Catalyst-free and controllable growth of SiC_xN_y nanorods

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Abstract

Non vapor–liquid–solid (VLS) method of growing high-purity silicon carbon nitride (SiC_xN_y) nanorods with rod widths ranging from 10 to 60 nm and lengths of microns is reported. Unlike the case for the ordinary VLS or catalyst-mediated growth, the two-stage process presented here is a catalyst-free approach since it does not involve any catalyst during the growth of the nanorods. The first stage involves formation of a buffer layer containing various densities of SiC_xN_y nanocrystals by electron cyclotron resonance plasma enhanced chemical vapor deposition (PECVD); whereas the second stage involves a high growth rate along a preferred orientation to produce high-aspect-ratio nanorods using microwave PECVD. Moreover, the number density and the diameter of the nanorods can be controlled by the number density and the size of the nanocrystals in the buffer layer. Production of quasi-aligned SiC_xN_y nanorods with a number density of the rods as high as 10^{10} cm^{-2} has been achieved. The SiC_xN_y nanorods thus produced exhibit good field emission characteristics with stable operation over 8 h. The approach presented here provides a new advance to synthesize nanorod materials in a controllable manner. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: A. Nanostructures; B. Vapor deposition

1. Introduction

The inherent anisotropy in one-dimension (1-D) systems, such as nanotubes, nanorods, and nanowires, is central to the unique properties and phases of these materials [1]. Besides the quantum size effect [2], the lattice orientation in a nanorod or nanowire can affect their optical properties in a manner unavailable in quantum dots [3]. Applications for 1-D systems include functional components in advanced mesoscopic electronic and optical devices, interconnects, probe microscopy tips, as well as superstrong and tough composites [4–7]. Among them, electron field emission of carbon nanotubes (CNT) exhibits rather promising features for flat-panel-display application [8]. The extremely large

field enhancement effect originated from the sharp curvature of CNT is the main factor responsible for their low threshold fields and high current densities. In view of this, nanorods and nanowires with similar geometric features have the potential as field emitters, and indeed good field emission properties from these nanostructures have been reported [9–11]. Nevertheless, researches on 1-D materials other than CNT are still quite scanty.

To explore and realize these exciting opportunities requires producing 1-D system in a well-controlled manner. To date, several techniques, such as laser ablation [12,13], template-based [14,15], solution-based [16], carbothermal reduction [17], powder-mixture reaction [18] oxide-assisted growth [19], and rapid thermal process [20] have been employed to synthesize 1-D nanostructures. Most of the techniques relate to the vapor–liquid–solid (VLS) process wherein a catalyst is involved. The catalyst usually remains in the 1-D system and may affect its intrinsic properties.

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This work presents a non-VLS and catalyst-free approach of growing SiC_xN_y nanorods directly on Si substrate.

The ternary SiC_xN_y compound has just been identified to be a new phase, distinct from those of crystallized Si_3N_4 -SiC or Si_3N_4 -C mixtures [21–25]. While the chemical bonding and the atomic local order can be quite complex in the ternary SiC_xN_y system, a simple class would be the one exhibiting crystal structure similar or isomorphic to a known phase with well-established structure details. For instance, a ternary solid solution of (Si; C) $_3\text{N}_4$ is a compound that falls on the tie line between the known Si_3N_4 and the hypothetical C_3N_4 . Assuming both phases exhibit β - Si_3N_4 structure and are miscible, the β -(Si; C) $_3\text{N}_4$ substitutional solid solution is a three-dimensional network wherein all the C and Si atoms are bonded to four N atoms and all the N atoms are bonded to three C and/or Si atoms. Theoretical studies for the series of hexagonal (mostly in the β - Si_3N_4 structure) and cubic (in the defect zinc-blende structure) $\text{Si}_{3-n}\text{C}_n\text{N}_4$ ($n = 0, 1, 2, 3$) indicated that they are potentially superhard materials [26–28]. Considering that all the three constituent elements of the SiC_xN_y compounds are light and usually light covalent compounds are hard materials with wide band gap energies, the newly discovered SiC_xN_y crystals are expected to possess mechanical and optical properties as such. Indeed, polycrystalline SiC_xN_y film exhibits a hardness value rivals to cBN [29] and a direct band gap at 3.8 eV [30], therefore, a great potential for blue and ultra-violet photo-electronic applications. Furthermore, ultra-high oxidation resistance up to 1600°C has also been reported in the amorphous SiC_xN_y phase [31].

In our previous works, polycrystalline SiC_xN_y films were deposited by microwave plasma enhanced chemical vapor deposition (MW-PECVD), wherein the nucleation density was low, while the growth rate was high, leading to formation of micron-sized crystals [22]. On the other hand, deposition of SiC_xN_y by using electron cyclotron resonance (ECR) PECVD led to formation of amorphous or nanocrystalline film with high nucleation density [32], presumably, due to the higher ionization fraction and more abundant nucleation species in the ECR-PECVD process [33]. In this report, a two-stage approach that combines the advantages of ECR- and MW-PECVD was used to produce dense SiC_xN_y nanorods. In the first stage, a thin SiC_xN_y buffer layer was deposited on Si (100) or (111) substrates using ECR-PECVD. Then, the substrates were transferred to the MW-PECVD reactor for directional growth with higher rate. The result is the formation of SiC_xN_y nanorods, surprisingly different from its poly- and nano-crystalline counterparts. Our approach to the nanorod growth is catalyst-free and self-mediated in that the buffer layer contains the same chemical elements as the nanorods. In addition, the buffer layer also controls the number density and the diameter of the nanorods. Moreover, direct growth of these nanorods on Si is advantageous for future integration into the existing micro-electronics technology.

2. Experiments

2.1. First stage growth of buffer layers

The SiC_xN_y films were deposited in an ECR-PECVD reactor, which consists of a 40 cm diameter chamber equipped with a substrate stage wherein a BN heater is used for independent control of the substrate temperature. A thermocouple placed underneath the substrate holder was used for monitoring the holder temperature. A 1.5 kW Astex2115 microwave source and an AX4400 electromagnet were employed to generate the ECR plasma as nitrogen or hydrogen was introduced into the reactor from the top shower ring right below the quartz window. The films were deposited on Si(100) and (111) substrates after standard HF acid deoxidization and distilled water cleaning followed by H_2 plasma etching of surface impurities. Prior to film deposition, the base pressure of the reactor was 1×10^{-6} Torr evacuated by a turbo molecular pump. A mixture of semiconductor grade H_2 , N_2 , CH_4 and SiH_4 (10% SiH_4 in N_2 dilution) was used as the source gas for film deposition with typical flow rates of 2.5, 2.5, 1.0 and 0.2 sccm, respectively. During the ECR-PECVD process, the chamber pressure was kept at 3 mTorr with a microwave power of 1200 W, while the substrate temperature was varied between 270 and 900°C.

2.2. Second stage growth of nanorods and nanowires

In the second stage, the Si substrates with pre-coated buffer layers were transferred to a microwave reactor (AsTex 5 kW model) for the growth of nanorods. Prior to the deposition process, the reactor was first evacuated to a base pressure of 10^{-3} Torr and a 10-min cleaning/etching of the substrate was performed using H_2 plasma at 1 kW. A mixture of semiconductor grade H_2 , N_2 , CH_4 and SiH_4 (10% SiH_4 in N_2 dilution) in various proportions was used as the source gas for the growth of SiC_xN_y nanorods. For the rest of this manuscript, we have only included the results for using H_2 , N_2 , and SiH_4 with flow rates of 80, 80 and 4 sccm, respectively, while varying CH_4 between 0 and 50 sccm. Notice that gas mixtures enriched in nitrogen are required because the dissociation rate and/or surface reaction rate of N_2 or NH_3 is much lower than that of CH_4 and SiH_4 . The experiments were performed with microwave power ranging from 1 to 2.5 kW. With no external temperature control of the substrate, the substrate temperature depends upon various growth parameters such as gas flow rate and gas composition, as well as chamber pressure and microwave power. For instance, with fixed gas composition and flow rate and at a given microwave power, the substrate temperature can be varied by changing the chamber pressure over a wide range within which the plasma remained stable. During deposition, a dual-wavelength optical pyrometer (Williamson 8220S-C-T) was used to read the temperature from the front surface of the substrate. Fig. 1 depicts the typical temperature-pressure curves at various operating

Fig. 1. Substrate temperature as a function of chamber pressure for the MW-PECVD process performed with different gas compositions and microwave powers.

microwave powers. As will be shown later in this manuscript, the substrate temperature is a critical physical parameter for the growth morphology.

2.3. Characterizations

Scanning electron microscopy (SEM) was performed with a Hitachi model S-800 SEM and a Hitachi model S-5000 Field Emission SEM (FESEM). A JEOL model 2010 TEM using an operating voltage of 160 kV was employed for high-resolution transmission electron microscopy (HRTEM) investigations. Energy dispersive X-ray spectroscopy (EDX) studies were conducted with an Oxford ISIS300 spectrometer that is integrated with the SEM.

For the photoluminescence (PL) measurements, an ArF Excimer pulsed laser operating at 193 nm (6.4 eV) with a repetition rate of 10 Hz and duration of about 50 ns for each pulse was used. The sample was placed in a closed-cycle He cryostat, which allows PL measurements to be recorded over a temperature range of 10–300 K. Further optical properties were studied by piezoreflectance (PzR) spectroscopy. For the PzR measurements, the sample was glued on a lead-zirconate-titanate piezoelectric transducer driven by a 200 V_{rms} sinusoidal wave at 200 Hz. The alternating expansion and contraction of the transducer subjects the sample to alternating strain thereby strain-induced changes of the inter-band transitions can be detected. A detailed description of the PzR experimental setup can be found elsewhere [34,35].

Field emission measurements were performed using parallel-plate configuration with spacing at about 30 μm . An indium-tin-oxide (ITO) glass plate was used as the anode of which the area was restricted to be smaller than

that of the sample to avoid the field emission at the sample edges due to their structure enhancement. The field emission I - V characteristics were obtained under a base pressure of 1×10^{-7} Torr at room temperature. A Keithly 237 electrometer was employed for sourcing the voltage and measuring the current.

3. Results and discussion

SiC_xN_y nanorods can be synthesized by MW-PECVD with a rather wide range of process parameters on SiC_xN_y buffer layers prepared by ECR-PECVD. The most critical parameters are the substrate temperature and the methane fraction in the source gas mixture during the MW-PECVD process. Nanorods can be formed at a substrate temperature higher than 950°C and up to a methane flow rate of 35 sccm (Fig. 2). When the substrate temperature was below 950°C or when the methane flow rate was higher than 45 sccm in the MW-PECVD process, microcrystalline and nanocrystalline phases were observed. Interestingly, wire-like materials were formed within very limited range of the substrate temperature and methane flow rate, typically at around 1050°C and 40 sccm, respectively, as indicated in Fig. 2. Representative morphologies of these phases are shown in Fig. 3. The nanowires exhibit microstructure quite different from that of the nanorods and the details will be described in a separate paper. For the rest of this manuscript, we would only discuss the results for the nanorods.

Fig. 4 shows a typical SEM micrograph of a cluster of SiC_xN_y nanorods. The length and width of these nanorods were 0.7–2 μm and 10–60 nm, respectively. The aspect ratio of the SiC_xN_y nanorods reaches 30–70, considerably

Fig. 2. 'Phase fields' of the SiC_xN_y nanorods, nanowires and nanocrystals as well as microcrystals are indicated as a function of the substrate temperature and methane flow rate.

larger than those of the SiC_xN_y crystals shown in our previous reports [22,29]. The remarkable aspect ratio of the SiC_xN_y nanorod is also among the tops of known fiber materials.

Cross-section transmission electron microscopic (TEM) investigation clearly shows that the cluster of nanorods

grown on top of a buffer layer with a layer thickness of about 100 nm and that the nanocrystalline phase was formed on top of the amorphous phase in the buffer layer (Fig. 5(a)). Interestingly, there was no detectable difference in composition between the nanocrystals and amorphous phase. A possible mechanism of this bi-layer structure of the buffer layer is

Fig. 3. SEM micrographs of the SiC_xN_y nanorods, nanowires and nanocrystals synthesized by MW-PECVD process using different methane flow rates but otherwise same growth parameters. For this specific set of experiments, the H_2 , N_2 and SiH_4 (10% SiH_4 in N_2 dilution) gases were used with flow rates of 80, 80 and 4 sccm, respectively. The methane flow rate used in this set of experiments was (a) 20, (b) 30, (c) 40, and (d) 50 sccm. During the MW-PECVD process, the chamber pressure was kept at 50 Torr with a microwave power of 2000 W. However, the substrate temperature gradually increased from 1000°C , when 20 sccm methane flow rate was used, to about 1080°C , when 50 sccm methane flow rate was used.

Fig. 4. SEM micrograph of a daisy-flower-like cluster of SiC_xN_y nanorods.

that the nanocrystals were formed by the strain induced in the amorphous film after a critical thickness (approximately 50 nm) in the ECR-PECVD process [36]. Apparently, the nanocrystals formed on top of the amorphous layer served as the ‘seeds’ for subsequent growth of nanorods. The process parameters in the second stage appear to favor growth along a preferred orientation, leading to very high aspect ratios of the rods. These rods are straight and well faceted with a hexagonal cross-section. High-resolution TEM images and their corresponding electron diffractions viewed in perpendicular and in parallel to the long axis of the rod are shown in Fig. 5(b) and (c), respectively. The electron diffraction taken along the axis of the nanorod shows hexagonal symmetry whereas the perpendicular one shows twofold symmetry.

While SiC_xN_y nanorods can be formed provided that the substrate temperature and the methane fraction in the source gas mixture during the MW-PECVD process were within the range indicated in Fig. 2, the number density and the diameter of the nanorods strongly depended on the microstructure details of the buffer layers. Fig. 6 shows two pairs of SEM images of the buffer layers and their corresponding

Fig. 5. (a) Cross-section TEM image of the SiC_xN_y nanorods grown on the Si substrate indicates that there exists an amorphous interlayer with nanocrystalline aggregates on top and that the nanorods only grow from the nanocrystals. High-resolution TEM images and the electron diffraction patterns of a SiC_xN_y nanorod viewed (b) in perpendicular and (c) in parallel to the long axis of the rod, indicating a two-fold and three-fold symmetry, respectively.

Fig. 6. Two pairs of SEM images of the SiC_xN_y buffer layers and their corresponding SiC_xN_y nanorods. The buffer layers were deposited by ECR-PECVD using a mixture of semiconductor grade H_2 , N_2 , CH_4 and SiH_4 (10% SiH_4 in N_2 dilution) gases with flow rates of 2.5, 2.5, 1.0 and 0.2 sccm, respectively. During the ECR-PECVD process, the chamber pressure was kept at 3 mTorr with a microwave power of 1200 W, while the substrate temperature was independently controlled with a BN heater. The buffer layers shown in (a) and (c) were deposited with substrate temperatures of 270 and 640°C, respectively. Figs. (b) and (d) were grown by MW-PECVD using the buffer layers shown in (a) and (c), respectively. In MW-PECVD process, the same H_2 , N_2 , CH_4 and SiH_4 (10% SiH_4 in N_2 dilution) gases were used but with flow rates of 80, 80, 20 and 4 sccm, respectively. During the MW-PECVD process, the chamber pressure was kept at 50 Torr with a microwave power of 2000 W and a substrate temperature of 1000°C.

nanorods. The buffer layers shown in Fig. 6(a) and (c) were deposited by ECR-PECVD process (of which the detailed process parameters have been described in Section 2.1) with substrate temperatures of 270 and 640°C, respectively. The buffer layer deposited at 270°C was primarily amorphous with few clusters of nanocrystalline aggregates (Fig. 6(a)). The number density of the nanocrystals increased significantly with substrate temperature in the ECR-PECVD process while the average grain size of the nanocrystals showed negligible change. At 640°C, nearly complete coverage of the nanocrystalline phase was observed (Fig. 6(c)). Fig. 6(b) and (d) show the SEM micrographs taken from the samples after MW-PECVD process using the buffer layers shown in Fig. 6(a) and (c), respectively. It should be noted that these two substrates with buffer layers were placed side by side in the same MW-PECVD run for subsequent growth of nanorods. The specific deposition parameters of the MW-PECVD process used for this pair of samples were: H_2 , N_2 , CH_4 and SiH_4 gases with flow rates of 80, 80, 20 and 4 sccm, respectively; the chamber pressure at 50 Torr; a microwave power of 2000 W and a substrate temperature of 1000°C. The number density of the nanorods for the sample shown in Fig. 6(d) is much higher

than that shown in Fig. 6(b). Moreover, the diameter of the nanorods is quite similar to that of the nanocrystals. These images clearly reveal that the number density and the size of the nanocrystals in the buffer layer are the key factors that control the number density and the diameter of the nanorods. Dense ($\sim 10^{10} \text{ cm}^{-2}$), uniformly distributed quasi-aligned nanorods in which their long axis grows almost in perpendicular to the substrate have been obtained (Fig. 7). However, the angular distribution for the tilting of the rod axis away from the substrate normal was still large ($\sim 15^\circ$). This tendency of quasi-alignment occurred when nucleation density was very high, while daisy-like clusters of nanorods (Fig. 4) were observed when nucleation density was low.

It should be noted that the diameter of the nanorod remained quite constant, whereas the length of the nanorod progressively increased with time during the MW-PECVD growth process. A rough estimate of the average growth rate of the SiC_xN_y nanorods gave a value at about $0.25 \mu\text{m/h}$, considerably lower than that of the nanowires (Fig. 8). The slow growth rate makes SiC_xN_y nanorods preferable for controlled growth.

Energy dispersive X-ray spectroscopic analyses of the SiC_xN_y nanorods indicated the presence of Si, C and N for

Fig. 7. SEM image of a dense ($\sim 10^{10} \text{ cm}^{-2}$), quasi-aligned SiC_xN_y -nanorods sample. High-resolution SEM image of an individual SiC_xN_y nanorod reveals hexagonal cross-section of the rod (inset).

all the samples, but accurate determination of the composition of the nanorods by this method is not possible at present time. For the ECR-PECVD deposited buffer layers, Rutherford back-scattering spectroscopy (RBS) was employed to determine their compositions [37,38]. It was found that all the SiC_xN_y films exhibited an N content very close to 57 at.% while the $[\text{C}]/[\text{Si}]$ ratio varied from 0 to 1, depending on the process gas compositions. This implied a solid solution of Si_3N_4 and C_3N_4 , which was further supported by

bonding characteristics from the X-ray photoelectron spectroscopic (XPS) analyses. For the specific buffer layers prepared by using process parameters described in Section 2.1, the $[\text{C}]/[\text{Si}]$ ratio was 0.6. Unfortunately, the RBS technique is not suitable for the determination of the composition of the nanorods due to their inherent irregular surface features on the substrate. However, the XPS data measured for the SiC_xN_y nanorods [10] showed bonding characteristics quite similar to those of the plane SiC_xN_y films [21,22].

Typical X-ray diffractions (XRD) of the SiC_xN_y nanorods showed that their peak positions were in close proximity to those known for $\alpha\text{-Si}_3\text{N}_4$ while significant differences in their peak intensities for most of the hkl reflections were observed [39]. The peculiar deviation in peak positions and intensities was observed even for Si_3N_4 containing a relatively small concentration (~ 5 at.%) of C [25]. Although an unambiguous interpretation of the experimental XRD data can not be fully established yet, we would refer the present case to a pseudo $\alpha\text{-Si}_3\text{N}_4$ structure in that the main structural framework of the $\alpha\text{-Si}_3\text{N}_4$ is preserved for the SiC_xN_y nanorods but their space groups are not the same in a strict sense. Preliminary lattice parameters a and c (as conventionally defined for the hexagonal structure), estimated from the XRD of the SiC_xN_y nanorods were 7.60 and 5.58 Å, respectively. In comparison to the reported values of $\alpha\text{-Si}_3\text{N}_4$, namely, $a = 7.75$ and $c = 5.62$ Å [40], these lattice parameters are slightly smaller, presumably due to the substitution of some Si sites by C and the fact that C atom is smaller than Si atom.

Optical properties of the SiC_xN_y nanorods were studied by photoluminescence (PL) spectroscopy in a wide range of temperatures using an ArF laser at 193 nm. At room temperature, the SiC_xN_y nanorods exhibited a broad intense emission centered at 4.2 eV (Fig. 9). Blue shift of the peak with decreasing temperatures was observed. The band gap emission was also confirmed by piezorefectance (PzR)

Fig. 8. Average length of the SiC_xN_y nanorods and nanowires versus growth time. Typical morphologies for this set of samples are shown in Fig. 3(a) and (c).

Fig. 9. Experimental PL and PzR (inset) spectra of SiC_xN_y nanorods at 300 K. The PzR curve has been fitted to the first derivative of a Lorentzian profile, which yields the direct band-to-band transition energy [35].

Fig. 10. Field emission J – E curves for two SiC_xN_y -nanorods samples in log-linear scale. Field emissions are characterized using parallel-plate configuration (with spacing at about $30\ \mu\text{m}$) under a base pressure of 8.0×10^{-8} Torr and over a voltage sweep from 0 to 1100 V. The maximum accessible current density for SiC_xN_y nanorods varies, presumably, due to the difference in the number density as well as the geometry and orientation of the rods. Typical temporal stability test for SiC_xN_y nanorods is shown in the inset.

spectroscopic technique [41]. As shown in the inset of Fig. 9, typical PzR spectrum of the SiC_xN_y nanorods measured at 300 K shows a direct band gap of 4.2 eV, consistent with the PL data. This value is smaller than that of the $\alpha\text{-Si}_3\text{N}_4$ (~4.8 eV) [42], but is larger than that for a polycrystalline $\text{Si}_{35}\text{C}_{26}\text{N}_{39}$ film (3.81 eV) [29]. The present results indicate a variation of the band gap of SiC_xN_y phase with its composition and crystal structure while their exact relation is yet to be clarified.

In Fig. 10, the field emission characteristics of two SiC_xN_y -nanorods samples are depicted. Emission current density at the maximum accessible voltage (i.e., a field of 36.7 V/ μm) in excess of 1 mA/ cm^2 can be routinely achieved for sample with high rod number density. This material also showed a low turn-on field at 10 V/ μm , which is defined as the field in which the I–V curve shows a sharp increase in the current density, or at a current density of 10 $\mu\text{A}/\text{cm}^2$ for convenience. While achieving highest emission current at lowest applied field is the goal in most field emission study, the long-term stability of the emission is also essential. The temporal stability test for the SiC_xN_y nanorods was carried out at a constant applied voltage that gave an initial emission current density of about 100 $\mu\text{A}/\text{cm}^2$. As shown in the inset of Fig. 10, there was no significant degradation and fluctuation ($\pm 10\%$) for over 8 h.

4. Conclusion

In summary, we have demonstrated controlled growth of SiC_xN_y nanorods with a catalyst-free two-stage approach, which is different from the ordinary VLS or other catalyst-mediated process. It is shown that the number density and the size of the nanorods are determined by those of the nanocrystals in the buffer layer containing the same chemical elements. The nanorods thus grown are well faceted with typical aspect ratio of 30–70. We also believe that the present technique of using nanocrystal-containing buffer layer followed by a directional growth can be a general method for preparing compositionally diverse nanorods. The 4.2 eV direct band gap determined by optical measurements manifests a potential of the SiC_xN_y nanorods for blue-UV applications. Finally, dense ($\sim 10^{10} \text{ cm}^{-2}$), uniformly distributed quasi-aligned SiC_xN_y nanorods exhibit low turn-on field ($\sim 10 \text{ V}/\mu\text{m}$), large emission current density ($> 1 \text{ mA}/\text{cm}^2$) and stable operation over 8 h.

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