Infrared absorption property of silicon carbide-silica nanocables synthesized by ethanol pyrolysis

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A controllable synthesis method for SiC-SiO2 nanocables has been proposed. The diameter of SiC core and thickness of SiO2 shell were changed by adjusting the flow ratio between Ar dilution gas and ethanol precursor. With increasing the flow, the enhancement of 1137 cm−1 peak was observed from Fourier transform infrared spectroscopy (FTIR) spectra. This peak is considered to be originated from a highly disordered surface structure of SiO2 shell which was enhanced with increasing the flow. The FTIR spectra show the 910 cm−1 peak which is attributed to surface phonon resonance in the nanostructure of SiC exited by p-polarized field component.

Keywords: Nanostructures, Fourier transform infrared spectroscopy (FTIR), Surface Phonon Resonance

I. INTRODUCTION

The discovery of carbon nanotubes in 1991 [1] and their unique properties differing from bulk material have stimulated the study of one-dimensional (1-D) nano-sized materials. Among them, silicon carbide nanocables have been focused as a potential candidate for light-emitting device, nano-reinforced composite materials, nanoelectronic devices and catalyst supports due to their outstanding properties such as wide band-gap, high hardness, excellent thermal conductivity, high electron mobility, high saturation drift velocity, good chemical inertness, etc [2]. In general, the as-synthesized SiC nanowires contain amorphous SiO2 on their surfaces and have SiC-SiO2 core-shell structure. Recently, this structure has been attracting much attention owing to their potential applications for optoelectronic device and field emitter [3,4]. For application of nano-materials, it is important to understand their several properties as well as to synthesize them in various forms.

Fourier transform infrared spectroscopy (FTIR) provides the important information about the several chemical bond states of the sample. The phonon states in nano-sized particle or wire differing from those in bulk will be reflected in infrared (IR) absorption spectra. But, to our knowledge, a few reports [5-8] related to IR absorption properties of SiC-SiO2 nanocables have been presented and most of them were restricted to confirm the characteristic band positions of Si-C and Si-O bonds. In our earlier study [10], we found a shoulder peak of SiO antisymmetric stretching mode centered at 1130 cm−1, and attributed it to the interface effect of the open structure of chainlike SiO2/SiC nanocables on the base of the comparison to the prior report [11]. But, our further study showed that the shoulder peak of SiO antisymmetric stretching mode could not be attributed to above mentioned origins. Furthermore, we found a novel peak centered at 910 cm−1 from SiC-SiO2 nanocables in the IR absorption measurement. In this paper, we discuss the likely origin of these two peaks based on some experimental data and theoretical calculations.

II. EXPERIMENTAL DETAILS

SiC-SiO2 nanocables were synthesized by use of ethanol pyrolysis. Ethanol is thermally decomposed into CO, H2O, C2H6, CH4, C2H4, and H2 at about 700°C and the higher temperature above 1000°C induces the decomposition of hydrocarbon into C and H2 [12]. At about 1100°C, the main products are CO and H2. Therefore, the use of thermal decomposition of ethanol allows us to obtain carbon source for synthesis of SiC-SiO2 nanocables at low cost [10]. In our experiment, silicon source for synthesis SiC-SiO2 nanocables was generated by use of the reaction between Si(111) substrate (0.09Ω·cm, n-type) and pyrolysis productions of ethanol [10-13].

The experimental details for synthesis of SiC-SiO2 nanocables were presented in our earlier report [10]. We used five flow ratios between Ar and (Ar+ethanol), 98:2, 96:4, 94:6, 92:8, and 90:10, for synthesis of nanocables having different core diameters and shell thicknesses. After synthesis, the whole surface of the Si substrate was covered with white-colored product. Beyond the range of the flow ratios used in this experiment, the surface of Si substrate showed no more white color and changed from wheat to black in color [10]. The synthesized products were characterized by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), energy-dispersive X-ray diffraction (EDS), FTIR, and Raman spectroscopy.
III. RESULTS AND DISCUSSION

SEM images of nanocables synthesized at the flow ratios of 98:2 Fig. 1(a) and 90:10 Fig. 1(a) were presented in Fig. 1. Randomly oriented large-scale nanocables have been uniformly synthesized on the surface of Si substrate. High-magnification SEM images show that the nanowires synthesized at 98:2 flow ratio have smooth surface and those synthesized at flow ratio of 90:10 have rough one. The mean diameter of nanowires synthesized at flow ratio of 98:2 and 90:10 were estimated to be about 140nm and 200nm, respectively.

Based on low-magnification TEM observation Fig. 2(a) and 2(b), the as-synthesized one dimensional nanostuructures have core-shell structure. With decreasing the ethanol flow, the thickness of shell increased and the core diameters decreased. For instant, mean diameter of cores and mean thickness of shells were estimated to be 40nm and 50 nm at 90:10 flow ratio, respectively. For those synthesized at 98:2 flow ratio, the values were estimated to be 10nm and 90 nm, respectively. Based on our previous reports [10], the nanocables synthesized by use of ethanol pyrolysis consisted of crystalline SiC cores and amorphous SiO$_2$ shells. SAED (selected area electron diffraction) patterns [inserts in Fig. 2(a) and (b)] recorded from the nanocables also confirm the existence of crystalline SiC and amorphous materials in nanocables.

Fig. 3 shows the IR spectra of the nanocables synthesized at different flow ratios. The two strong absorption bands centered at $\sim 1090$ and $\sim 796$cm$^{-1}$ in all spectra can be attributed to Si-O antisymmetric stretching mode [14] and SiC transverse optical (TO) mode [5–8], respectively. Therefore the amorphous material is confirmed to be SiO$_2$.

It is interesting to note the change of SiO main stretching band with ethanol flow. At low ethanol flow, SiO main stretching band shows a strong absorption peak centered at $1090$cm$^{-1}$ and a weak shoulder centered at $1137$cm$^{-1}$. With increasing ethanol flow, the intensity of $1090$cm$^{-1}$ peak becomes weak, while $1137$cm$^{-1}$ shoulder peak is enhanced. At high ethanol flow, the two bands are clearly distinguished and the $1137$cm$^{-1}$ peak becomes stronger.

Similar shoulder peaks centered at about $1130$cm$^{-1}$ have been found from Si-SiO$_2$ nanocables [11], amor-
Hu et al. [11] considered that this shoulder peak from Si-SiO$_2$ nanocables resulted from the interface effect of the open structure of chainlike SiO$_2$/Si nanowires and the vibration of an interstitial oxygen atom in a silicon single-crystalline core of nanowire. For SiO$_2$ nanowires [14], the origin of this shoulder peak was attributed to the structural disorder in amorphous SiO$_2$. There was no explanation about this peak for SiC-SiO$_2$ nanocables [15]. In previous reports [11, 14], the origin of this shoulder peak was interpreted on the base of the experimental result performed by Gaskell et al. [16] and refer it to the structural disorder in amorphous SiO$_2$ shells. The problem is why the structural disorder is created and where the structural disorder in SiO$_2$ exists. The rough surface [Fig. 1(d)] implies the structural disorder of SiO$_2$ surface. At this time, it is not clear why the shortening of Si-O bond occur in the surface of SiO$_2$ shell of SiC-SiO$_2$ nanocable. It needs further study.

Next interest comes from a sharp band ranged from 870 cm$^{-1}$ to 960 cm$^{-1}$ in Fig. 3. At low ethanol flow, an obvious peak centered at 910 cm$^{-1}$ comes into view. With increasing ethanol flow, this peak becomes weak and finally a broad and weak absorption band appears in this region. To our knowledge, there is no report with respect to the sharp 910 cm$^{-1}$ peak in SiC-SiO$_2$ nanocables. This peak is difficult to be attributed to the terminal SiOH deformation band absorption having its maximum position at 958 cm$^{-1}$ [14] due to the large frequency difference. Moreover, this peak decreased with increasing ethanol flow. If we assign this peak to the OH group, the intensity of this band should be increased with increasing ethanol flow because more OH groups would be formed.
FIG. 4. SEM (a) and TEM (b) images of etched nanocables and EDS spectra before (c) and after (d) etching.

FIG. 5. FTIR spectrum of etched nanocables.

on the surface of SiO₂ shell at high ethanol concentration. This peak also differs from the SiC IF (interface) modes often observed in Raman measurement [17], because no dominant peak appears in this range from etched nanocables as shown in Fig. 5.

To find out nature of the 910 cm⁻¹ peak, we simulate infrared field in a SiC nanorod inserted into a transparent host medium. Absorption in the SiC nanorod is calculated by \( \vec{J} \cdot \vec{E} = \omega \text{Im}[\varepsilon(\omega)] \langle \vec{E}^2 \rangle \) [18], where \( \langle \rangle \) signifies field-averaging over one optical cycle, Im signifies imaginary part, \( \omega \) is the frequency of interest, \( \varepsilon(\omega) \) is the infrared permittivity of SiC at the frequency \( \omega \), \( \vec{J} \) is the displacement current density, and \( \vec{E} \) is the electric field strength. Fig. 6(a) shows infrared absorption spectra for incident fields with the s- (blue circle) and p- (red cross) polarizations. For the s-polarization perpendicular to the cross section of SiC nanorod, there is one peak near 795 cm⁻¹ obviously corresponding to TO-mode of SiC, which is naturally observed in bulk SiC. For the p-polarization parallel to the cross section of SiC nanorod, there is one peak between TO-frequency and LO-frequency of SiC. This peak is attributed to resonant coupling of p-polarized field to the nanostructure of SiC, corresponding to surface phonon resonance (SPR) in the SiC nanorod. Fig. 6(c) shows field enhancement in the SiC nanorod at the surface phonon resonance, while (b) shows no field enhancement at the TO-frequency for the s-polarization. An analytical treatment of an ellipsoid in the electrostatic approximation [19] can make nature of the two peaks more clear. The analytical study leads to the following expression for the polarizabilities \( \alpha_i \) along
the principal axes \((i = 1, 2, 3)\)

\[
\alpha_i = \frac{4\pi a_1 a_2 a_3}{3\varepsilon_h + 3L_i} \frac{\varepsilon(\omega) - \varepsilon_h}{\varepsilon(\omega) - \varepsilon_h}.
\]  

Here \(a_1, a_2, a_3\) is semiaxes of the ellipsoid, \(\varepsilon_h\) is the permittivity of host medium, \(L_i\) is a geometrical factor given by

\[
L_i = \frac{a_1 a_2 a_3}{2} \int_0^\infty \frac{dq}{(a_i^2 + q)} f(q),
\]

\[f(q) = \sqrt{(q + a_1^2)(q + a_2^2)(q + a_3^2)} \]  

The geometrical factors satisfy \(\sum L_i = 1\), and for a sphere \(L_1 = L_2 = L_3 = \frac{1}{3}\). If the nanorod is considered as a kind of ellipsoid with \(a_1 = a_2, a_3 = \infty, L_1 = L_2 = \frac{1}{2}, L_3 = 0\). If we remind the resonance arises at a pole of the polarizability, a surface-resonance peak \((L_1 = L_2 = L_3)\) centered between the TO-frequency and the LO-frequency and no peak exactly centered at the TO-frequency should be observed in FTIR spectra of spherical nanoparticles of SiC as were in [20, 21]. However, for the case of nanorod, both of the surface-resonance peak \((L_1 = L_2)\) between the TO-frequency and the LO-frequency and the bulk-peak at the TO-frequency \((L_3 = 0)\) should be observed as were clearly in our FTIR spectra.

Our experimental result (Fig. 3) shows weakening and disappearing of the 910 cm\(^{-1}\) band with increasing the flow of ethanol precursor, contrary to the theoretical deduction. It is assumed that the discrepancy is attributed to the highly disordered surface of SiO\(_2\) shell and a transient layer between the SiO\(_2\) shell and the SiC core, which would be enhanced with increasing the flow of ethanol precursor, suppressing coupling of incident infrared field to the SiC core.

### IV. CONCLUSION

The enhancement of a peak centered at 1130 cm\(^{-1}\) at higher frequency of Si-O stretching band was observed. The origin of this peak was referred to the structural disordering of SiO\(_2\) shell surface. Below 1000 cm\(^{-1}\), our nanostructure reveals in its FTIR spectra both of the peak centered at 910 cm\(^{-1}\) and the peak centered at 795 cm\(^{-1}\). The 910 cm\(^{-1}\) peak is attributed to surface phonon resonance in the SiC part which is characteristic of SiC nanoparticles. The 795 cm\(^{-1}\) peak is attributed to TO-mode absorption in the SiC part, which is characteristic of bulk SiC.

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