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Al-Doped Single-Crystalline SiC Nanowires Synthesized by Pyrolysis of Polymer Precursors

Weiyou Yang[1,*], Fengmei Gao[1], Yi Fan[2], and Linan An[3]

[1] *Institute of Materials, Ningbo University of Technology, Ningbo, 315016, P. R. China*
[2] *Laboratory of Excited State Process, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, 130033, P. R. China*
[3] *Advanced Materials Processing and Analysis Center, University of Central Florida, Orlando, FL 32816, USA*

Al-doped 6*H*-SiC nanowires are synthesized by catalyst-assisted pyrolysis of polymer precursors. The obtained nanowires were characterized using scanning electron microscopy, X-ray diffraction, transmission electron microscopy and selective area electron diffraction. We demonstrate that doping concentrations can be controlled by tailoring the Al concentrations in the precursors. We also find that Al-doping has a profound effect on the morphology and emission behavior of the SiC nanowires. The current results suggest a simple technique for synthesizing Al-doped SiC nanomaterials in a controlled manner, which are promising for applications in optical and electronic nanodevices.

Keywords: SiC Nanostructures, Pyrolysis, Polymer Precursors, Doping.

RESEARCH ARTICLE

INTRODUCTION

Silicon carbide is one of the most important wide bandgap semiconductors with widespread applications in high-temperature/high-voltage electronics and short-wavelength optics.[1–5] Recently, one-dimensional (1D) SiC nanostructures have attracted extensive attention since they could be useful as the building blocks in the fabrication of electronic/optic nanodevices.[6–8] To date, significant progress have been made in the synthesis of SiC nanostructures with varied morphologies, including nanowires,[9–13] nanorods,[14–19] nanobelts,[20,21] nanotubes,[22,23] nanocables,[24,25] nanosprings,[26] and nanospheres.[27] In spite of these efforts, little has been done on the synthesis of doped SiC 1D nanostructures.

In this paper, we report the synthesis of Al-doped single-crystalline SiC nanowires with high yield and high quality by catalyst-assisted pyrolysis of Al-containing polymer precursors. As compared to our previously published paper,[28] current work has achieved to synthesize Al-doped SiC nanowires with controlled doping levels by tailoring the experimental parameters directed by the Si–C–N phase diagram.[29]

*Author to whom correspondence should be addressed.

2. EXPERIMENTAL DETAILS

Al-doped SiC nanowires were synthesized by the catalyst-assisted pyrolysis of polyaluminasilazane precursors. The precursors were obtained by reaction of polyureamethylvinylsilazane (Ceraset, Kion Corporation, USA) and aluminum isopropoxide (AIP, Beijing Bei Hua Fine Chemicals Company, Beijing, China) using the procedure reported previously.[30] In order to control the doping concentration of the nanowires, three kinds of polyaluminasilazanes containing different amounts of aluminum were synthesized by adding 0.5 wt%, 1 wt% and 5 wt% AIP to Ceraset, respectively, referred as to PAS05, PAS1 and PAS5. The obtained polyaluminasilazanes, which were liquid as synthesized, were then solidified by heat-treatment at 260 °C for 0.5 hour in N_2. The solids were crushed into fine powders by high-energy ball milling for 24 hours, with 3 wt% of $FeCl_2$ powder (analytical purity: 99.99%, Beijing Bei Hua Fine Chemicals Company, Beijing, China) additive as the catalyst. Nylon bottles and high-pure Si_3N_4 balls are used for the milling media. The powder mixtures were put into a high-pure alumina crucible (99.9%, 3 cm in diameter and 2.5 cm in height, respectively) and then pyrolyzed in a conventional furnace with a graphite resistance under flowing ultra-high purity N_2 of ~200 sccm and 0.1 MPa. The pyrolysis was carried

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out at 1700 °C for 2 hours followed by furnace-cool to ambient temperature.

The obtained products were then characterized using field emission scanning electron microscopy (SEM, JSM-6301F, JEOL, Japan) equipped with energy-dispersive X-ray spectroscopy (EDX, GENESIS2000MS 60S), X-ray diffraction (XRD, Automated D/Max-RB, Rigaku, Japan) with CuK_α radiation ($\lambda = 1.54178$ Å), and high-resolution transmission electron microscopy (HRTEM, JEOL-2011, Japan). Photoluminescence (PL) spectra of the nanowires were recorded using a UV-lamp micro-zone Raman spectrometer under the excitation of a 325 nm HeCd laser at room temperature.

3. RESULTS AND DISCUSSION

Figure 1(a) is a typical low-magnification SEM image of the nanowires obtained from PAS5, showing high-density growth of the nanowires. The average lengths of the nanowires can be up to tens of micrometers. The compositions of the nanowires of the different samples were measured using EDX under SEM. A typical EDX spectrum recorded from the nanowires of PAS5 is presented as the inset picture in Figure 1(a), which reveals that the nanowires consist of Si, C and Al, as well as a small amount of O (Cu comes from the copper substrate to support the samples). The EDX spectra obtained from different areas are identical, indicating the uniform distribution of Al-doping, which suggests that the SiC nanowires are *p*-type doped. The measured Al concentrations are 0.88, 1.13 and 1.35 at% for the nanowires synthesized from PAS05, PAS1 and PAS5, respectively (as plotted in Fig. 1(b)). This suggests that the Al-doping level of the SiC nanowires can be tailored by varying the Al-concentration in the precursors, implying that the current method offers a simple way to synthesize SiC nanowires with controlled doping concentrations. Closer examinations of the three samples under TEM (Figs. 1(c–e)) reveal that the obtained nanowires exhibit a cylindrical shape with smooth surfaces. The average diameters are ~200, ~300 and ~500 nm for the nanowires synthesized from PAS05, PAS1 and PAS5, respectively. The diameter of an individual nanowire is uniform along its entire length for the three samples. Figure 1(f) is a HRTEM image of the nanowire labeled by a white arrowhead in Figure 1(c). The HRTEM image discloses that there is an amorphous layer on the surface of the nanowire. The lattice fringe spacing are 0.26 and 0.25 nm, in good agreement with {101} and {102} planes of bulk 6*H*-SiC, where $a = 0.308$ nm and $c = 1.509$ nm (JCPDS Card No. 29-1128). The inset in Figure 1(f) is a corresponding selected area electron diffraction (SAED) pattern recorded from the same nanowire. The SAED patterns recorded from different positions are identical, indicating that the nanowire is a single crystal. Both the SAED pattern and HRTEM image suggest that the nanowires grow along [102], as indicated in Figure 1(c).

To investigate the effect of Al-doping on crystal structure, the nanowires were carefully studied using XRD. The typical XRD patterns for three different kinds of nanowires are presented in Figure 2. All diffraction peaks are in good agreement with JCPDS 29-1128, confirming that all of

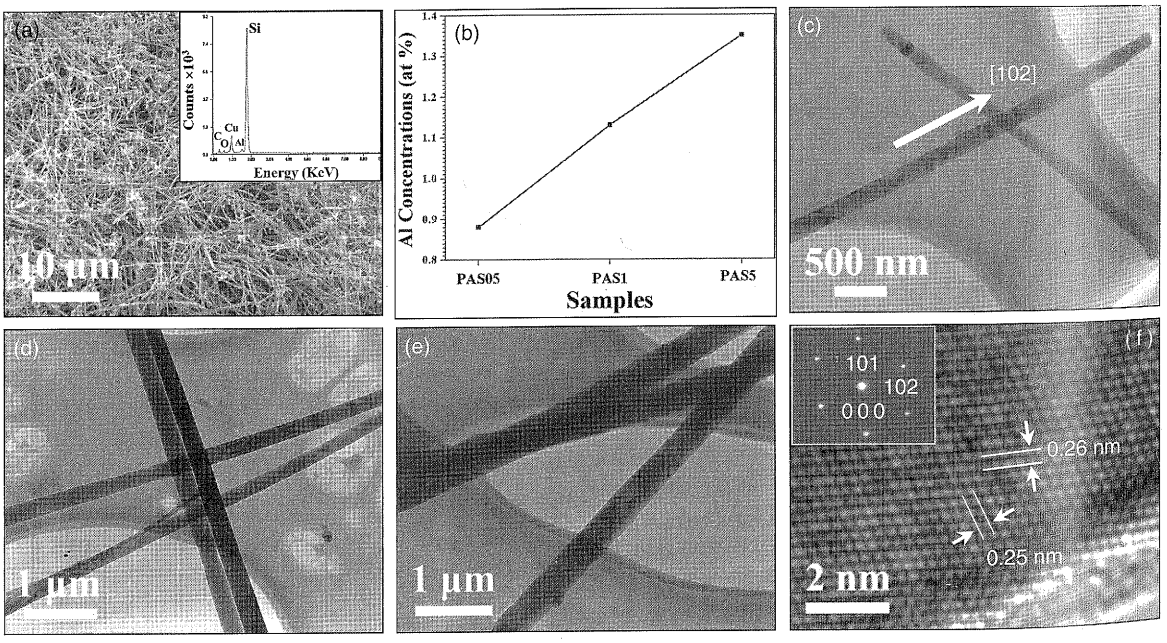
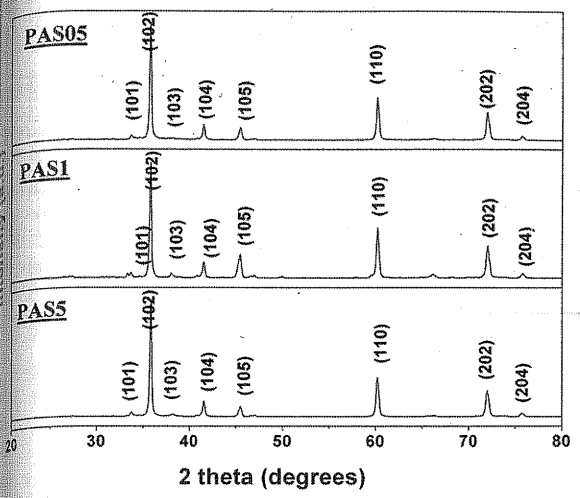


Fig. 1. (a) A typical Low magnification SEM image of the SiC nanowires obtained from PAS5, the inset picture is a representative EDX spectrum of the nanowires; (b) Al concentrations in different nanowires. (c–e) Typical TEM images of the nanowires obtained from PAS05, PAS1 and PAS5, respectively; (f) a HRTEM image of a SiC nanowire, the inset is a corresponding SAED pattern recorded from the nanowire.



2. XRD patterns of the SiC nanowires synthesized from different ursors.

nanowires are 6*H*-SiC, regardless of the different pre-sors used. The lattice parameters of the nanowires are ulated from the diffraction patterns and summarized Table I. It is seen that Al-doping causes a decrease in lattice parameters as compared with the values of pure There are two possible doping mechanisms:[28]

$$\mathrm{Al} \xrightarrow{\mathrm{SiC}} \mathrm{Al_{Si}} + V_C \quad (1)$$

$$\mathrm{Al} \xrightarrow{\mathrm{SiC}} \mathrm{Si_{Si}} + \mathrm{Al}_i + C_C \quad (2)$$

first reaction leads to the formation of a substitutional d solution, which should lead to a decrease in lattice meters; while the second reaction leads to the forma- of an interstitial solid solution, which should leads an increase in the lattice parameters. Our experimen- results indicate that the Al-doped SiC nanowires form stitutional solid solutions.

The growth of the Al-doped SiC nanowires via a alyst-assisted pyrolysis of polymer precursors should low the solid–liquid–solid (SLS) growth mechanism

le I. Lattice parameters of the SiC nanowires with different oping concentrations.

ples	Cryst. Plane	2θ (°)	Latt. Const. (Å)		Decrease	
			a	*c*	Δ*a* (%)	Δ*c* (%)
oped*	(102)	35.68	3.081	15.092	0	0
	(110)	60.05				
30.5	(102)	37.76	3.074	14.939	0.23	1.01
	(110)	60.12				
31	(102)	35.82	3.072	14.832	0.31	1.72
	(110)	60.18				
35	(102)	35.84	3.071	14.796	0.33	1.96
	(110)	60.20				

From JCPDS Card No. 29-1128.

since there are no gas/vapor phases involved in the formation process.[17] In this process, the precursors were first thermally decomposed into amorphous SiAlCNs at ~1000 °C.[30] The SiAlCNs were then reacted with Fe to form liquid Si–Fe–C–Al alloy droplets at a temperature higher than the eutectic temperature of the quaternary system. Further reaction of the SiAlCN and the liquid droplets results in the formation of supersaturated alloys which in turn leads to the precipitation of Al-doped SiC nanowires. The formation of SiC phase is because the SiC is a stable phase at 1700 °C in pure N_2 atmosphere.[29]

To investigate the effect of Al-doping on the optical properties of the SiC nanwires, the photoluminescence (PL) spectra were recorded from the three samples at room temperature (Fig. 3). All three kinds of nanowires exhibit intense light emission, which can even be seen by the naked eyes. While all three samples show similar PL spectra with a strong and broad emission peak ranging from 1.7 to 3.4 eV, the peaks show clear red-shifts with increasing Al-doping concentration. The peaks are centered at ~2.56, ~2.45 and ~2.43 eV for the nanowires made from PAS05, PAS1 and PAS5, respectively, revealing the doping concentration effects. These peaks are dramatically different from that of pure single crystal 6*H*-SiC which shows a major emission peak centered at 2.93 eV, ascribed to the band-edge emission.[31] Previous studies on *n*-type doped 6*H*-SiC revealed a major PL peak centered at ~2.65 eV,[32, 33] which was attributed to a Al-related donor–accepter recombination process. Our PL peaks are red-shifted as compared to these previous results. Since the nanowires are too large to have any confinement effect, we attribute the red shifts to the effects of doping concentrations. While the detailed mechanisms that determine the emissions of these nanowires are not clear at this moment, the current results suggest that the optical properties of the SiC nanowires can be tailored by Al-doping.

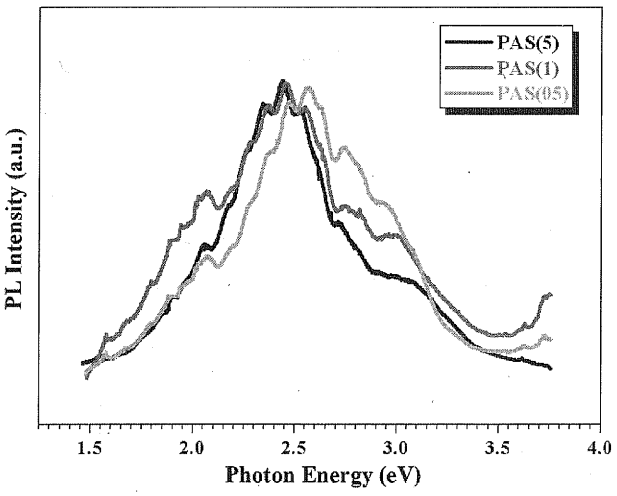


Fig. 3. Photoluminescence spectra of the SiC nanowires recorded from the different samples.

4. CONCLUSIONS

In summary, we have reported the synthesis of Al-doped 6*H*-SiC nanowires, which were synthesized by the catalyst-assisted pyrolysis of polymer precursors in the presence of $FeCl_2$ as the catalyst at 1700 °C for 2 hours in N_2. The results suggest that the Al-doping levels can be tailored by varying the Al-concentration in the precursors. The PL spectra reveal that the Al-doping causes a red-shift of the emission band. The current results suggest a new and simple technique to synthesize low-dimensional SiC with controlled doping levels, which could be extended to other doping elements. The obtained *p*-type doped SiC nanowires could be promising to be used in optical and electronic nanodevices.

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