SiC COATED GRAPHITE IN SEMICONDUCTOR APPLICATIONS

Julian Norley
UCAR Carbon Company Inc.
12900 Snow Road, Parma, OH 44130 USA

Introduction

CVD silicon carbide (SiC) coated graphite is finding increasing usage in the semi-conductor industry with applications in polysilicon reactors, silicon crystal growers, epitaxial susceptors and wafer fabrication. The SiC coating performs multiple functions, including prevention of oxidation and methanation, reduction of dusting and prevention of diffusion of impurities from the graphite. To be successful in this application the coating should be crack free and of sufficiently high purity to be used in the semiconductor applications.

The purpose of this study was to establish the desirable graphite thermal expansion and grain size requirements to produce crack-free coatings. The purity of the SiC coating has been determined to see whether it meets the standards for semiconductor applications. SiC coatings from six industrial coaters have been evaluated.

Experimental

The graphite grades used in the study are listed in Table 1. The superfine-grain graphite (SFGG) materials had an average particle size of <5 μm with coefficients of thermal expansion (measured from room temperature to 1200°C) varying from 4.86 to 6.38 x 10^{-6}/°C. The fine-grain graphite (FGG) and medium-grain graphite (MGG) had average particle sizes of 25μm and 640μm, respectively.

Graphite coupons of dimensions 50mm x 50mm x 12.5mm (t) were machined from each grade. The samples were surface ground with a 120-grit wheel. All edges were machine-radiused with a 1.6mm tool to minimize edge or corner cracking. Samples for glow discharge-mass spectroscopy (GD-MS) were of the flat cell type, being of dimensions 25 mm x 25mm x 3.2mm (t).

Samples of each grade were sent to six CVD coaters with the instruction to provide a gas-tight SiC coating of their highest purity. A methyltrichlorosilane/hydrogen mixture was used as the precursor. Temperatures were in the 1125-1200°C range, with pressures ranging from 10's of torr up to atmospheric. Coating times were of the order of four hours, with coating thicknesses in the 55 – 110μm range.

Coated samples from each vendor were weighed and measured to estimate coating thickness. Representative samples were examined by SEM to determine whether the coating was cracked. Oxidation testing was conducted at 650°C for 24 hours to measure gas-tightness. Coating purity was evaluated by GD-MS at Shiva Technologies. Samples were sectioned for optical microscopy to verify SiC coating thickness and uniformity.

Results and Discussion

Influence of Graphite Grain Size on SiC Coating

The medium-grain graphite studied had an average particle size of 640μm. For the range of coating thickneses investigated (55μm - 110μm), large surface pores could not be sealed. The interior of the pore is coated only with a very thin layer of SiC, this being insufficient to seal the graphite effectively from gas attack. By contrast, the average particle sizes of the fine-grain and superfine-grain graphite materials were of the order of 25μm and <5μm respectively. Surface pores in these materials were rapidly covered and sealed, rendering the graphite gas-tight provided the thermal expansion coefficient was in the right range as described below.

Influence of Thermal Expansion Coefficient on Cracking

There was no evidence of any cracking in the SiC coating for graphite thermal expansion coefficients in the range 4.86-6.38 x 10^{-6}/°C (RT-1200°C). This was verified both by SEM and by the more sensitive oxidation test. Any cracking present in the coating would have resulted in measurable weight loss during the oxidation test. Furthermore, thermal cycling of the coupons from room temperature to 1200°C, at a rate of 240°C/min for 20 cycles did not generate any cracking. By contrast, the low thermal expansion graphite (grade F) cracked on cooling from the coating deposition temperature. The average value of thermal expansion coefficient for this grade is 3.98 x 10^{-6}/°C. This is well below the thermal expansion coefficient of SiC (4.97 x 10^{-6}/°C)[1] with the result that the coating is placed in tension on cooling from the deposition temperature. Values of stress in the coating were calculated using the equation $\sigma = E\ (\alpha_{sic}-\alpha_g)/(T_d\text{-RT})$, where: E is the Modulus of SiC (460 GPa); α_{sic} and α_g are the average thermal expansion coefficients of silicon carbide and graphite, respectively, over the range RT-1200°C; and T_d is the coating deposition temperature (assumed to be 1200°C). These stress values are listed in Table 1. From these results, it is apparent that the coating can withstand compressive stresses up to 765 MPa but is less tolerant to tensile stresses, with cracking occurring somewhere in the range of 62 to 537 MPa. Based on this analysis the minimum graphite thermal expansion coefficient to achieve crack-free SiC coatings is somewhere in the range of 3.98 – 4.86 x 10^{-6}/°C. The study did not establish any maximum value of thermal expansion coefficient beyond which other coating failure mechanisms may be induced; however, there is no cracking problem in coating graphite substrates up to a thermal expansion coefficient of 6.38 x 10^{-6} °C^{-1}.

Purity Analysis of SiC Coatings

Samples from each coater were analyzed for purity of the SiC coating using GD-MS. The results are shown in Table 2. Measurements are in parts per million (ppm) unless indicated. Blanks in the table indicate values below detection limits [0.01 ppm for all elements except copper, potassium, calcium (0.05 ppm) and chromium (0.1ppm)]. Total impurity levels (oxygen, nitrogen and chlorine were not regarded as impurities) ranged from 1.9 to 9ppm, with an average of 4.5ppm. Typical semiconductor purity standards require <5 ppm total impurities. 50% of the data does not meet this standard and it can be argued that in some cases the purity is not as good as the graphite which it is sealing. The five major contaminants are: boron (1.4 ppm), iron (0.8ppm), potassium (0.5 ppm), aluminum (0.5 ppm) and sodium (0.3 ppm). The average iron levels are not acceptable for the more stringent semiconductor applications, although some coaters have attained < 0.1 ppm.

Conclusions

For SiC coating applications where gas-tightness is critical, SFGG and FGG materials are the most suitable. Crack-free coatings can be achieved over a graphite CTE range of 4.86-6.38 x 10^{-6}/°C (RT-1200°C). Cracking can occur for CTE's of < 3.98 x 10^{-6}/°C . Total impurity levels in SiC coatings average ~ 5 ppm.

References

[1] Morton Advanced Materials. Material Specification CVD Silicon Carbide, 1998. Morton Advanced Materials, Woburn, MA 01801.

Table 1. Summary of Graphite Grades

Substrate	Grain Size Category	Average CTE RT-1200°C x 10^{-6}/°C	Coating Stress MPa	Cracked
A	SFGG	4.86	62	No
B	SFGG	5.43	-251	No
C	SFGG	5.65	-371	No
D	SFGG	5.92	-514	No
E	SFGG	6.38	-765	No
F	FGG	3.98	537	Yes
G	MGG	5.13	-87	No
Coatable Grades		5.16-5.66	-103 to -375	
SiC		4.97		

Table 2. Summary of Purity Data on SiC Coatings

Supplier	Side	C wt%	Si wt%	N	O	Cl	B	Na	Mg	Al	P	S	K	Ca	Ti	V	Cu	Cr	Mn	Fe	Ni	W	Total
A	1	35	65	2400	2000	6.5	3.3	1.8		.6		.04	.6	.7	.02			.9		1.0			9.0
B	1	31	69	1000	2000	1100	.7	.3	.08	1.2	.03	0.6	1.0	.7	.03	.07	.1	.9	.02	1.4	.03	.25	7.4
	2	34	66	1300	1400	1300	.87	.08		.24	.01	.05	2.0	.8	.02	.07		.3	.03	0.3		.35	5.1
C	1	35	65	2000	800	2	1.3			.25		.2	.2					.05					2.0
	2	35	65	2000	1000	1	1.4	.1		.17		.1	.3	.2				.07		.05		.07	2.5
D	1	33	67	1500	240	3	.36	.4		.75	.14	.25	.1					.05		.09			2.1
	2	34	66	3000	900	3	.45	.2		.45	.27	.14	.2					.17		.09			2.0
E	1	36	64	8000	300	.8	.75	.05		.05	.08	.04						.10		.85			1.9
	2	36	64	4000	200	1.5	.8	.05	.1	.30	.05	.12	.2	.15	.2			.40	.15	3	1.5		7.0
E(2)	1	37	63	5000	4000	2	4.5	.40		.50	.08	.05	.15		.02					.05			5.8
Average		34.6	65.4	3020	1284	242	1.4	.34	.03	.45	.07	.16	.48	.28	.02	.02		.30	.03	.76	.16	.07	4.5
Stdev		1.7	1.68	2147	1160	507	1.4	.53	.03	.34	.08	.17	.61	.32	.06	.03		.33	.04	.98	.47	.13	2.7