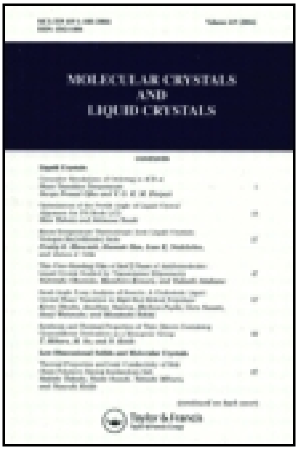

Molecular Crystals and Liquid Crystals

Silicon Dicarbide Synthesis

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SILICON DICARBIDE SYNTHESIS

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A method for the synthesis of the hypothetical silicon dicarbide structure is proposed. This structure with tetragonal symmetry has been synthesized in matrixes of hardened novolac with silicon powder. Thermal treatment up to 1200°C induces in these matrixes spiroconjugation features with subsequent organizing in tetragonal symmetry. XRD, HRTEM patterns and SAED confirmed that the hypothetical structures proposed are synthetically realizable.

Keywords: hardened novolac; pyroylisis; silicon dicarbide; tetragonal structure

INTRODUCTION

M. J. Bucknum and R. J. Hoffman have proposed a new hypothetical structure, described with the chemical formula SiC_2 like the parent carbon allotrope glitter [1]. Silicon dicarbide is a tetragonal structure with $\mathbf{a} = 3.07$ Å and $\mathbf{c} = 7.02$ Å and lies in space group $P4_2/mmc$, with 6 atoms in the unit of pattern and 2.61 g/cm^3 density. If the tetrahedral carbon atoms from glitter are replaced with tetrahedral silicon atoms and retains the trigonal carbon

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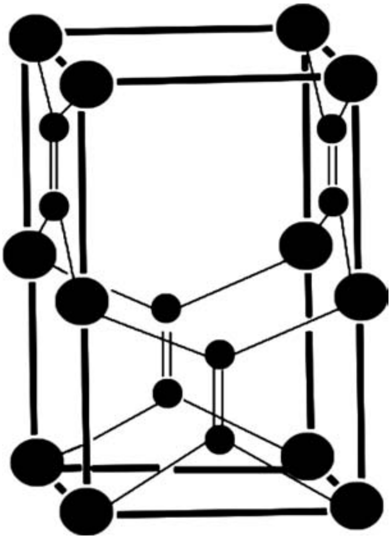

FIGURE 1 The elementary cell of silicon dicarbide (the large sized is silicon atom and the small is carbon atom) with $a = 3.07$ Å, $c = 7.02$ Å, $P4_2/mmc$.

atom pairs in the structure then is obtained the elementary cell of silicon dicarbide as shown in Figure 1.

The history of the silicon dicarbide (SiC_2) started with the spectroscopic survey of cool carbon stars (N stars) when in 1926 Merrill and Sanford observe un-catalogued blue-green bands in cool carbon stars. The green region, where the Merrill-Sanford bands of the SiC_2 molecule are prominent, was observed at 1 Å resolution [3]. In, 1984, the Smalley group achieved full rotational resolution of the 4977 Å band system of SiC_2 using resonant two-photon ionization accomplishing the reassigning $^1B_2 \rightarrow {}^1A_1$transition of a T-shaped SiC_2 ring, the Merrill-Sanford bands [4].

Through a targeted search of the literature, have been identified several experiments regarding to the silicon dicarbide synthesis.

Therefore in 1955, Kleman reproduces stellar bands in silicon-charged graphite furnace and ascribes them to SiC_2. Sakurai *et al.* [5] working with hydrosilicon-carbon oligomeric structures synthesized and partially characterized several “spiroquinoid” oligomers of a 1,4-disilaquinoid monomer,

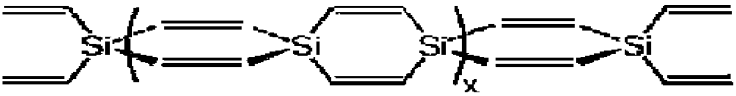

FIGURE 2 Spiroquinoid polymer of 1,4-disilaquinoid.

as shown in Figure 2. They correspond precisely to the substructures of a silicon dicarbide, SiC_2. It appears that the extension of the oligo-1,4-disilaspiroquinoid chain can be carried out essentially repeatedly.

Further, Naka *et al.* [6] synthesized "quinoid" oligomers of a 1,4-disilaquinoid monomer as are shown in Figure 3. They also contain substructures of the silicon dicarbide phase and appears that such chains extended indefinitely, just as in the case of the oligo-1,4-disilaspiroquinoid molecules.

There is enough evidence that another fundamental substructure of an eventual fully three-dimensional silicon dicarbide crystal structure, SiC_2, is synthetically realizable as well.

More recently our group working on Novolac pyrolysis with different adds of silicon powder observe some interesting features of spiroconjugation in C-SiC composites [7]. Studying these features, we identify a tetragonal phase similar with silicon dicarbide obtained from pyrolysis of Novolac matrix mixed with micron-sized silicon.

The Novlolac resin is well known because in the photoresist technology, this material in presence of UV sensitizer rises to well align phenolic molecules bridged with CH_2, methylenes, in 1–5 positions.

The Novolac resin hardened with hexamethylenetetramine (HMTA), that is a rich methlyene source, it connects the aromatics from novolac molecules in a proper configuration. During the hardening time a highly cross-linked lattice of the hardened novolac surrounds the silicon particles, embedded in the initial mixture. After a subsequent pyrolysis the hydrogen and OH-groups are released and the resulted lattice it reconfigures close to a SiC_2-spiroconjugated structure similar as Figure 2 and Figure 3.

Based on above considerations the principal aim of our work is to investigate the interaction between carbon structure with silicon powder and PCS (polycarbosilane) during the pyrolysis to obtain the spiro-substructures. The PCS decomposition is expected to release silicon at nanometric level or to have a catalytic effect due to the methylene or

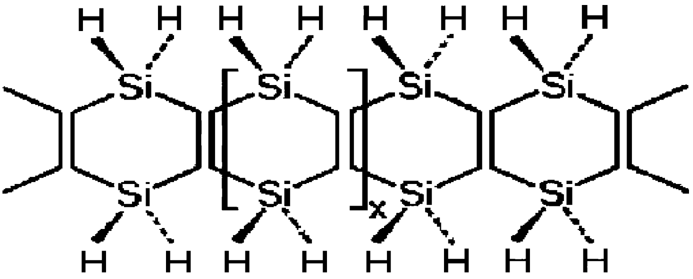

FIGURE 3 Quinoid polymer of 1,4-disilaquinoid.

methyl groups on spirostructures. A new experimental method that suggests a route for synthesis of this hypothetical tetragonal structures-silicon dicarbide is proposed.

EXPERIMENTAL METHOD

The starting materials for silicon dicarbide synthesis are the mixtures of Novolac-type phenolic resin with HMTA and Silicon or PCS powder.

PCS produced by plasma polymerization of HMDS (hexamethyldisilane) in Ar/H_2 as carrier gases are usual applied as precursors for SiC ceramics. PCS was synthesized in a homemade RF-reactor, 2.5 MHz, inductively coupled. The deposition conditions are: $2{,}6 \times 10^3$ Pa, monomer flux of 1.3 ml/h and 275 W plasma power discharge.

The Novolac resin of commercial use, micron size powder, 10% wt hardener (HMTA) and 5 wt% micron size Silicon powder are homogenized in ethylic alcohol (the percents are reported to Novolac). Another mixture is Novolac type phenolic resin and HMTA were mixed and homogenized with PCS powder (5% wt reported at Novolac) in ethylic alcohol.

After homogenization in ethylic alcohol the mixtures were transferred in sintered Alumina boat and dried for 24 h at 70°C.

The following steps were hardening and pyrolysis. Hardening: samples have been heated under Ar atmosphere with 2°C/min up to 300°C and hold for 30 min., followed by a free cooling till room temperature. During the hardening it takes place the connecting by methylenes of the aromatics from Novolac, resulting a high cross linking lattice in a specific configuration, close with spiroconjugated ones, containing embedded silicon particles.

Pyrolysis: the samples were heated with 5°C/min up to 300°C and then with 3°C/min up to the pyrolysis temperature. The soaking time for each sample was established at 30 min. Finally the samples were free cooled to room temperature.

Depending on the final pyrolysis temperature and the starting materials the samples were indexed as in Table 1.

An X-ray powder diffraction (XRD) pattern of the samples was collected using Bruker D8 powder diffractometer equipped with a copper target X-ray tube and a diffracted-beam monochromator. The samples were packed into disk "well holder" with 25 mm diameter and 2 mm deep. We used fixed 1 degree and antiscatter slits and an 0.6 mm receiving slit for all the samples.

Philips CM120ST (Customized Microscope 120 Super Twin) was used for collecting the high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) images.

TABLE 1 The Index of the Samples Depending on the Final Pyrolysis Temperature and the Starting Materials

Sample	Sample Cod	Hardening temperature (°C)	Pyrolysis temperature (°C)	Sample index
Novolac 10% HMTA 5% PCS	NHPCS	300	900	900-NHPCS
(in bulk)			1200	1200-NHPCS
Novolac with 10% HMTA and 5% Si	NHSi	300	800	800-NHSi
(in bulk)			1200	1200-NHSi

RESULTS AND DISCUSSION

The XRD pattern on NHPCS shows only a conversion of Novolac to turbostratic –like structure showed in Figure 4. That is a consequence of the high thermal stability of PCS up to 1200°C.

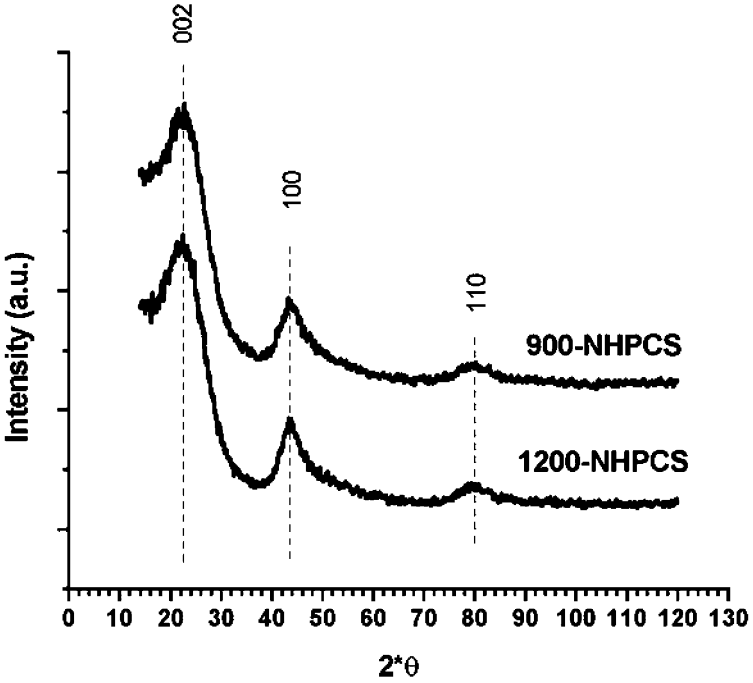

FIGURE 4 XRD pattern on NHPCS at 900 and 1200°C.

The number of graphene sheets, L_c, which are stacked in a roughly parallel layers is estimated from the width of the (002) Bragg peak and the lateral dimension La of the graphene sheets which is estimated from the width of a particular set of powder diffraction peaks (the (100) and (110) peaks), both using the Debye-Scherrer formula. The turbostratic-like structures developed in NHPCS are small domains with: $L_C = 12.5\,Å$, $L_A(100) = 21.03\,Å$ and $L_A(110) = 17.4\,Å$. These dimensions indicate small free graphene sheets in samples.

Figure 5 presents the XRD pattern on NHSi and the corresponding theoretical index of diffraction lines of SiC_2. From this pattern in NHSi samples are observed three different phases: silicon dicarbide, glitter and turbostratic-like structures. In this case, the turobstratic-like structures developed in NHSi are domains with: $L_C = 12.8\,Å$, $L_A(100) = 20.8\,Å$ and $L_A(110) = 16.4\,Å$. For both samples, NHSi and NHPCS, the dimensions calculated have similar values. This means the silicon and PCS favors the forming of the small graphene sheets during the Novolac pyrolysis.

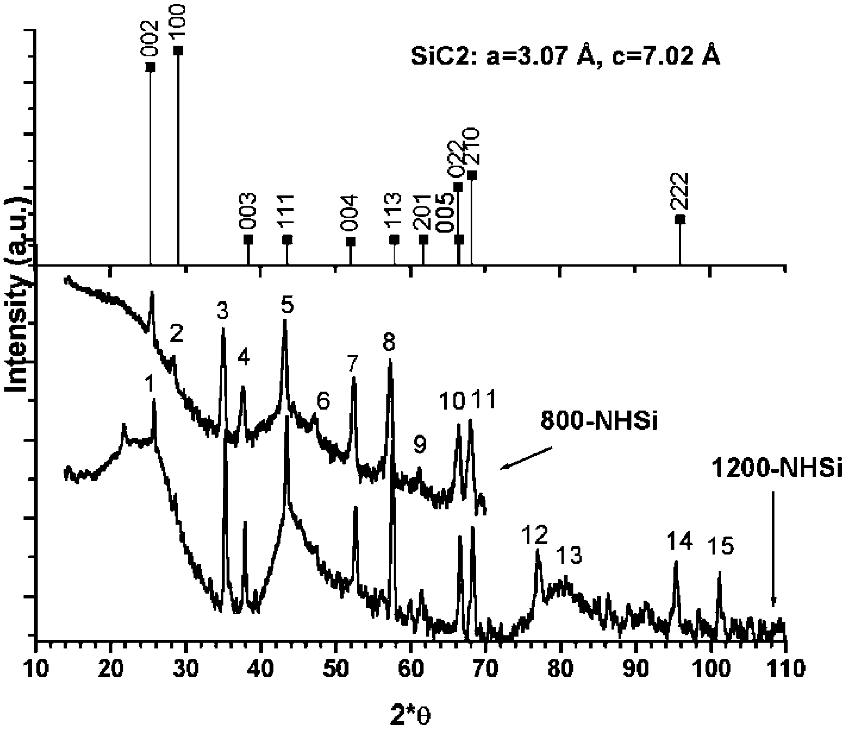

FIGURE 5 XRD pattern on NHSi at 800 and 1200°C and indexed diffraction lines of SiC_2.

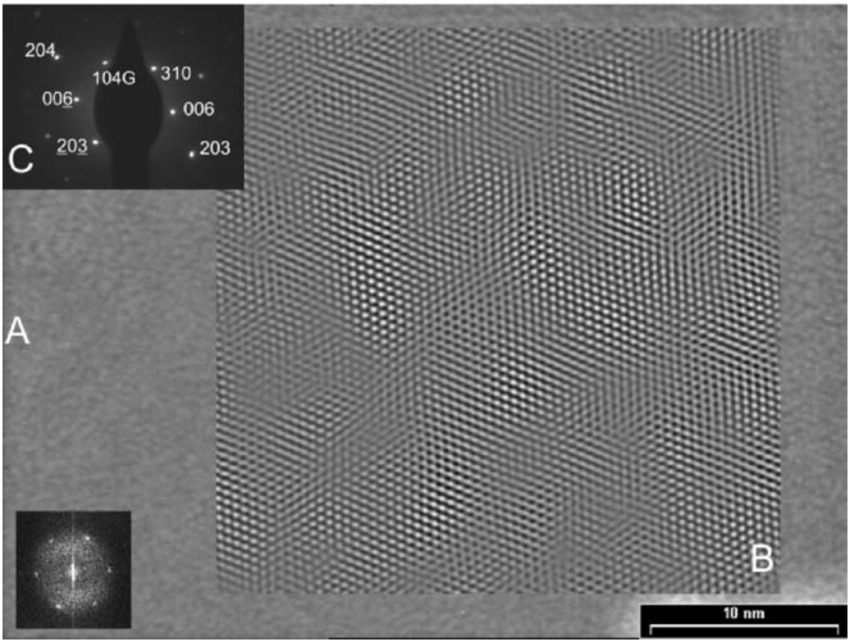

FIGURE 6 TEM/SAED of NHSi: a) TEM image of well ordered area, b) details of this area and c) SiC_2 and Glitter ((204) and (104) lines) as identified by SAED.

A representative TEM and SAED images are shown in Figure 6. In the TEM image (Figure 6A) was identified a well ordered area with details in Figure 6B. Visible, the well ordered domains have structures similar with SiC_2 and Glitter as identified using SAED (Figure 6C).

Table 2 presents the experimental data (XRD and SAED) and the matching with theoretical calculations of silicon dicarbide and glitter structures.

CONCLUSION

The presence of Silicon in cross-linking Novolac and their pyrolysis has a favorable effect to give the spiroconjugation substructures, which are transforming into a tetragonal structure of silicon dicarbide and small quantity of glitter, beside large amount of free graphene sheets. XRD, HRTEM patterns and SAED of NHSi samples confirm the three phases which are well defined. (corresponding to the silicon dicarbide structure, glitter and turbostratic-like structures). On the other hand, due to the high thermal stability of PCS, the interactions between Novolac and PCS during the

TABLE 2 The Correspondences between the Experimental and Theoretical Data

	Experimental						Theoretical					
	800-NHSi XRD		1200-NHSi XRD		TEM/SAED		SiC_2: a = 3.07 Å, c = 7.02 Å			Glitter a = 2 Å.53, c = 5.98 Å		
Peak no.	d(Å)	2θ	d(Å)	2θ	hkl	d(Å)	hkl	d(Å)	2θ	hkl	d(Å)	2θ
1	3.47	25.6	3.46	25.7			002	3.51	25.37			
2	3.14	28.4	3.12	28.6			100	3.07	29.08			
3	2.56	35	2.54	35.3						100	2.53	35.48
4	2.39	37.6	2.37	37.9			003	2.34	38.4			
5	2.09	43.2	2.07	43.5			111	2.07	43.6			
6	1.92	47.2								102	1.93	47.04
7	1.74	52.4	1.69	52.7			004	1.75	52.1			
8	1.60	57.3	1.59	57.6			113	1.59	57.9			
9	1.51	61.2	1.50	61.5			201	1.49	61.8			
10	1.40	66.4	1.40	66.6			022	1.40	66.4			
							005	1.40	66.6			
11	1.37	68	1.37	68.3			210	1.37	68.3			
					203	1.28	203	1.28	73.8			
					104	1.29				104	1.29	73.5
12			1.23	77						021	1.23	77.05
13			1.19	80.4						005	1.19	80.26
					006	1.17	006	1.17	82.43			
14			1.04	95.4								
15			1.001	101.2						006	0.99	101.3
					310	0.971	310	0.970	105.1			
					204	0.97				204	0.965	105.9

pyrolysis give just turbostratic-like structure with small free graphene sheets in samples. Finally Novolac with HMTA and Si is a good precursor in building of spiro structures confirming the hypothetical structures proposed.

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