

Controlled Al-Doped Single-Crystalline 6H-SiC Nanowires

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ABSTRACT: We report for the first time the synthesis of Al-doped 6H-SiC nanowires with high yield and high quality. The nanowires were obtained by the catalyst-assisted pyrolysis of polymeric precursors with FeCl₂ as the catalyst. The doping concentrations were controlled by tailoring the Al concentrations in the precursors. It was observed that the Al dopants caused red-shifts of the photoluminescence bands. The results suggest a simple technique to synthesize Al-doped SiC nanomaterials in a controlled manner. The obtained nanowires could be useful for making optical and electronic nanodevices.

Silicon carbide (SiC) is one of the most important wide bandgap semiconductors with widespread applications in high-temperature/high-voltage electronics and short-wavelength optics.¹ 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.² To date, significant progress has been made in the synthesis of SiC nanostructures with varied morphologies, including nanowires,³ nanorods,^{4,5} nanobelts,⁶ nanotubes,⁷ nanocables,⁸ nanosprings,⁹ and nanospheres.¹⁰ In spite of these efforts, little has been done on the synthesis of doped SiC 1D nanostructures.

Doping has been used to tailor the electronic and optical properties of SiC and is critical for potential applications of the material.¹¹ For bulk SiC and SiC thin films, doping can be realized by vapor phase codeposition,¹² ion-implantation,¹³ and diffusion.¹⁴ However, these methods are difficult to apply to 1D nanostructures.

In this paper, we report for the first time a simple method to synthesize Al-doped single-crystalline 6H-SiC nanowires, namely, catalyst-assisted pyrolysis of Al-containing polymeric precursors. By this technique, high-quality SiC nanowires have been synthesized with high yield. We also demonstrate that the doping concentrations can be controlled by controlling the Al-concentration in the precursors. The results suggest a unique technique for synthesizing Al-doped SiC nanomaterials, which could be extended to other doping elements.

Experimental Procedures. Al-doped SiC nanowires were synthesized by the catalyst-assisted pyrolysis of polyaluminasilazane precursors. The precursors were obtained by reaction of polyurea-methylvinylsilazane (Cerset, Kion Corporation, USA) and aluminum isopropoxide (AIP, Beijing Bei Hua Fine Chemicals Company, Beijing, China) using the procedure reported previously.¹⁵ In order to control the doping concentration of the nanowires, three kinds of polyaluminasilazanes containing different amounts of aluminum were synthesized by adding 0.2 wt%, 1 wt%, and 5 wt% AIP to Cerset, respectively, referred as to PAS02, PAS1, and PAS5. The obtained polyaluminasilazanes, which were liquid as synthesized, were then solidified by heat-treatment at 260 °C for 0.5 h in N₂. The solids were crushed into fine powders by high-energy ball milling for 24 h, with 3 wt% of FeCl₂ powder (analytical purity: 99.99%, Beijing Bei Hua Fine Chemicals

Company, Beijing, China) additive as the catalyst. The powder mixtures were pyrolyzed in a conventional furnace with a graphite resistance under flowing ultrahigh purity Ar (99.99%) of 0.1 MPa. The pyrolysis was carried out at 1450 °C for 2 h 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 Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$), and high-resolution transmission electron microscopy (HRTEM, JEOL-2011, Japan). Photoluminescence (PL) spectra of the nanowires were recorded using a UV-lamp microzone Raman spectrometer under the excitation of a 325 nm HeCd laser at room temperature.

Results and Discussion. The obtained products were first analyzed using SEM. Figure 1a is a typical SEM image of the nanowires obtained from PAS5, showing high-density growth of the nanowires. For all three precursors, ~80 wt% of the raw materials was converted to SiC nanowires under the present processing conditions. Closer examination at higher magnification reveals that the nanowires exhibit a cylindrical shape with smooth surfaces (Figure 2b–d). The average diameters are ~150, ~250, and ~300 nm for the nanowires synthesized from PAS02, PAS1, and PAS5, respectively. The diameter of an individual nanowire is uniform along its entire length. The average lengths of the nanowires are a few micrometers for the sample synthesized from PAS02, and several tens to hundreds of micrometers for the samples synthesized from PAS1 and PAS5. These results suggest that Al-doping may promote the growth of SiC nanowires.

The compositions of the nanowires were measured using energy dispersive X-ray analysis (EDX) under SEM. A typical EDX spectrum recorded from the nanowires obtained from PAS5 is presented in Figure 1e, which reveals that the nanowires consist of Si, C, and Al, as well as a small amount of O. The EDX spectra obtained from different areas are identical, indicating the uniform distribution of Al-doping. The measured Al concentrations are 0.52, 1.05, and 1.25 at% for the nanowires synthesized from PAS02, PAS1, and PAS5, respectively (Figure 1f). This suggests that the Al-doping level of the SiC precursors 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.

Further characterization of the nanowires was carried out using TEM. Figure 2a–c shows typical TEM images of the nanowires synthesized from PAS02, PAS1, and PAS5, respectively, confirming that the nanowires made from PAS02 are much shorter than those

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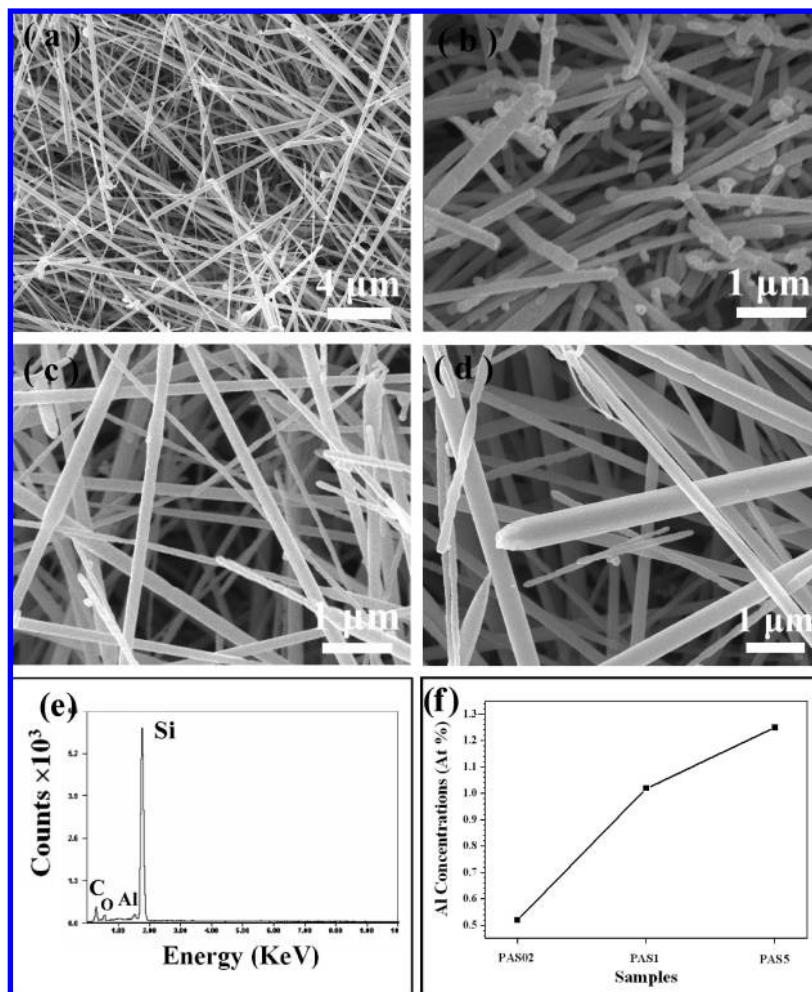


Figure 1. (a) Low magnification SEM image of the SiC nanowires obtained from PAS5; (b–d) high magnification SEM images of the SiC nanowires obtained from PAS02, PAS1, and PAS5, respectively; (e) a typical EDX spectrum of the nanowires; (f) Al concentrations in different nanowires.

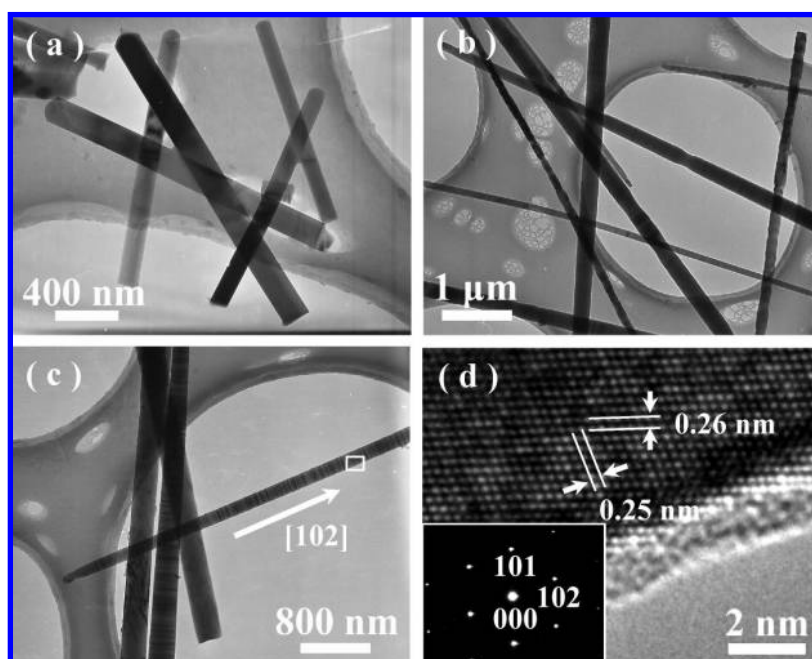


Figure 2. (a–c) Typical TEM images of the nanowires obtained from PAS02, PAS1, and PAS5, respectively; (d) a HRTEM image of a SiC nanowire; the inset is a corresponding SAED pattern recorded from the nanowire.

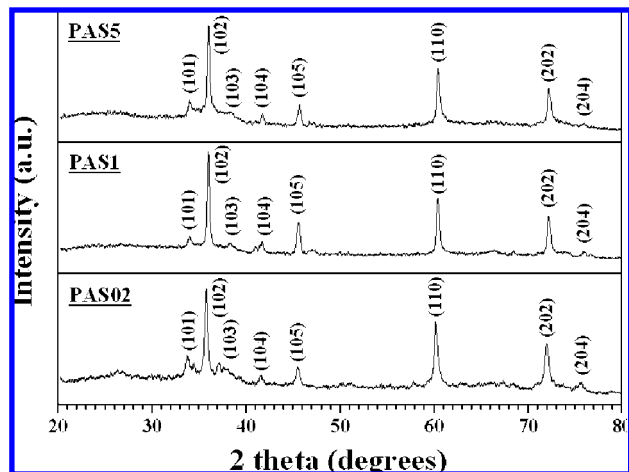


Figure 3. XRD patterns of the SiC nanowires synthesized from different precursors.

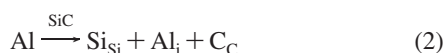
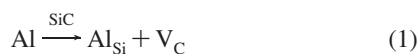
Table 1. Lattice Parameters of the SiC Nanowires with Different Al-Doping Concentrations

samples	cryst plane	2θ (°)	latt const (Å)		decrease	
			a	c	Δa%	Δc%
undoped ^a	(102)	35.68	3.081	15.092	0	0
	(110)	60.05				
PAS02	(102)	35.74	3.0744	15.0126	0.21	0.53
	(110)	60.12				
PAS1	(102)	35.78	3.0716	14.9738	0.31	0.78
	(110)	60.18				
PAS5	(102)	35.80	3.0698	14.9720	0.36	0.8
	(110)	60.22				

^a Data from JCPDS Card No. 29-1128.

made from PAS1 and PAS5. The images also confirm that the nanowire is uniform in size along its entire length. Figure 2d is a HRTEM image of the nanowire labeled by a white rectangle in Figure 2c. The HRTEM image discloses that there is an amorphous layer of ~1 nm on the surface of the nanowire, which could account for the O detected by the EDX spectrum (Figure 1e). The lattice fringe spacings are 0.26 and 0.25 nm, in good agreement with {101} and {102} planes of bulk 6H-SiC, where a = 0.308 nm and c = 1.509 nm (JCPDS Card No. 29-1128). The inset in Figure 2d 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 2c.

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 3. All diffraction peaks are in good agreement with JCPDS 29-1128, confirming that all of the nanowires are 6H-SiC, regardless of the different precursors used. The lattice parameters of the nanowires are calculated from the diffraction patterns and summarized in Table 1. It is seen that Al-doping causes a decrease in the lattice parameters as compared with standard values. There are two possible doping mechanisms:



The first reaction leads to the formation of a substitutional solid solution, which should lead to a decrease in lattice parameters, while

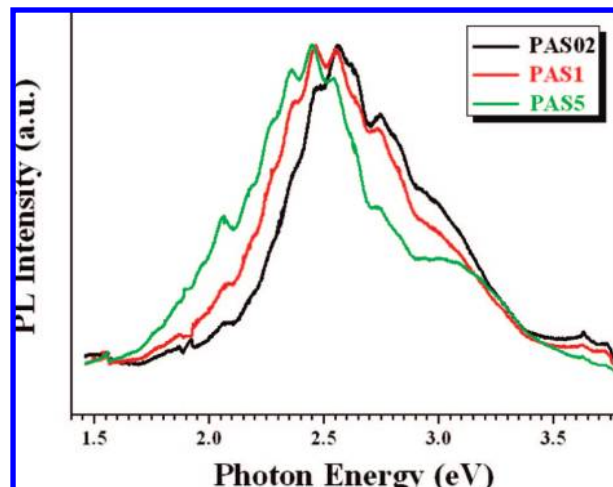


Figure 4. Photoluminescence spectra of the SiC nanowires recorded from the different samples.

the second reaction leads to the formation of an interstitial solid solution, which should lead to an increase in the lattice parameters. Our experimental results indicate that the Al-doped SiC nanowires form substitutional solid solutions.

Previous studies demonstrated that the SiC nanowires synthesized by catalyst-assisted pyrolysis of polymeric precursors were grown via a solid-liquid-solid (SLS) process.⁴ In this process, the precursors were first thermally decomposed into amorphous SiAl-CN_x at ~1000 °C.¹⁵ The SiAlCN_x 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_x and the liquid droplets results in the formation of supersaturated alloys and leads to the Al-doped SiC nanowires precipitating on the liquid/gas interface. The formation of the SiC phase is due to its stability at 1450 °C in a pure Ar atmosphere.¹⁶

To investigate the effect of Al-doping on the optical properties of the SiC nanowires, the photoluminescence (PL) spectra were recorded from the three samples at room temperature (Figure 4). 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, 2.50, and 2.44 eV for the nanowires made from PAS02, PAS1, and PAS5, respectively. These peaks are dramatically different from that of pure single crystal 6H-SiC which shows a major emission peak centered at 2.93 eV, ascribed to the band-edge emission.¹⁷ Previous studies on n-type 6H-SiC (much lower doping level than the nanowires reported here) revealed a major PL peak centered at ~2.65 eV,^{18,19} which was attributed to a Al-related donor-acceptor 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.

Conclusions. In summary, we have demonstrated for the first time the synthesis of Al-doped 6H-SiC nanowires, which were synthesized by the catalyst-assisted pyrolysis of polymeric precursors in the presence of FeCl₂ as the catalyst. The Al-doping levels can be tailored by varying the Al-concentration in the precursors. The growth yield of the nanowire is high and their quality is very good. The growth of the nanowires is attributed to a SLS mechanism. 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 Al-doped low-dimensional SiC. The obtained SiC nanowires could be useful in optical and electronic nanodevices.

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