

THE EFFECT OF SILICON IN SYNTHESIS OF THE TETRAGONAL STRUCTURES: SILICON DICARBIDE AND GLITTER

Ioan Stamatina¹, Anca Dumitru¹, V. Ciupina², G. Prodan², Adina Moroza¹

¹*University of Bucharest, Faculty of Physics, 3-NANO-SAE Res. Center, Bucharest, MG-11, 76900, Romania*

²*“Ovidius” University of Constanta, Bd. Mamaia 124, Constanta, Romania*

Corresponding author e-mail address: ancad@polymer.fizica.unibuc.ro;

ancadumitru@lycos.com

Introduction

Silicon dicarbide and glitter are two tetragonal structure theoretically proposed by M.J. Bucknum and R.J. Hoffman [1]. Silicon dicarbide is a tetragonal structure with $a = 3.07 \text{ \AA}$ and $c = 7.02 \text{ \AA}$ and lies in space group $P4_2/mmc$, with 6 atoms in the unit of pattern and 2.61 g/cm^3 density, described with the chemical formula SiC_2 [1,2]. Glitter is a heretofore-hypothetical tetragonal allotrope of carbon first reported in 1994, as a theoretical construction, by Bucknum and Hoffmann with the theoretical dimensions of the lattice are $a = 2.53 \text{ \AA}$ and $c = 5.98 \text{ \AA}$ and lies in space group $P4_2/mmc$. It is a 3-,4-connected net containing trigonal and tetrahedral atoms in a ratio of 2:1, with a calculated density of 3.12 gm/cm^3 ; intermediate between graphite and diamond.

Working on novolac resin (a phenol-formaldehyde resin similar to Bakelite) pyrolysis with add-on of silicon powder it was identified two tetragonal phases similar with silicon dicarbide (observed in C-SiC composites [3]). Combining the novolac property which have a great affinity to methylenes with a rich methylene source as HMTA (hexamethylenetetramine), have been elaborated an experimental procedure with aim to synthesise tetragonal structures, glitter and silicon dicarbide [4-6].

The paper aim is provide supplementary data to the estimation the effect of silicon in synthesis of tetragonal structures. The role of silicon in synthesis of the tetragonal structures was established for the samples obtained from novolac matrix deposited onto silicon substrate and the bulk samples of novolac matrixes mixed with different adds of silicon.

Transmission electron microscope (TEM), selected area diffraction (SAED), X-ray diffraction (XRD) and Raman spectroscopy were used to characterize the synthesis products of the thermal treatment. The results show a good correspondence between diffraction pattern and theoretical estimations of silicon dicarbide and glitter. Also Raman gives some supplementary peaks beside G and D regularly carbon structures.

Experimental Details

The starting materials are: the novoloc resin- type phenol-formaldehyde condensation similar with Bakelite, crosslinked agent called hexamethylenetetramine (HMTA) and silicon powder. Two types of samples thin were investigated: bulk and thin film deposited onto silicon substrate.

Bulk samples: The mixture for the bulk samples were the resin, hardener (HMTA) and silicon powder. Novolac resin and HMTA (10% wt) were mixed with different percent of silicon 5, 10 and 15% wt (reported at novolac resin) in ethylic alcohol. After homogenization in ethylic alcohol the mixtures were transferred in sintered Alumina boat and after that dried for 24 h at 70 °C in air.

Thin layer samples: Novolac resin with 10%wt HMTA (reported at novolac resin) have been ultrasonically homogenized in ethylic alcohol and deposited by spin coating onto silicon substrate with a subsequent drying in similar conditions.

The process will follow the next steps for all samples: hardening and pyrolysis.

Hardening: The curing samples took place in oven under Ar atmosphere and heated with 2°C/min up to 300°C, 30 min soaking time with free cooling in final stage. During the hardening it takes place the connecting by methylene groups of the aromatics from novolac resin then result a high cross linking lattice. For the bulk samples the hardening leads to a high cross linking lattice of novolac resin containing embedded silicon particles.

Pyrolysis: samples were heated with 5°C/min and then 3°C/min up to final pyrolysis (holding) temperature. The soaking time for each sample was established at 30 min. Finally the samples were free cooled to room temperature. Depending on the pyrolysis temperature and the starting materials the samples were indexed as in Table 1.

Table 1. Samples indexing

Sample	Cod	Hardening temperature (°C)	Pyrolysis temperature (°C)	Sample indexing
Novolac 10% HMTA 5% Si (in bulk)	NHSi	300	800	800-NH_5%Si
			900	900- NH_5%Si
			1200	1200_ NH_5%Si
Novolac resin with 10%HMTA and 10% Si (in bulk)	NHSi	300	1200	1200- NH_10%Si
Novolac resin with 10%HMTA and 15% Si (in bulk)	NHSi	300	1200	1200- NH_15%Si
Novolac resin with 10% HMTA in thin layer, onto Si substrate	NH	300	700	700- NH
Novolac with 10% HMTA in thin layer, onto Si substrate	NH	300	800	800- NH

X-ray powder diffraction (XRD) pattern of the samples was collected using Bruker D8 powder diffractometer utilizing Cu K α radiation ($\lambda=1.548$ Å) and 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 0.5 degree at incident plan and antiscatter slits and a 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.

The Raman spectrum was collected with Raman spectrometer, model 2001, Ocean Optics, using as source GaAs laser diode with power 500 mW. The range of measurements: 0 -2800 cm $^{-1}$ with step of 1.36 cm $^{-1}$.

Results and Discussions

Figure 1 show the XRD patterns of NHSi with 5, 10 and 15% adds of silicon after a thermal treatment at 1200°C. In Figure 2 are presented the XRD patterns of NH_5%Si at different temperatures. The sharp peaks from Fig. 1 and Fig.2 were from silicon dicarbide and glitter phases identified in Table 1. The experimental dates and the matching theoretical calculations of silicon dicarbide and glitter structures are presented in the Table 2. From these patterns the bulk samples are observed to have three different phases: silicon dicarbide, the carbon allotrope glitter and turbostratic-like graphite structure.

It is well known that a typical carbon structure obtained at low temperatures (500–1200°C) exhibits a XRD pattern consisting of a few broad bands located near the (002), (100) and (110) reflections of graphite.

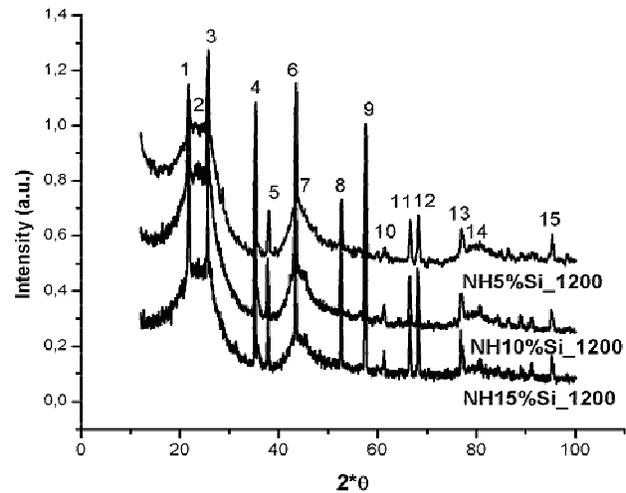


Figure 1 XRD patterns of NHSi with different adds of silicon after pyrolysis at 1200°C

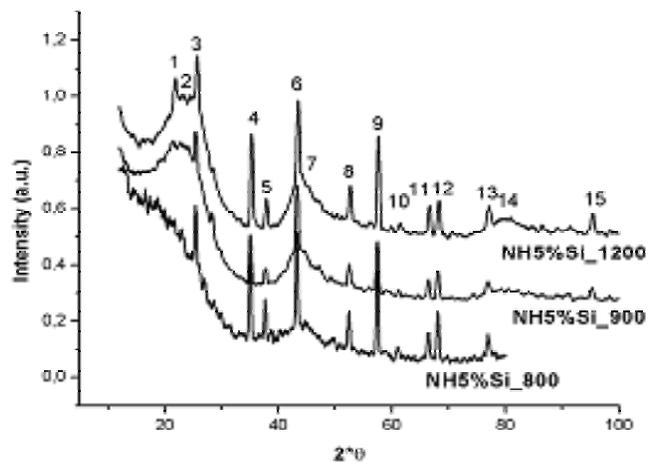


Figure 2 XRD patterns of NH_5%Si at different pyrolysis temperatures

Table 2. The correspondences between the experimental and theoretical data of the bulk samples

Peak No.	Experimental		Theoretical						Observations
	1200_NH_5%Si		SiC ₂ : a=3.07 Å, c=7.02 Å			Glitter: a=2 Å.53, c= 5.98 Å			
	d(Å)	2θ	hkl	d(Å)	2θ	hkl	d(Å)	2θ	
1	4,07	21.8							N/A
2	3,76	23.65							Disordered carbon structure close with graphite (002)
3	3,47	25.6	002	3.51	25.4				Al ₂ O ₃ (d=3,48)
4	2,54	35.2				100	2.53	35.5	Al ₂ O ₃ (d=2,55)
5	2,38	37.8	003	2.34	38.4	011	2.33	38.6	Al ₂ O ₃ (d=2,38)
6	2,08	43.4	111	2.07	43.6				Al ₂ O ₃ (d=2,09)
7	2,05	44.2							Disordered carbon structure close with graphite (101)
8	1,74	52.6	004	1.75	52.1				Al ₂ O ₃ (d=1,74)
9	1,6	57.5	113	1.59	57.9				Al ₂ O ₃ (d=1,62)
10	1,51	61.35	201	1.49	61.8				
11	1,4	66.55	022	1.40	66.4				
			005	1.40	66.6				
12	1,37	68.25	210	1.37	68.3				Al ₂ O ₃ (d=1,37)
13	1,24	76.85				021	1.23	77.0	Al ₂ O ₃ (d=1,23)
14	1,2	80							Disordered carbon structure close with graphite (110)
15	1,04	95.25	222	1.03	96.0				Al ₂ O ₃ (d=1,09)

*N/A Not Assigned

In this case, the turbostratic-like graphite structures developed in the bulk samples contain domains with: R, L_C, L_A(100), and L_A(110) presented in Table 3. 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 L_A 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. Liu et al. [7] showed how the empirical parameter R could be used to estimate the fraction of graphene sheets which have no parallel neighbor in the samples. R is defined in Fig. 3, and measured as the ratio of the height of the (002) Bragg peak to the background.

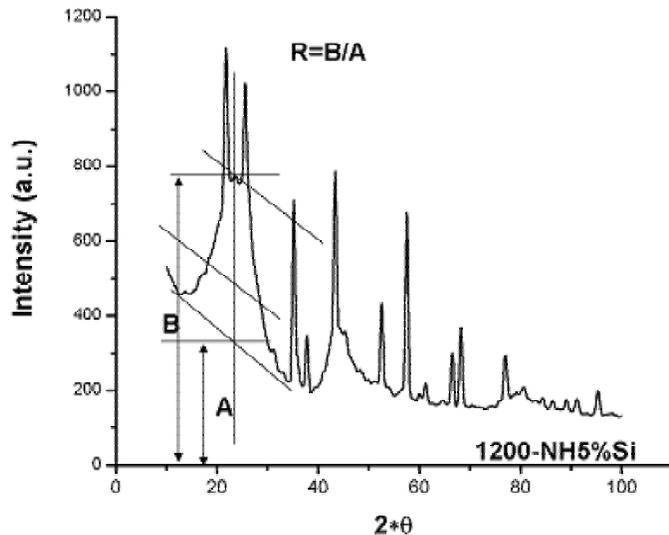


Figure 3. Schematic representation of the definition of the empirical parameter R for 1200-NH5%Si

R is defined in Fig. 3, and measured as the ratio of the height of the (002) Bragg peak to the background.

Table 3. R , L_a and L_c for all the samples indexed as NHSi

Samples	$R(\text{\AA})$	$L_c(\text{\AA})$	$L_a(100) (\text{\AA})$	$L_a(110) (\text{\AA})$
800- NH_5%Si	1.31	12.63	18.69	N/A
900- NH_5%Si	1.91	12.84	18.53	18.18
1200- NH_5%Si	2.20	12.86	20.87	16.42
1200- NH_10%Si	2.51	13,82	22,4	21,14
1200-NH_15%Si	2,36	12,09	22,65	23,45

For the bulk samples the free graphene dimensions calculated have approaching values. This means that the silicon favor the formation of small graphene sheets during the novolac resin pyrolysis.

Figure 4 show the XRD patterns of NH at 700^oC (for 800^oC, XRD pattern are same) pyrolysis temperatures. In Table 4 are shown the experimental dates and the matching theoretical calculations of silicon dicarbide and glitter structures. Due to the very strong diffraction peak of silicon substrate was necessarily to detail the XRD patterns for detecting the diffraction peaks of the samples. The correspondences between the experimental and theoretical data for thin film samples could be observed the presence of both phases: silicon dicarbide and glitter.

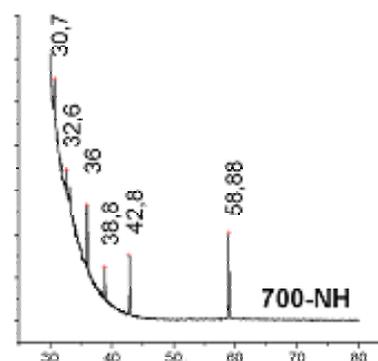


Figure 4. XRD patterns of 700-NH

Table 4. The correspondences between the experimental and theoretical data for thin film samples

Experimental		Theoretical						Observations
700- NH		SiC ₂ : a=3.07 Å, c=7.02 Å			Glitter: a=2 Å.53, c= 5.98 Å			
d(Å)	2θ	hkl	d(Å)	2θ	hkl	d(Å)	2θ	
2,9	30,7				002	2,99	29,9	
2,74	32,6	011	2,81	31,8				
2,49	36				100	2.53	35,5	
2,31	38,8	102	2.31	38,9	011	2.33	38,6	
2,1	42,8	110 111	2.17 2.07	41,6 43,6				Graphite rhom. (d ₍₁₀₁₎ =2,1;) or Al ₂ O ₃ (d=2,09)
1,56	58,88				013	1.56	58,9	

In Figure 5 are presented the Raman spectra for the bulk samples at 1200^oC pyrolysis temperature. The Raman spectroscopy shows the D and G Raman shifts at 1275 cm⁻¹ and 1572 cm⁻¹, due to the presence of disordered carbon structure. In addition, Raman spectrum is presented a peak at 138 cm⁻¹, which are not attributable to disordered carbon structure

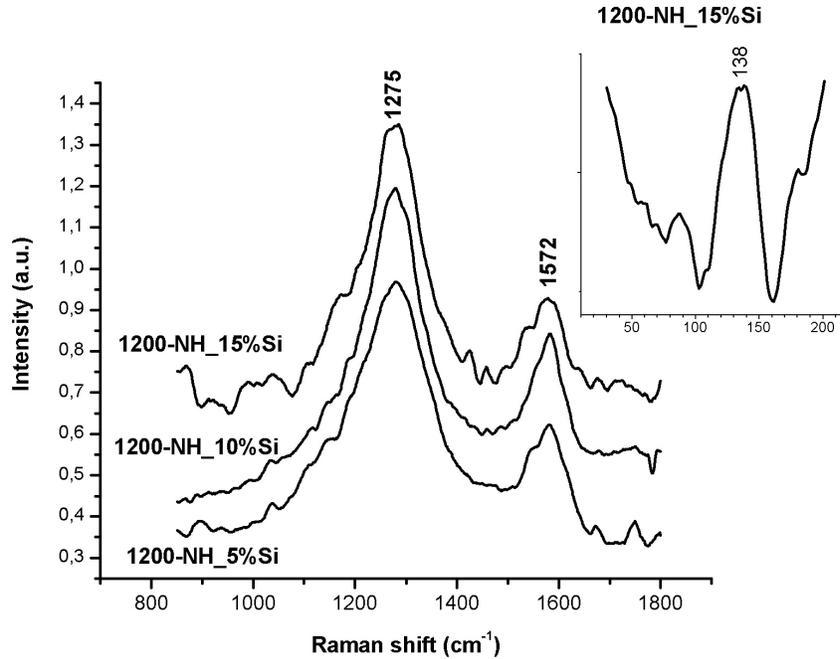


Figure 5. Raman shift of NHSi with different adds of silicon after pyrolysis at 1200°C

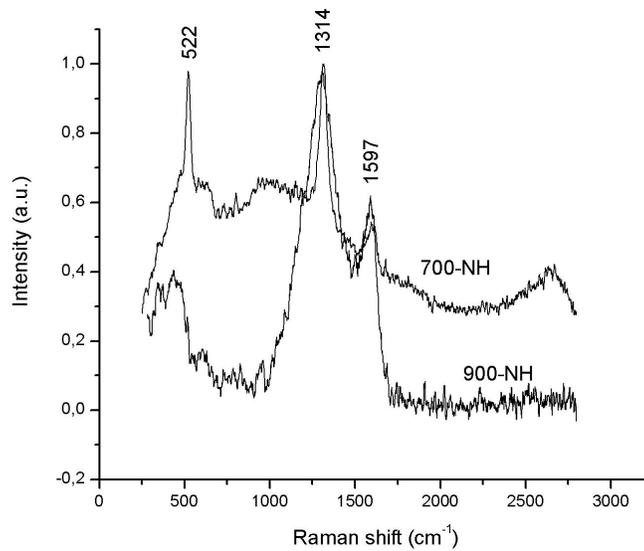


Figure 6. Raman spectra of NH samples at 700 and 900°C

Raman spectra for thin film samples are presented in Figure 6. They show D and G shifts due to the disordered carbon structure. The Raman peak at 522 cm^{-1} is attributed to the silicon substrate. It could be observed that D Raman shift for the thin film samples compared with bulk samples is shifted with 36 cm^{-1} to regularly D line placed at 1350 cm^{-1} . When novolac resin is simple pyrolyzed, with no curer, and graphitized D and G are very close to a turbostratic carbons and gives the evolution of the graphene stacking

along c-axis. In the presence of HMTA the methylene bridges many aromatics hindering the tendency to flattening and condensation in graphene. It is more possible as many aromatics in the polycondensation process to take positions in spiroconjugation. In this case Raman lines are shifted down to lower frequencies.

Representative selected area electron diffraction (SAED) image is presented in Figure 7 with correspondent assignments in table 5. They show a good matching with theoretical calculations for silicon dicarbide structures.

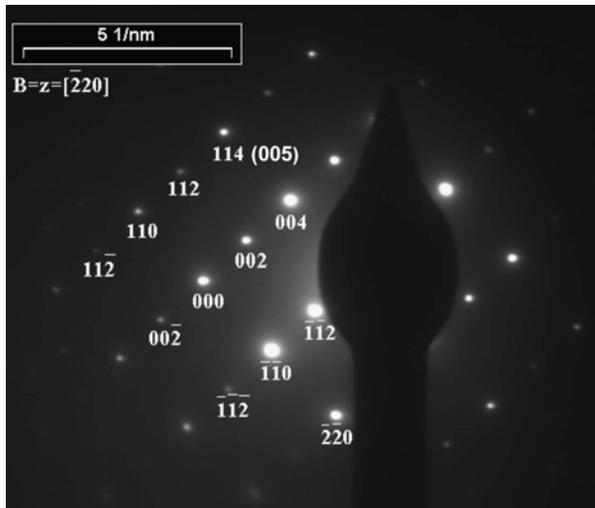


Table 5. The correspondences between SAED and theoretical data

SAED		Theoretical SiC ₂ : a=0,27 Å, c=7,02 Å	
		hkl	d (Å)
002	3,55	002	3,51
110	2,13	110	2,17
112	1,84	112	1,84
004	1,70	004	1,75
114	1,40	114	1,36
		005	1,40
220	1,08	220	1,08

Figure 7. Representative SAED of 1200-NH_15%Si

Conclusions

The presence of silicon either as substrate for thin film samples or powder mixed with novolac resin for bulk samples give the tetragonal structures: silicon dicarbide and carbon allotrope glitter, after thermal treatment. XRD patterns and SAED of NHSi samples confirm the three phases which are well defined which are attributable to the silicon dicarbide structure, glitter and turbostratic-like structures. In the XRD patterns the diffraction peaks could be interpreted either as silicon dicarbide and glitter or as alumina diffraction due to some impurities (Al and O) presented in the starting materials.

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