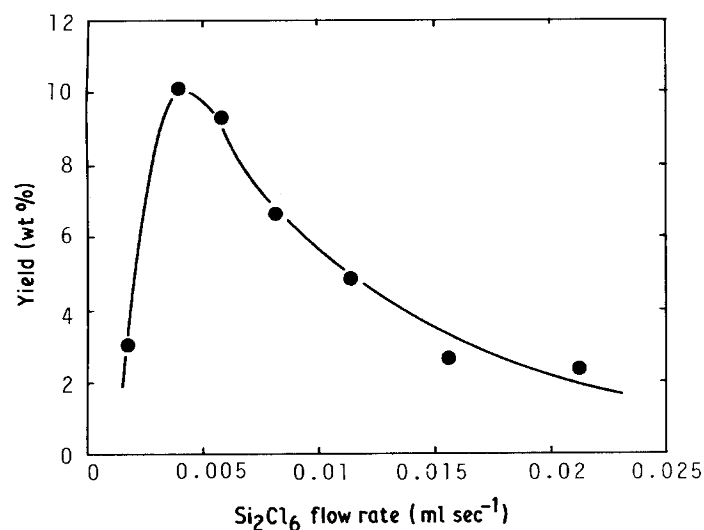

Figure 3 Effect of Si_2Cl_6 flow rate on the deposition yield. Reaction temperature 1000° C, reaction time 30 min, H_2 flow rate 3.0 ml sec^{-1}, C_3H_8 flow rate 0.05 ml sec^{-1}.

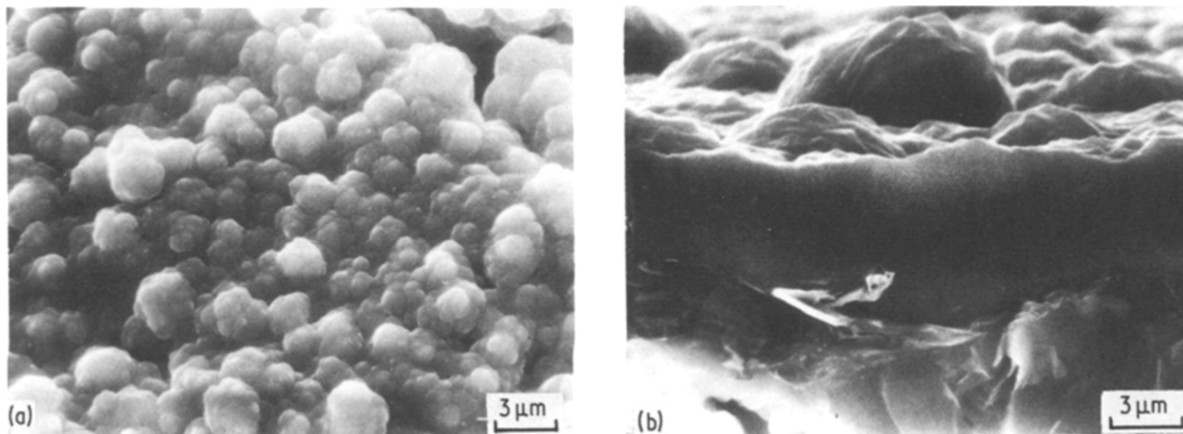

Figure 4 Micrographs of (a) surface and (b) a ruptured cross-section of SiC coating layers. (a) Reaction temperatures 950° C, reaction time 30 min, H_2 flow rate 3.0 ml sec^{-1}, Si_2Cl_6 flow rate 0.043 ml sec^{-1}, C_3H_8 flow rate 0.1 ml sec^{-1}. (b) Reaction temperature 1000° C, reaction time 30 min, H_2 flow rate 3.0 ml sec^{-1}, Si_2Cl_6 flow rate 0.0082 ml sec^{-1}, C_3H_8 flow rate 0.05 ml sec^{-1}.

etched at all, indicating the presence of pure SiC. The lowest deposition temperature of SiC is considered to be 750 to 800° C.

3.2. Effect of reaction parameters on the contents of carbon, silicon and chlorine in the deposits

The effect of the reaction temperature on the contents (peak ratios) of carbon and silicon in the deposits is shown in Fig. 6. The silicon content in the deposits was constant in the reaction temperature range 900 to 1050° C, and decreased rapidly at temperatures below 900° C or above 1050° C. On the other hand, the carbon content decreased with increasing reaction temperature and attained a minimum at about 1000° C, increasing again with increasing reaction temperature. It can be seen that SiC layers with a relatively constant composition are obtained in the reaction temperature range 950 to 1050° C. The decrease in the silicon content at reaction temperatures above 1050° C is probably caused by the co-deposition of some amount of free carbon. On the other hand, the rapid decrease in silicon content at reaction temperatures below 900° C is probably caused by the inclusion of carbon residues and/or chlorine into the deposits, as will be shown later.

The effect of the Si_2Cl_6 flow rate or flow ratio (H/Cl) in the source gas on the contents of carbon and silicon is shown in Fig. 7, in which the reaction temperature was fixed at 1000° C. It can be seen that these deposition parameters have no effect at all on the contents of carbon and silicon in the deposits; constant contents of carbon and silicon in the deposits are obtained irrespective of the Si_2Cl_6 flow rate and flow ratio (H/Cl) in the source gas.

The effect of the Si_2Cl_6 flow rate and reaction temperature on the chlorine content (peak ratio) in the deposits is shown in Fig. 8, in which the reaction temperature in examining the effect of Si_2Cl_6 flow rate was fixed at 1000° C. Effect of Si_2Cl_6 flow rate on chlorine content in the deposits was not observed in the flow rate range 0.005 to 0.03 ml sec^{-1}. On the other hand, the chlorine content decreased rapidly with increasing reaction temperature, and attained a con-

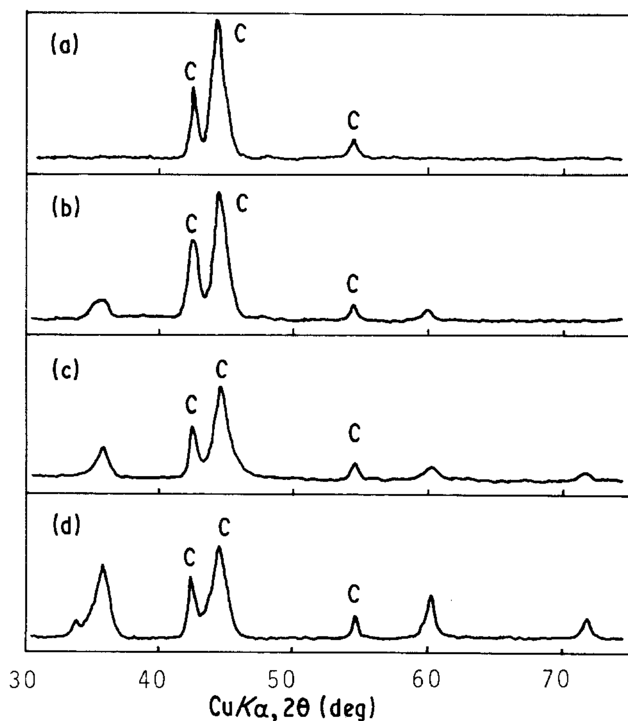

Figure 5 X-ray diffraction profiles obtained with Cu*Kα* radiation. Reaction temperature (a) 800° C, (b) 850° C, (c) 900° C, (d) 950° C.

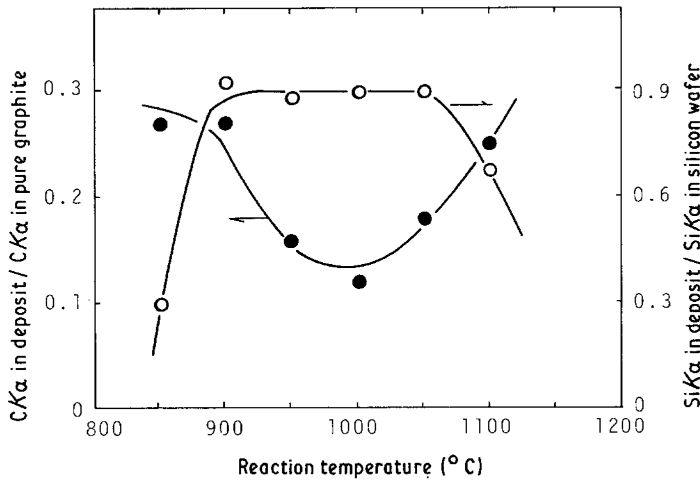

Figure 6 Effect of the reaction temperature on carbon and silicon contents (peak ratios) in the deposits. H_2 flow rate $3.0\,ml\,sec^{-1}$, Si_2Cl_6 flow rate $0.016\,ml\,sec^{-1}$, C_3H_8 flow rate $0.05\,ml\,sec^{-1}$. $CK\alpha$ and $SiK\alpha$ refer to the areas of the respective peaks in EPMA. (●) Carbon, (○) silicon.

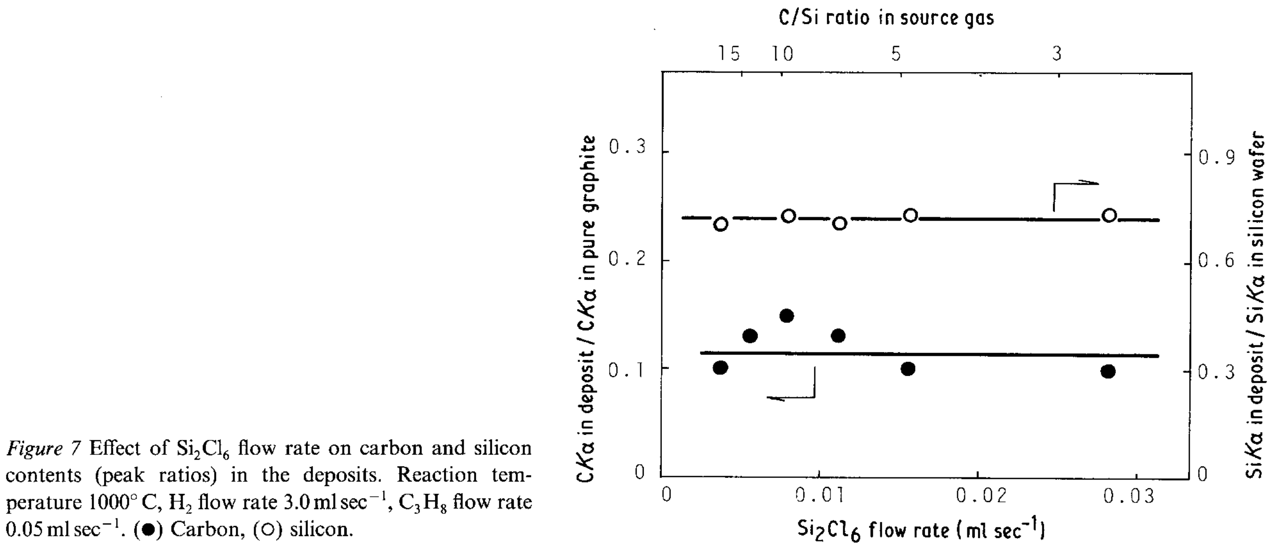

Figure 7 Effect of Si_2Cl_6 flow rate on carbon and silicon contents (peak ratios) in the deposits. Reaction temperature 1000° C, H_2 flow rate $3.0\,ml\,sec^{-1}$, C_3H_8 flow rate $0.05\,ml\,sec^{-1}$. (●) Carbon, (○) silicon.

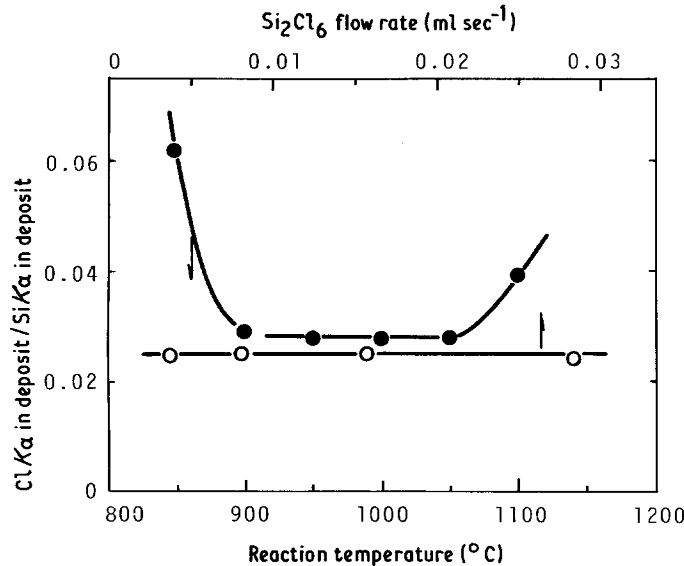

Figure 8 Effect of deposition parameters on the chlorine content (peak ratio) in the deposits. (●) H_2 flow rate $3.0\,ml\,sec^{-1}$, Si_2Cl_6 flow rate $0.016\,ml\,sec^{-1}$, C_3H_8 flow rate $0.05\,ml\,sec^{-1}$. (○) Reaction temperature 1000° C, H_2 flow rate $3.0\,ml\,sec^{-1}$, C_3H_8 flow rate $0.05\,ml\,sec^{-1}$.

stant value of about 0.03 at temperatures above 900° C. The high chlorine content at low reaction temperatures is presumably due to the co-deposition of some amount of polychlorosilanes with the SiC deposition. The reason for the increased chlorine content at the higher temperature of 1100° C is not clear at the present time.

It has been reported that the flank wear of TiN coatings increased exponentially with increasing chlorine content in TiN coatings [20]. Thus, it is considered that SiC layers with high resistance to wear are obtained in the reaction temperature range 900 to 1050° C because SiC layers with low chlorine contents are obtained.

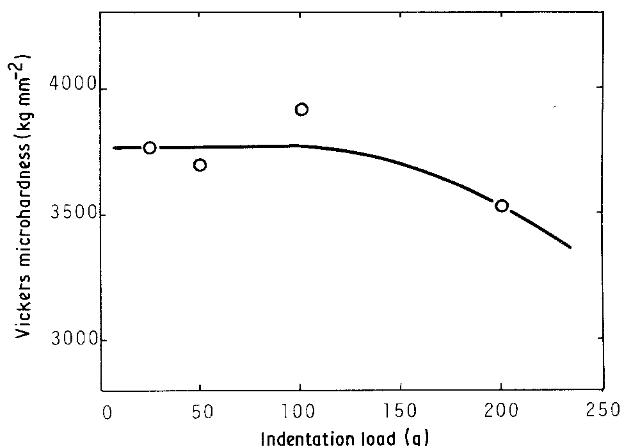

Figure 9 Room temperatures Vickers microhardness of the SiC coating layers. Reaction temperature 1000° C, reaction time 24 h, H_2 flow rate 3.0 ml sec^{-1}, Si_2Cl_6 flow rate 0.016 ml sec^{-1}, C_3H_8 flow rate 0.05 ml sec^{-1}.

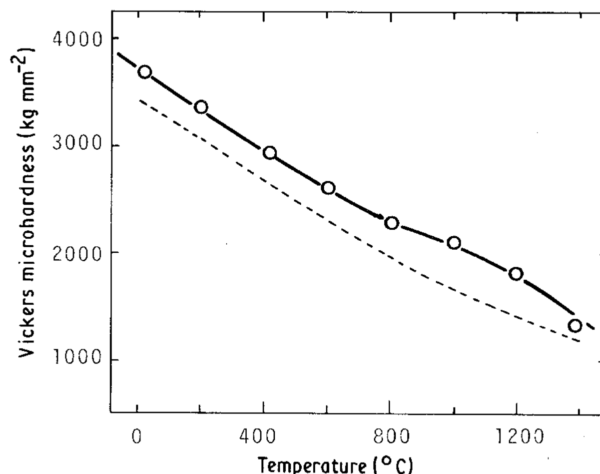

Figure 10 High-temperature Vickers microhardness of SiC coating layers. Deposition conditions are the same as for Fig. 9. (---) Data from Niihara [22].

3.3. Microhardness

The Vickers microhardness of an SiC layer obtained at 1000° C is shown in Fig. 9 as a function of the indentation load. A constant hardness value of about 3800 kg mm^{-2} was obtained in the indentation load range 25 to 100 g, and the hardness decreased gradually with increasing indentation load. These hardness values are higher than the reported values of 2600 to 3100 kg mm^{-2} [21] and 3400 kg mm^{-2} [22]. The change of hardness with indentation load is very similar to that of Si_3N_4 [23]. The dependence of the Vickers microhardness of layers deposited at 1000° C on the hardness measurement temperature is shown in Fig. 10, together with published data [23]. The Vickers microhardness decreased monotonically with increasing measuring temperature, and was about 2150 kg mm^{-2} at 1000° C. This pattern of hardness decrease with temperature is very similar to that reported by Niihara [22], except that values were 250 to 400 kg mm^{-2} higher at all measuring temperatures compared with his values of SiC, which were obtained at 1500° C.

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