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Preparation and characterization of polymer-derived amorphous silicon carbide with silicon-rich stoichiometry

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ABSTRACT

Polydihydrosilane with pendant hexyl groups was synthesized to obtain silicon-rich amorphous silicon carbide (a-SiC) films via the solution route. Unlike conventional polymeric precursors, this polymer requires neither catalysts nor oxidation for its synthesis and cross-linkage. Therefore, the polymer provides sufficient purity for the fabrication of semiconducting a-SiC. Here, we investigated the correlation of Si/C stoichiometry between the polymer and the resultant a-SiC film. The structural, optical, and electrical properties of the films with various carbon contents were also explored. Experimental results suggested that the excess carbon that did not participate in Si—C configurations was decomposed and was evaporated during polymer-to-SiC conversion. Consequently, the upper limit of the carbon in resultant a-SiC film was <50 at.%; namely, the polymer provided silicon-rich a-SiC, whereas the conventionally used polycarbosilane inevitably provides carbon-rich one. These features of this unusual polymer open up a frontier of polymer-derived SiC and solution-processed SiC electronics.

1. Introduction

Amorphous silicon carbide (a-SiC) films have numerous attractive properties such as higher thermal conductivity, better chemical stability, and wider optical gap than those of amorphous silicon (a-Si) [1]. These features make a-SiC attractive for use as a semiconducting material in light-emitting diodes [2], thin-film transistors [3], color sensors [4], and silicon solar cells [5]. In general, a-SiC is obtained using expensive vacuum-based equipment and large quantities of hazardous silane gases, leading to inconvenience such as high production cost, environmental load, and deposition area limitation.

Synthesis of SiC has been attempted by pyrolysis of polymeric precursors [6]. This approach offers potential processing advantage over conventional vacuum-based processes because it is compatible with solution processes, environmental friendly, low-cost, and safe. Since the early work of Yajima et al. [7], the SiC synthesized by pyrolysis of polycarbosilane has led to numerous publications [8,9]. The polycarbosilanes are obtained by pyrolysis of various polysilanes [10–12]. These precursors are typically synthesized using vinyl/chlorinated silanes with metal catalyst [12]. The polycarbosilane is pyrolyzed in argon at 400 °C to induce a partially cross-linked structure. Then, it is oxidized in air for complete cross-linkage and converted to SiC with excess carbon and SiO_2 on heating in N_2 at a higher temperature [7,10].

This approach is well investigated as a means for providing SiC fiber with good mechanical properties [7,13,14]. In contrast, polycarbosilane-derived SiC has not been applied in the field of electrical components because the remained oxygen and metal catalysts in resultant SiC negatively affect the electrical properties. Recently, we synthesized a polymeric precursor for semiconducting SiC with silicon-rich stoichiometry [15]. The polymer is based on polydihydrosilane with pendant hexyl groups (PSH). A distinguished feature of PSH is that the synthesis procedure and cross-linking require neither catalysts nor oxidation, resulting in high purity SiC. Therefore, the PSH can be p- or n-doped by dissolving appropriate amounts of borane or phosphorus compounds, respectively, before polymerization [16,17]. These unusual features satisfy the requirement as a solution-based semiconducting material.

PSH-derived SiC has silicon-rich stoichiometry, whereas the polycarbosilane-derived SiC is inevitably carbon-rich. Although the well-defined controllability of Si/C stoichiometry in the silicon-rich phase is absolutely important as semiconducting SiC, systematic studies of the PSH-derived SiC with varying Si/C stoichiometry have not been conducted. Therefore, in this study, we synthesized PSH with varying Si/C stoichiometry and clarified the correlation of Si/C stoichiometry in the PSH and resultant a-SiC films. We also studied the structural, optical, and electrical properties of the films. We developed silicon-rich a-SiC,

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which is difficult to obtain using conventionally used polycarbosilane, and would open up possibilities of solution-processed SiC electronics.

2. Experimental

2.1. Polymer preparation

PSH is a polymeric precursor for semiconducting SiC. Therefore, PSH solution is called SiC-ink in this study. The polymer was synthesized by hydrosilylation and heat polymerization of a mixture of 1-hexyne and cyclopentasilane (CPS) at 50 °C for 2 h, as shown in Scheme 1. CPS was originally synthesized as a solution precursor for semiconducting silicon in our previous studies [18]. CPS was synthesized according to the method described in one of our previous studies [19].

The Si—Si bond in CPS underwent cleavage by heating at 50 °C because of its weaker bond energy than other bonds such as Si—C, Si—H, C—H, and C—C [10,20]. The generated radicals react by insertion into Si—H bonds in the CPS to form a larger polydihydrosilane, along with incorporation of a hexyl group via hydrosilylation between the radical and the unsaturated bond in 1-hexyne. Ab initio theoretical calculations of the hydrosilylation of SiH_2 with C_2H_4 indicate that the reaction has no energy barriers, which is consistent with the high rate constants reported for these reactions [21–23].

CPS and 1-hexyne were purified by vacuum distillation before use, and were used as sources of elemental Si and C in PSH, respectively. The carbon content in PSH was controlled by changing the molar ratio of [1-hexyne] to [1-hexyne + CPS], denoted as X; X is varied from 0.07 (1-hexyne = 7%, CPS = 93%) to 0.67 (1-hexyne = 67%, CPS = 33%). The resultant PSH was a low viscosity, transparent, liquid-state polymer. Size-exclusion chromatography measurements revealed that the relative molecular weight of the PSH to polystyrene was 200–3000 g/mol [15]. All procedures were conducted in a glove box under a nitrogen atmosphere with oxygen content <0.5 ppm and dew point of −75 °C.

2.2. Film preparation

PSH was dissolved in cyclooctane at a concentration of 30 vol%. The SiC-ink was then spun on a Si wafer or glass substrate at 2000 rpm for 30 s, and the coated PSH film was transformed into an a-SiC film by thermal decomposition on a hot plate at 400 °C for 15 min under a nitrogen atmosphere. The thickness of the a-SiC film was ~250 nm. The Si wafer was cleaned with hydrofluoric acid to remove the native oxide layer prior to use for Fourier transform infrared (FTIR) measurements, while glass substrates were cleaned with ultraviolet ozone treatment and used for optical and electrical characterization.

2.3. Sample analysis

The chemical structures of PSH and the a-SiC films were analyzed by FTIR. IR spectra were obtained using a Bruker Alpha spectrometer operated in the attenuated total reflectance mode for PSH and in the transmittance mode for a-SiC films. The chemical bonding of the films was characterized by X-ray photoelectron spectroscopy (XPS). The binding energy of Si 2p, C 1s, and O 1s was measured using a Shimadzu Kratos AXIS ULTRA DLD with monochromatized Al Kα radiation (1486.6 eV). The carbon and oxygen content in the a-SiC films was estimated using the integrated intensity of Si 2p, C 1s, and O 1s bands with relative sensitivity factors. The films were etched before measurement to remove the surface contaminants. The etching rate was 5 nm/min with the condition of Ar + 2.0 kV. The oxygen content in a-SiC films was confirmed to be <3 at.%. The film thickness and optical absorption coefficient were determined from transmittance and reflectance (TR) data collected using a Scientific Computing International FilmTek 3000. The optical gap (E_{opt}) was estimated from the equation $\alpha E = B(E - E_{opt})^2$, i.e., a Tauc plot [24], where, α is the optical absorption coefficient, B is a constant, and E is the photon energy in eV. The valence band energy (E_v) of each a-SiC film was measured by photoemission spectroscopy (Riken Keiki AC2). Dark conductivity (σ_d) and photoconductivity (σ_p) at room temperature were measured by an Agilent 4155C semiconductor parameter analyzer using an aluminum contact with a coplanar configuration of 250 μm gap width. An AM-1.5G solar simulator with an intensity of 100 mW/cm^2 was used to determine the σ_p.

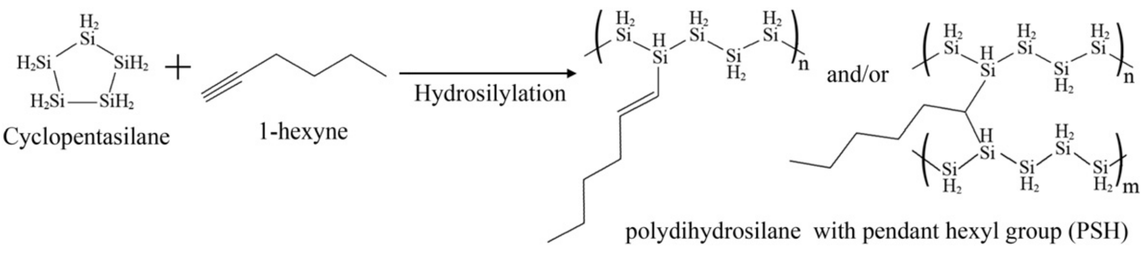
3. Results and discussion

3.1. Correlation between PSH and a-SiC

Here, we compare the FTIR spectra between PSH and a-SiC film to clarify the correlation. Fig. 1 shows the absorbance spectra of PSH with various X values, in which the intensity was normalized to the height of the 2100 cm^{-1} peak. The spectrum of polydihydrosilane without pendant hexyl groups is also shown for comparison as $X = 0$. The peaks appearing at 570, 700, 850–900, 2100, and 2850–2950 cm^{-1} correspond to Si—Si wagging, Si—Si rocking, Si—H_2 bending, Si—$H_{1,2}$ stretching, and C—$H_{2,3}$ stretching modes, respectively [25,26]. A broad peak at 790 cm^{-1} appears in the spectra of PSH with larger X values, which is assigned to the Si—C stretching mode in alkylsilane [27]. The Si—C bonds increase with the X values due to the hydrosilylation between CPS and 1-hexyne.

Fig. 2 shows the absorption coefficient spectra of a-SiC films prepared using SiC-inks with various X values. The spectrum of the film prepared using SiC-ink with $X = 0$, amorphous silicon (a-Si), is also shown for comparison. The main absorption peaks appearing at 640, 990–1000, 2000–2100, and 2850–2920 cm^{-1} correspond to Si—H wagging, C–H_n wagging, Si—$H_{1,2}$ stretching, and C—$H_{2,3}$ stretching modes, respectively [28]. The peak of Si—C stretching mode shifts from 790 cm^{-1} in PSH to 760 cm^{-1} in the films, indicating that the Si—C bond configuration in a-SiC film differs somewhat from that in alkylsilane. The peak positions are the same for all films, whereas the intensity of the carbon related peaks increases with the X value.

Various hydrocarbons were tested as carbon sources. Many Si—C bonds were detected in the FTIR spectra of the polymer as well as the resultant films when sp- or sp^2-containing hydrocarbons were used as carbon sources. In contrast, sp^3-containing hydrocarbons did not react with CPS, leading to few Si—C bonds in the PSH and resultant films. The unsaturated carbon played an essential role in the formation of Si—C bonds.



Scheme 1. Synthesis route for PSH from a mixture of CPS and 1-hexyne. Unsaturated carbon in 1-hexyne reacts with CPS via hydrosilylation.