



# Liquid polycarbosilane derived SiC coating on silicon (1 1 1) wafer for enhanced mechanical properties

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## ABSTRACT

Silicon carbide coating on silicon (1 1 1) wafer was deposited by modified chemical vapor deposition (CVD) method using liquid polycarbosilane (LPCS) as precursor at three different moderately high temperatures in presence of Argon gas. Glancing angle X-ray diffractometer and Fourier Transform Infrared Spectroscopy reveals smooth  $\beta$ -SiC coating and its subsequent transformation into  $\alpha$ -SiC on silicon substrate. In all the temperature the film was found to be uniform with a thickness ranging from 0.6–1.2  $\mu\text{m}$ . The average particle size as can be seen from FESEM ranges from 7 to 385 nm approximately, the lowest range being (7–20 nm) which hitherto has not yet been reported using LPCS as precursor for SiC. Moreover the coated samples show substantial increment of hardness ( $\sim 18.8$  GPa) and toughness ( $\sim 1.51$   $\text{MPa m}^{1/2}$ ), both of which increases with increase in deposition temperature. The smooth and thin SiC coating on silicon formed in three different moderate temperatures compared to very high temperature for other CVD assisted coating along with enhanced hardness and toughness makes this a promising material in critically harsh environment required for microelectromechanical systems (MEMS) application.

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## 1. Introduction

Over two decades microelectromechanical systems (MEMS) have been developed using Si micromachining technology and have been applied in many fields, such as automotive, aerospace, ship, nuclear power instrumentation, satellites, space exploration, geothermal wells and sensors. Unfortunately, many of the physical properties that make Si attractive for MEMS, restrict the applications where Si-based devices can be used. For instance, the reduction in the elastic modulus above 600 °C and the degradation of pn-junctions above 150 °C limits the high temperature operating limit for Si-based MEMS devices to about 200 °C, cutting off many high temperature application areas using Si in MEMS technology. Recently, there is an increasing demands for MEMS devices that can operate in harsh environments, including high temperatures [1–5]. It is well known that silicon is the most conducive material for MEMS application hence extensive research is going on for its proper utilization in all environments. Mostly the research is centred around hard coatings on the surface so as to make it applicable in all environments. Wide bandgap semiconductors such as silicon carbide (SiC) offer promise for the development of high-temperature MEMS, because the wide bandgap allows for stable

electronic properties at high temperatures. SiC has long been noted for its excellent mechanical properties, specifically hardness and wear resistance and corrosion resistance properties [6]. Its mechanical strength, high thermal conductivity, ability to operate at high temperatures and extreme chemical inertness in several liquid electrolytes, makes it a potential candidate as structural material and as coated layers for MEMS application. A thin protective coating of SiC has found to be very effective in harsh environments [7], although there are reports that Si structures fabricated by deep reactive ion etching (DRIE) do not perform well in erosive environments [8], since SiC is a semiconductor with wide bandgap so it offers a promising coating material on silicon for MEMS application. Chemical vapor deposition (CVD), physical vapor deposition (PVD), atomic layer epitaxy, molecular beam epitaxy, sputtering, or laser ablation have been successfully employed to deposit single and polycrystalline forms of SiC thin films on substrate [9–12]. Each technique has its own merits and limitations. In comparison to other coating techniques CVD gives a uniform and crack free coating on simple and complex surfaces. However, the formation of voids and defects are observed at the SiC/substrate interface in the initial stage of the growth, which leads to serious problems in the realization of SiC MEMS devices [13]. Hence, there has been a considerable amount of interest in the development of alternative technique for producing SiC films to overcome these difficulties.

Formation of ceramic coating such as SiC and  $\text{Si}_3\text{N}_4$  from organosilicon precursors is now well documented [14,15]. Yajima et al. [16] pioneered the process of forming continuous SiC fibres

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by pyrolysis of polycarbosilane precursors in the 1970s owing to its distinct advantage of processability. Moreover, polymer derived ceramics have high thermal stability, good thermal and mechanical properties, and resistance to oxidation in dry and wet environments which render them potential materials for high temperature structural applications [17,18]. Polycarbosilanes have attracted particular interest because they are important precursors to synthesize SiC based ceramics. Previous works on a novel processing technique for making SiC MEMS from polymeric precursors referred to as polymer derived ceramics (PDC) have been reported. Chung have used a polydimethylsilazane (PDMS) mold to fabricate SiCN microstructures for a high-temperature environment (exceeding 1400 °C) [2]. Liew et al. have reported another method of using precursor photopolymerization as a simpler alternative to micro casting as a fabrication technique for SiCN MEMS, which is capable of withstanding over 1500 °C [19]. However, there are still some disadvantages, such as cantilever structure curling, demolding difficulty and the large difference of shrinkage ratio between the SiC and substrate, which causes serious defects. Lee et al. [20] have demonstrated that epitaxial cubic-SiC films can be formed on single-crystalline Si at temperatures of 900–1000 °C utilizing 1,3-disilabutane (DSB) as a single precursor.

The low temperature, low pressure single source precursor CVD method for realization of SiC-based MEMS and SiC-coated Si MEMS has several key advantages over the conventional CVD SiC deposition method such as (1) high quality polycrystalline films at low temperatures [21]. (2) The use of single precursor insures the stoichiometry of the CVD reactor base feed gas, eliminating the need for an elaborate gas handling system. (3) No pre-carbonization step is needed for deposition on Si and SiO<sub>2</sub>. In this work we have mainly focused on the deposition of coating (SiC) at different temperatures by CVD process at low pressure and temperature using liquid polycarbosilane (LPCS) as single precursors on silicon (1 1 1) substrate to enhance its mechanical properties so that it can be used in harsh environments. Efforts are also made to deposit a smooth crystalline coating without defects and voids at lower temperatures ranging from 800 °C to 1000 °C.

## 2. Material and methods

A liquid polycarbosilane (LPCS) with highly branched structure was synthesized by Defence Materials and Stores Research and Development Establishment (DMSRDE), Kanpur, India. The molecular weight of the material as measured by GPC was found to be ( $M_n$ ) 500 and having a structure in the form of  $[\text{Si}(\text{CH}_3)_2\text{CH}_2\text{SiH}(\text{CH}_3)\text{CH}_2]_n$ . The FTIR of the LPCS was analyzed to ascertain the presence of stretching bonds. The DTA/TG was performed in controlled Argon atmosphere by NETZSCH STA 449 C to measure the weight loss of the polymer. Silicon (1 1 1) wafers (Montco silicon Technologies Inc.) with 975–1025 μm thickness were used as substrates. The wafers were procured in a polished state with 7–8 nm surface roughness. The wafers were sliced into pieces, cleaned ultrasonically and placed inside the inert atmosphere furnace, where continuous flow of Argon gas at a flow rate of 12 ml min<sup>-1</sup> was maintained. The experiment was carried out at a pressure of 76 cm of Hg. At three different temperatures (800 °C, 900 °C and 1000 °C) the Argon gas was bubbled through LPCS (at 12 ml min<sup>-1</sup>) so as to carry the PCS vapours inside the furnace. Inside the furnace the PCS vapours decomposed to form a SiC which get coated on silicon (1 1 1) substrate. After a soaking period of one hour the furnace was slowly cooled down to room temperature, keeping all the parameters same. Glancing angle X-ray diffraction (GA-XRD) (PANalytical, UK) at a  $\Omega$  of 1.5° and using Cu K $\alpha$  radiation at 40 KV/30 mA, was used to observe crystallization of the coating. Microstructural analysis was carried out by field emission scanning electron microscopy (FESEM) (SUPRA™ 35VP,

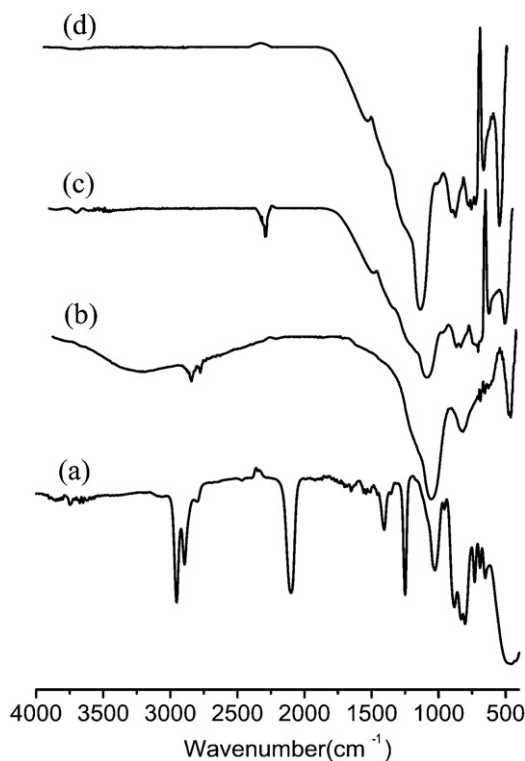


Fig. 1. FTIR spectra of polycarbosilane (a) uncured, (b) cured at 800 °C, (c) cured at 900 °C and (d) cured at 1000 °C.

Gemini Column, UK) to ascertain the particle size and the film thickness was viewed by scanning electron microscopy (SEM) (S430i LEO, LEO Electron Microscopy Ltd., UK) and transmission electron microscopy (TEM) (Tecnai G<sup>2</sup> 30ST (FEI), USA). FTIR (PerkinElmer, USA) absorbance spectra of the LPCS derived coating was taken to identify the stretching modes of SiC. Finally microhardness and fracture toughness measurement on coated and uncoated samples were carried out using digital Vickers microhardness tester (402MVD, Wilson Instruments, USA). Fracture toughness ( $K_{IC}$ ) was evaluated from cracklengths at Vickers indentations in the high load region using standard formulation by Evans et al. [22].

## 3. Results and discussions

Fig. 1 compares the FT-IR spectrum of the as-received liquid PCS with the spectrum of the films deposited at 800 °C, 900 °C and 1000 °C from LPCS. The functionalities in as received liquid polycarbosilanes were identified by FTIR (Fig. 1(a)). The deformation band at around 1250 cm<sup>-1</sup> (Si-CH<sub>3</sub> stretching) and the stretching band at 2953 cm<sup>-1</sup> (C-H stretching in Si-CH<sub>3</sub>) indicate the existence of Si-CH<sub>3</sub>. The strong band at 2099 cm<sup>-1</sup> is assigned to Si-H. The CH<sub>2</sub> bending in Si-CH<sub>2</sub>-Si at around 1026 cm<sup>-1</sup> and the C-H stretching in Si-CH<sub>2</sub> at around 2890 cm<sup>-1</sup> indicate the Si-CH<sub>2</sub>-Si chain, the backbone of the polymer, exists in this LPCS. Peaks at around 802 cm<sup>-1</sup> are assigned to Si-CH<sub>3</sub> rocking and Si-C stretching [23–25]. The stretching vibration band at around 3749 cm<sup>-1</sup> is due to the water adsorbed in KBr during FTIR testing [17]. The absorption peaks related to Si-H (2099 cm<sup>-1</sup>) and C-H stretching (2953, 2890 cm<sup>-1</sup>) greatly decreases in intensity in the 800 °C and 900 °C cured films and ultimately disappears in the 1000 °C cured films which is due to the polymer to ceramic conversion. Several SiC stretching modes are also observed corresponding to wavenumbers 750, 798 and 832 cm<sup>-1</sup> in the high temperature cured films [26–28]. The intensity of these SiC stretching modes increases with the curing temperature of films [29]. Si-O stretching mode was

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