Synthesis of SiC from poly(silyne-*co*-hydridocarbyne) under CO_2 atmosphere

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It is well known that advanced ceramics from polymer precursor have been producing upon heating under an ambient and inert atmosphere, like argon or nitrogen gases over 40 years. However, the effect of these gases on the production and on the crystal form of ceramic obtained are not well understood during thermal treatments. Here, we report to demonstrate a novel, simple and a common method for the production of crystalline SiC ceramic species using a polymeric precursor, which is poly(silyne-co-hydridocarbyne) (PSC), upon heating under an ambient and CO_2 atmosphere. The Raman and X-ray analysis showed that polycrystalline SiC production was successfully achieved at 1000 and 750°C under CO_2 atmosphere. Amorphous ceramic material was obtained at 500°C under CO_2 atmosphere. Also, the results showed that SiC powder produced under CO_2 has not crucial differences in crystal forms that is produced under argon atmosphere. SiC produced at 1000°C is mostly Moissanite-5H, at which temperature there is also a small amount of Moissanite-8H and Moissanite-84R. SiC produced at 750°C is mostly Moissanite-5H. There is also the trace of Moganite and Coesite, which are crystal forms of SiO_2. As a result, the type of produced SiC depends on process temperature and production atmosphere.

Keywords: Electropolymerization; pre-ceramic polymer; silicon carbide; ceramic

1. INTRODUCTION

Organo-silicon compounds have been widely recognized over 40 years as polymeric precursors for the production of advanced ceramics. Unlike the conventional synthesis procedures, they can be adopted to plastic-forming techniques such as fiber spinning, foaming, extrusion, injection molding or resin transfer molding to generate some special components in desired shape, or advanced ceramics known as polymer-derived ceramics or PDCs by pyrolysis above 750°C, especially under a non-oxidative atmosphere like nitrogen or argon atmosphere [1–12]. Pre-ceramic polymers are an important class of polymers since they stand as the interface between polymers and ceramics [2, 3, 10]. They easily produce ceramic materials upon moderate heating. Generally, the most crucial properties of these types of polymers are to form tough, hard-wearing ceramic materials with high thermal stabilities. A many kinds of ceramics that is not achievable by other techniques can be produced by using polymeric precursors. The composition of ceramic strictly depends on the nature and chemistry of polymeric precursors [1-12]. For example, an amorphous SiCO residue is produced from silicones upon heating in a non-oxidative atmosphere, which is considered as a silica glass [5-8]. Polysilazanes, another well investigated class of preceramic polymers, yield a SiCN ceramic at low pyrolysis temperature and after further heating to higher temperatures a similar microstructural evolution in materials will take place to form Si_3N_4 and SiC nano-sized regions [9]. Moreover, PMSi forms silicon carbide (SiC) [10,11], or PHC easily yields diamond and diamond-like carbon (DLC) [12] via pyrolysis under argon atmosphere. Likewise, since it already contains silicon and organic carbon atoms on its backbone, poly(silyne-co-hydridocarbyne) (PSC) can be transformed into silicon carbide without requiring additional carbon source and a catalyst [2].

Silicon carbide (SiC) is a wide band gap semi-conducting material and exhibits many excellent properties for high temperature, high frequency and high power applications. SiC has extensive usage such as in field emission display, nanosensors and nanoscale electro-devices [7]. Besides, SiC is used an abrasive and a wear resistant material in the form of powder or protective coatings, and also widely used in high temperature and high power electronic devices. In addition, amorphous SiC thin film has been recently used as a functional material for micro-electro-mechanical systems (MEMS) to prevent corrosion [8, 9].

The synthesis of silicon carbide (SiC) is accomplished with methods such as carbon nanotubes-confined growth [13], chemical vapor deposition (CVD) [14] and carbon-thermal reduction with catalyst [15] or without catalyst [16] etc. However, the most of these synthetic approaches comprise of complicated processes and manipulations. For example, it is quite difficult to get rid of the resident metal catalyst from the vapor–liquid–solid growth process, or CVD needs some complex equipment with well-controlled

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atmosphere. The method for the production of ceramics via pyrolysis using polymeric precursors has been applying since 1970's [17]. The advantages of this method are to be low impurity level and low cost production, to yield homogeneous element distribution, and to need low processing temperatures [2, 3, 10-12]. SiC can also be formed as a film upon heating on a surface because polymeric precursors are soluble in common organic solvents like, THF or chloroform etc [2, 3, 10-12].

In this research project, PSC was synthesized and characterized as reported in references 2 and 3 and its structure is presented in Figure 1. Advanced ceramic, like SiC, is mostly produced via thermal process of polymeric precursor under an inert media i.e. argon (Ar) or nitrogen (N_2) gas during thermal process [1-12]. In this article, it is aimed to investigate the type of SiC produced from PSC upon heating under CO_2 atmosphere. There is no such a work to demonstrate the production of SiC under CO_2 atmosphere.
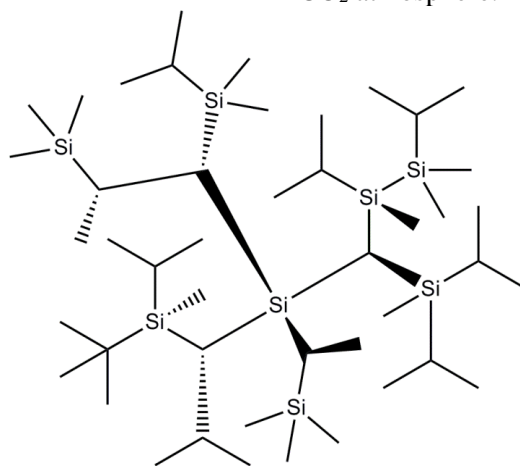

Fig. 1. Schematic representation of structure of poly(silyne-co-hydridocarbyne).

2. EXPERIMENTAL

2.1 Materials and methods

The reagents were bought from Sigma-Aldrich and used without further purification. The chemicals and materials used are trichloro(dichloromethyl) silane (96%), dimethoxy ethane (DME, anhydrous, 99.5%), tetrabutylammonium tetrafluoroborate (TBAFB, 99%), lithium aluminum hydrate (LAH, powder, 95%), methyl lithium (MeLi, 3.1 M in diethoxymethane), 430 stainless steel and copper electrode.

2.2. Equipment

The electrolysis of monomer was done via a DC power supply. [1]H Nuclear Magnetic Resonance (^{1}H-NMR) spectra were obtained using a Bruker-Spectrospin Avance DPX 400 Ultra-Shield (400 MHz, CDCl₃ solvent). Attenuated Total Reflectance-Fourier Transform Infrared (FTIR) spectra were collected using a Bruker Vertex 70 spectrophotometer by an Attenuated Total Reflectance (ATR) module. UV/visible spectra were taken using an HP8453A UV/visible spectrometer (Hexane as solvent). Gel Permeation Chromatography (GPC) was performed by a Perkin-Elmer Series 200 apparatus with a refractive index (RI) detector using TSKgel AM GPC Gel column and N,N-dimethyl form amide (DMF) eluent at a flow rate of 1.0 ml/min and calibrated via

polystyrene standards. Heat treatment of the polymer was carried out in an alumina ceramic boat using Protherm brand PTF12/50/450 model a tube furnace fitted with an alumina tube under a constant flow of carbon dioxide (CO_2). FEI Quanta 250 FEG instrument was run for Scanning electron microscopy (SEM). Raman spectroscopy was carried out using a Bruker FRA 106/S spectrograph fitted with a He-Ne laser (wavelength 532 nm) as the excitation source. X-ray diffraction (XRD) patterns were taken with a Rigaku Miniflex Diffractometer and CuKα (30 kV, 15 mA, λ=1.54051 Å) radiation. Scanning was done between 5∘<2θ<100∘. All measurements were made with 0.05 degree steps and 2 degree/minute rate. The divergence slit was variable, and the scattering and receiving slits were 4.2 degrees and 0.3 mm, respectively.

2.3. Synthesis of poly(silyne-co-hydridocarbyne)

The synthesis and characterization of PSC was performed as reported in references 2 and 3. Shortly, electrochemical synthesis of PSC was accomplished in 250 ml of an undivided cell. A 2 ml of trichloro(dichloro methyl) silane (0.007 M, in 60 ml DME) and 200 mg of TBAFB (0.01 M, in 60 ml DME) was mixed in 60 ml of DME to prepare electrolyte solution while it was purged with Ar. The cell was equipped with a 430 stainless steel as the cathode (10 cm × 5 cm × 0.5 mm) and copper as the

anode (10 cm × 5 cm × 0.5 mm). −8.0 V potential was applied to achieve the electrolysis for 8 h at room temperature and under Ar atmosphere. Once the electrolysis was finished, 150 mg of LAH was added to the solution and refluxed for 12 h. After evaporation of solvent and then re-dissolving the residue in DME, 4 ml of MeLi (3.0 M in DME) was added dropwise into this solution to replace chlorine atoms with methyl substituents, which makes PSC resistant against moisture being in the air by increasing hydrophobicity of the polymer backbone. The polymer formed was a light-brown powder and about 70% yields as reported in references 2 and 3.

2.4. Synthesis of SiC

SiC was synthesized and characterized as reported in previous works [2,3, 10-12]. Shortly, PSC was put into alumina ceramic boats and then heated at 1000◦C, at 750◦C and at 500◦C in a tube furnace under CO_2, at a ramp rate of 10◦C/min, held for 24 h to produce SiC and then cooled to room temperature. The crystalline SiC obtained was about 25% yields. All SiC samples were characterized by Raman, X-ray spectroscopy and SEM.

3. RESULTS AND DISCUSSION
3.1 Poly(silyne-co-hydridocarbyne)

The network structure of PSC with tetrahedral bounded carbon and silicon atoms is presented in Fig. 1. Like polycarbynes and polysilynes, PSC can be easily converted to SiC ceramic unless it has any functional groups like double bound which gives an intense absorption band in the visible region [2, 3, 10, 11]. UV/Vis spectroscopy, hence, was used to figure out whether the polymer has or not a functional group on its backbone. The characteristic structure of PSC results in a unique electronic spectrum with broad absorption starting in the ultraviolet (UV) region (at ~200 nm) tailing off the visible region (Fig. 2a) [2,3]. A small amount of aliphatic SiH_x (1–3) and CH_x (x: 2–3) groups on the backbone cause some weak absorptions appearing in the visible region (Fig. 1a), which may explain the dissolution of PSC in common solvents. FTIR spectrum of PSC (Fig. 2b) showed the usual broad Si-C absorption (δSi-C) at ~750 cm^{-1}, which is the combination of the peaks at 770 (antisym), 688 (sym) and 650 cm^{-1} [2,3]. A peak at ~1450 cm^{-1} is due to Si-CH$_3$ and Si-CH$_2$- absorptions [2, 3, 10, 11]. FTIR of PSC (Fig. 2b) is consistent with a primarily network backbone structure of the formula (SiCH)n. All characterization data for PSC shown here is consistent with the product being poly(silyne-co-hydridocarbyne), [(SiCH)n]. The ^{1}H-NMR of PSC is shown in Fig. 2c.
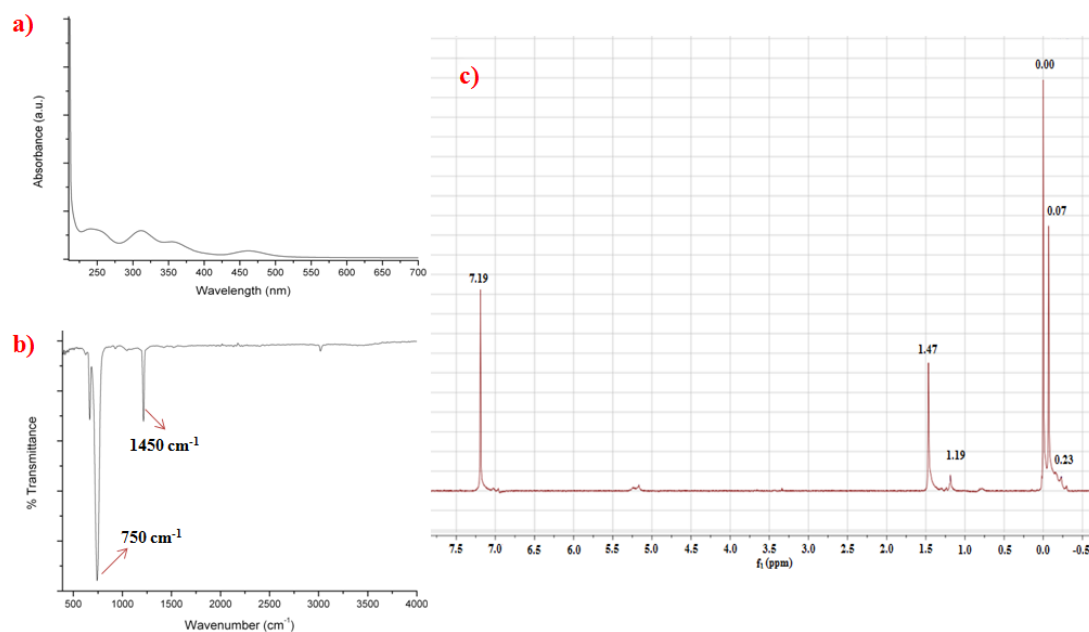

Fig. 2. a) UV/Vis; b) FTIR and c) ^{1}H NMR spectrum of poly(silyne-co-hydridocarbyne).

Fig. 2c shows the broad ^{1}H-NMR resonances, which is common spectrum for this type of polymer [2, 3, 18, 19]. The peaks between -0.1 and 0.10 ppm correspond to the protons of methyl (CH$_3$) and methine (CH) attached to silicon (νCH$_3$-Si: 0.02 and νCH-Si: 0.08), other peaks at 1.19 and 1.47 ppm correspond to aliphatic -CH-, -CH$_2$-and -CH$_3$ protons [2, 3, 13–19]. Average molecular weight of PSC was determined by GPC (GPC of PSC: Mn = 4589, Mw = 6404, PD = 1.40). This low molecular

weight result of PSC is due to the calibration of GPC instrument with linear polystyrene [2, 3, 10–19].

3.2 Polymer derived ceramic, SiC

Heat treatment of PSC produces a hard crystalline substance in high yield; typically in the range of 20–50%, depending on pyrolysis conditions. Pyrolysis at 1000 and 750∘C nearly resulted with 25% yield ceramic, while the material at 500∘C was obtained in approximately 42% yield.
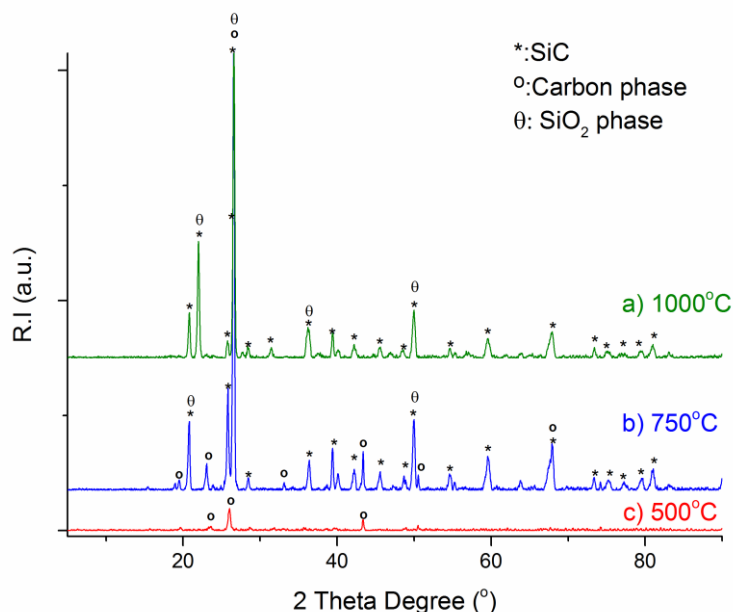

Fig. 3. X-ray powder diffraction patterns of SiC ceramics produced at **a)** 1000ºC, **b)** 750ºC and **c)** 500ºC.

The X-ray diffraction pattern of the SiC specimens is shown in Fig. 3. Wide angle X-ray powder diffraction patterns showed that SiC ceramics were successfully produced from PSC under CO_2 and ambient atmosphere. While SiC produced at 500ºC (Fig. 3c) was X-ray amorphous, the samples produced at higher temperature, at 750 and 1000ºC (Fig. 3a and 3b) , were crystalline, and their reflections were consistent with the mixture of Moissanite-5H, Moissanite-8H and Moissanite-84R, reflections of which were assigned according to "The International Center for Diffraction Data (ICDD))" ("PDF- 42-1360", "PDF-72-1625", "PDF-73-2082" and "PDF-73-2086, PDF-14-0654, PDF-38-0360 and PDF-42-1360). These crystalline samples are mostly composed of Moissanite-5H, which results are consistent with ICDD [2,3]. There are also some small reflections in Fig. 3a that cannot be assigned to Moissanite-5H or any other SiC phase [3]. Pyrolysis of the sample was carried out in an alumina crucible and an alumina tube and thus, it is believed that these peaks probably arose from Al_2O_3 contamination or SiO_2 formation during heat process [2].

The polycrystalline SiC has several overtone peaks in the range of 1000–2000 cm^{-1} (Fig. 4) [20–23]. SiC has a weak peak about 1620 cm^{-1} [21, 23]. The Raman spectrum of the samples (Fig. 4) showed very broad peaks in the vicinity of 1340 and 1600 cm^{-1}. The peaks around 1300 cm^{-1} are the so-called defect-induced D band, the peaks around 1600 cm^{-1} are the in-plane vibrational G band, which are respectively related with a strong sp^3-like resonant contribution and a sp^2-like doublet as observed in carbonous materials [21, 23]. Raman signals (Fig. 4) related to carbon and SiC interfered with each other since they appeared at the same Raman shift region and were very broad shifts. The weak peaks of SiC corresponding to the transversal optic at 796 cm^{-1} and the longitudinal optic at 972 cm^{-1} phonon modes were not clearly observed since D and G band in the spectra were significantly intense in Fig. 4. D and G bands emerging in Fig. 4a are nearly at same heights; however these are obviously different for SiC produced at 750 and 500ºC. Also, SiC formed at 500ºC (Fig. 4c) might be attributed to be crystalline SiC material from its Raman analysis; however, it revealed that the X-ray diffraction pattern obtained is more likely for an amorphous material. It can be concluded that the composition of SiC produced at 500ºC is mainly graphitic carbonous material. Thus, this is the reason why D and G band in the Raman analysis strongly appeared. Moreover, D band clearly appeared with lower intensity than that of G-band (Fig. 4c) which is another evidence for it to be amorphous. This result is also very consistent with X-ray and SEM (Fig. 3c and 5c) analyses.
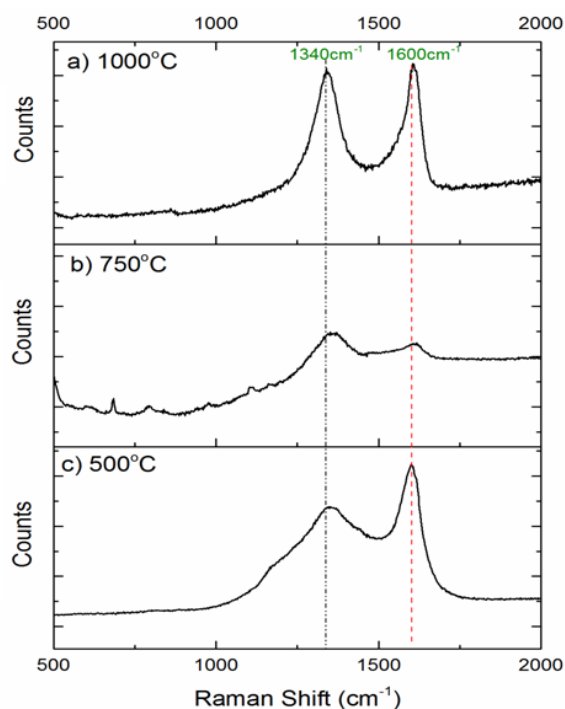
Fig. 4. Raman spectrum of SiC ceramics produced at **a)** 1000ºC, **b)** 750ºC and **c)** 500ºC.
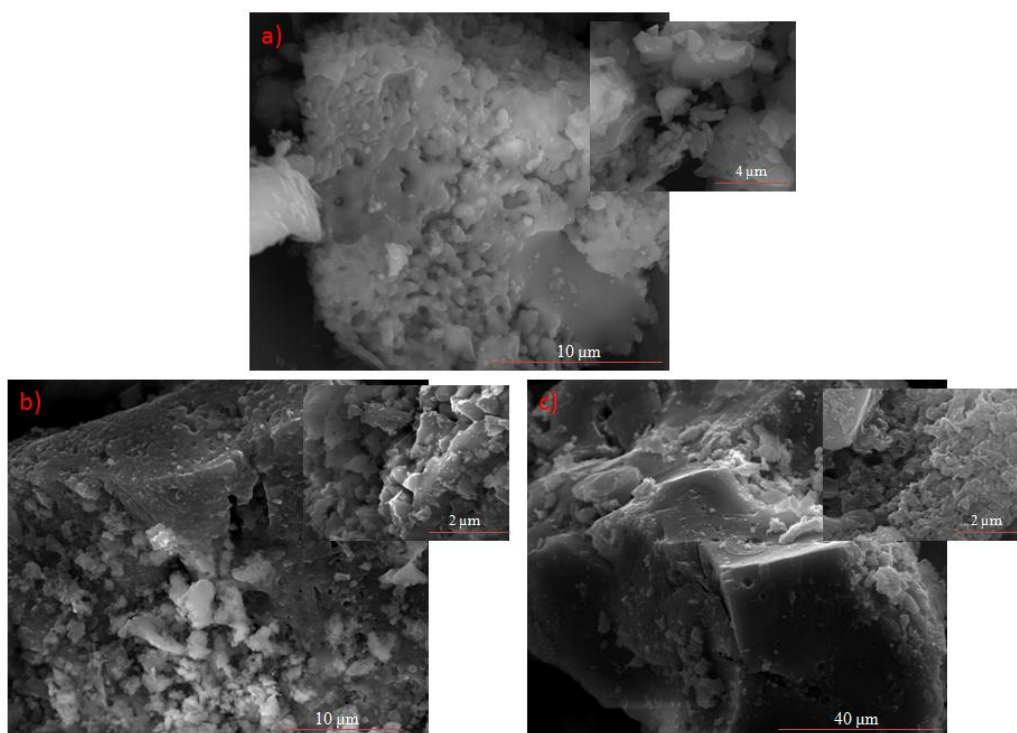

Fig. 5. SEM images of SiC ceramics produced at **a)** 1000ºC, **b)** 750ºC and **c)** 500ºC.

The SEM micrographs of SiC produced at different temperatures are shown in Fig. 5. In terms of morphology, it can be seen from Fig. 5 that ceramics are made up of particles which are irregular in shape and form as agglomerates. The size of the crystals is also mostly in the micrometer scale as seen clearly in SEM images in Fig. 5. At the moment, we have no significant means to control the crystal size and shape. It is obviously seen that SiC produced at 500ºC is amorphous (Fig. 5c) which is very consistent with other analyses (Fig. 3c).

4. CONCLUSIONS

The results showed that the synthesis of both the polymer and the resulting ceramic is relatively straightforward and simple. In the production of advanced ceramic, argon or nitrogen gas is used to create an inert media during thermal process, however, there is no such a work to demonstrate the production of SiC under CO$_2$ atmosphere. The Raman and X-ray analysis showed that polycrystalline SiC production was successfully achieved at 1000 and 750∘C under CO$_2$ atmosphere. The material produced at 500∘C was amorphous and the X-ray analysis showed it clearly. XRD results seem to indicate that the SiC was not a single Moissanite-5H, but the mixture of Moissanite-5H, Moissanite-8H and Moissanite-84R.

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