Temperature dependence of Raman scattering in defect-free AlN nanorods grown on multilayer graphene by van der Waals epitaxy

Xianjie Xiong1,2,4, Yu Xu1,3,5, Shunan Zheng1, Tong Liu1, Xujun Su1, Bing Cao1,2,4, Chinhua Wang1,2 and Ke Xu1,3,4

1 School of Optoelectronic Science and Engineering & Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215006, People’s Republic of China
2 Key Lab of Advanced Optical Manufacturing Technologies of Jiangsu Province & Key Lab of Modern Optical Technologies of Education Ministry of China, Soochow University, Suzhou 215006, People’s Republic of China
3 Suzhou Institute of Nano-Tech and Nano-Bionics (SINANO), Chinese Academy Sciences (CAS), Suzhou 215123, People’s Republic of China
4 Suzhou Nanowin Science and Technology Co Ltd, Suzhou 215123, People’s Republic of China
5 Authors to whom any correspondence should be addressed.

E-mail: yxu2007@sinano.ac.cn and bcao2006@163.com

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Abstract

The crystalline quality of traditional epitaxy is hampered by the lattice and thermal mismatch of epilayer and substrate. Van der Waals epitaxy (vdWE) allows the epilayer to show no excessive strain and results in low defects density. Here, the multilayer graphene as a substrate for c-axis-oriented growth of vertically aligned AlN nanorods by vdWE have been presented. Defect-free of the AlN nanorods was evidenced through transmission electron microscopy (TEM). The strain of AlN nanorods was reduced with the exponential of height, which was characterized by micro-Raman spectroscopy. Moreover, the temperature dependence of Raman scattering of AlN has been further studied for clarifying the relationship of optical phonons and temperature. This temperature dependence was well matched by an empirical relationship which has proved to be applicable for other III-Nitride (such as GaN, InN) semiconductors.

1. Introduction

Van der Waals epitaxy (vdWE) requires no satisfy of lattice match between the growing crystal and underlying 2D materials, thereby improving crystal quality and simplifying the epitaxy process [1]. In addition, due to weak van der Waals interaction between the crystal and substrate, the crystal will be allowed to transfer to foreign substrate as well as leave a clean substrate for reuse [2]. Recent developments of growth of the wide band gap [WBG, generally the band gap (Eg) in the range of 3–6 eV] semiconductors on 2D layered materials have attracted renewed attentions [3, 4].

Several excellent reports described different researches of luminescence [5], ultraviolet photodetector [6], deep ultraviolet light emitting diodes [7], strain [8] and defects [9] of the WBG semiconductors grown on 2D layered materials. Considerable research efforts have been devoted to the thin film and bulk structures. Compared with traditional thin film and bulk structure [10–13], the nanostructures of WBG semiconductors with large surface-to-volume ratio can be applied for more comprehensive fields. However, the published data on vdWE of AlN nanostructures is still insufficient, and its optical properties, especially the optical phonons of AlN, is not very well-documented to date.

Here, the high-quality AlN nanorods via vdWE using graphene as a substrate, which is directly obtained by the sublimation of 4H-SiC and preserved the consistent orientation of the crystal with substrate have been demonstrated. The crystalline quality of AlN nanorods has also been illustrated by high-resolution TEM (HRTEM) and selected area electron diffraction (SAED). The multilayer graphene (MLG) are confirmed by energy dispersive x-ray spectroscopy (EDX) after the growth of the AlN nanorods. Raman spectrum are used to
investigate the typical phonon frequency and residual strain of AlN nanorods. Furthermore, the temperature dependence of the optical phonons and the Raman linewidth on single crystal AlN nanorods over a temperature range from 4 K to room temperature have been reported, which appears to follow the same empirical functional form which has been found for diamond [14, 15] and other semiconductors [16–18]. This research extends our knowledge of the AlN nanostructures direct growth via vdWE and also raises to be potentially attractive of photon-assisted optoelectronic devices.

2. Experimental

2.1. Growth of AlN nanorods
Catalyst-free AlN nanorods were grown on MLG/4H-SiC substrates using a hydride vapor phase epitaxy (HVPE) system. MLG was grown on Si-terminated face 4 H–SiC of the (0001) plane by sublimation (TankeBlue Semiconductor Co., Ltd), which serves as a template to promote the formation of AlN nanorods. Our group has reported the AlN films grown on MLG/SiC by HVPE, and found that pretreated MLG by NH3 was propitious to nucleation of AlN [10]. Here, we elevate the growth temperature to 1300 °C and cut off the pretreatment for nonplanar growth of AlN. Therefore, high-quality AlN nanorods has been fabricated on MLG by vdWE.

2.2. Characterization
The surface morphology of AlN nanorods were exhibited by scanning electron microscope (SEM) (FEI Quanta 400 FEG, 10 kV). The microcosmic structure was investigated by TEM (FEI; Tecnai G2 F20 S-Twin; equipped with high-resolution TEM). For the TEM sample, a Pt and C protective layer was deposited onto the surface of the sample using the ion beams in a dual-beam focused ion beam (FIB) system. TEM milling voltage was changed from 10 to 2 kV to minimize the beam-induced damage, and a standard copper Omniprobe grid was used to fix the TEM lamella. MLG is characterized by EDX. Temperature dependence of Raman spectrum (F1; LabRam HR 800, 532 nm) was used to analyze the strain and optical phonons of AlN. A quartz chamber equipped with a homemade temperature stage was used to heat the sample from 4 to 300 K in flowing liquid helium. The laser power supplied through the 50x objective lens was estimated to be less than 2.78 mW incident on the sample. The wave number position was calibrated with a standardized single crystal silicon. For each measurement point at each given temperature, the temperature was stabilized for ten minutes before acquiring experimental spectrum, which was measured twice and averaged to obtain.

3. Result and discussion
The SEM vertical view of AlN nanorods grown on MLG/4H-SiC was shown in figure 1(a). It can be seen that AlN nanorods are hexagonal and the in-plane orientation is uniform (the red dotted line in figure 1(a) marks the m-plane of the hexagonal nanorods). Nanorods vary in diameter, and a few nanorods have been merged due to the close of nucleation. The representative SEM aerial view of AlN was shown in figure 1(b). The AlN grown along the C axis with similar height exhibited a pyramidal tip, indicating Al-polarity. Figure 2 shows that the C element (green) and N element (blue). Conversely, the double dashed line below approves the complete overlapping of Al (green) and N element (blue). Mixed dislocations would be found under both vector conditions. No dislocation was observed by two-beam bright/dark field TEM at g = (0002) and g = (0110), respectively. Mixed dislocations would be found under both vector conditions. No dislocation was observed by two-beam bright/dark field TEM at g = (0002) and g = (0110) as shown in figures 2(a)–(d), identifying the high quality of the crystal [21], which was also confirmed by HRTEM images. The microstructure and compositional distribution of the nanocrystals were further investigated by scanning-TEM (STEM) and EDX mapping. Elemental mapping under STEM mode is a powerful technique to characterize the element distribution in an individual nanoparticle. Figure 2(c) is a typical STEM image of the interface between the nanorod and substrate, on which elemental mapping analysis was induced. Figure 2(f) shows EDX elemental mapping of Al, N, Si, and C, respectively. Single dashed line above approves the complete overlapping of Al (green) and N element (blue). Conversely, the double dashed line below shows that the C element (yellow) is significantly higher than the Si element (red) layer, about 5 nm thick, further confirming the MLG in STEM of figure 2(e). As for the sporadic element C observed above the interface, it should be a residual C protective layer during FIB processing. The growth direction (0001) and the semipolar planes (1011) and (0111) have been marked in the TEM morphology at the top of the single nanorod of figure 2(g). Figure 2(h) shows the HRTEM image at the position of the red box in figure 2(g), the lattice arrangement is neat. The interlayer spacing a = 0.489 nm which is consistent with the lattice constant of AlN.
Figure 1. (a) SEM vertical view of AlN nanorods grown on MLG/4H-SiC. (b) SEM aerial view of AlN nanorods grown on MLG/4H-SiC. (c) Diameter distribution of AlN nanorods on MLG/4H-SiC. The nanorods are mostly 550 nm in diameter. (d) Height distribution of AlN nanorods on MLG/4H-SiC. The height of the nanorods is mostly 5.2 μm.

Figure 2. (a) Two-beam bright field TEM image at $g = \langle 0002 \rangle$. (b) Two-beam bright field TEM image at $g = \langle 01\bar{1}0 \rangle$. (c) Two-beam dark field TEM image at $g = \langle 0002 \rangle$. (d) Two-beam dark field TEM image at $g = \langle 01\bar{1}0 \rangle$. (e) The TEM at the interface exhibits about 5 nm thick of graphene. (f) The EDX spectrum corresponding to the Figure (e) shows the distribution of Al, N, Si, and C element, respectively. (g) The TEM morphology at the top of a single nanorod. (h) The HRTEM image at the position of the red box in (g). The inset is the SAED of the corresponding area.
The inset is the SAED pattern of the corresponding area, which show that AlN present the close-packed hexagonal lattice.

AlN normally has the hexagonal wurtzite-type crystal structure. For the purpose of a better confirmation on the optical phonons of AlN, Raman scattering investigation was also conducted. Micro-Raman experiments were performed at room temperature with a 532 nm laser. Figure 3(a) shows a complete Raman spectrum of AlN nanorods. (d) Lorentz fitting of the Raman spectrum of AlN nanorods measured at 4 K. $A_1$(TO), $E_2$(high), $E_1$(TO) had been marked. (e) Temperature dependence of the Raman shift for the active $E_2$(high) and $E_1$(LO) mode in AlN nanorods. (f) Temperature dependence of FWHM of $E_2$(high) mode of AlN nanorods.

Figure 3. (a) Raman spectrum of AlN nanorods measured at temperature of 300 K. (b) Following the position of the $E_2$(high) peak of the Raman spectrum of AlN permits a strain estimation along the nanorods c-axis, showing a decreased strain away the interface. (c) Variable temperature Raman of AlN nanorods. (d) Lorentz fitting of the Raman spectrum of AlN nanorods measured at 4 K. $A_1$(TO), $E_2$(high), $E_1$(TO) had been marked. (e) Temperature dependence of the Raman shift for the active $E_2$(high) and $E_1$(LO) mode in AlN nanorods. (f) Temperature dependence of FWHM of $E_2$(high) mode of AlN nanorods.

The inset is the SAED pattern of the corresponding area, which show that AlN present the close-packed hexagonal lattice.
The direction of Raman excitation and detection have been marked with the red arrow line. In this study, a negligible shift is observed in the $E_2$ (high) mode (less than 0.2 cm$^{-1}$), compared with that measured in AlN film [22], confirming that the AlN nanorods are nearly free of strain as discussed above [23]. In order to further support this conclusion, temperature dependence Raman scattering was employed to characterize the Raman shift and full width at half maximum (FWHM) of the $E_2$ (high) peak of single crystal AlN. Figure 3(c) shows the typical Raman spectrum of AlN detected at different temperatures. The Raman shift measured at 4 K of each active mode was determined using the Lorentzian line shape fitting as being given in figure 3(d). Changes in the Raman line positions and FWHMs are clearly evident at different temperatures. In more detail, to achieve a better understanding of how the spectrum respond to the temperature system, figures 3(e) and (f) describe the Raman shift and FWHMs of $E_2$ (high) modes during 4–300 K, respectively. And the Raman shift were fitted [lines in figure 3(e)] using the following relationship previously proposed by Cui et al [15] for modeling the temperature dependence of the Raman modes of diamond and used by Liu et al [16] for GaN films and Kazan et al [17] and Jonathan et al [18] for bulk AlN:

$$\omega(T) = \omega_0 - \frac{A}{\exp \left( \frac{h\omega_0}{k_B T} \right) - 1},$$

where $\omega_0$ is the Raman frequency at 0 K, $A$ and $B$ are fitting parameters, $h$ is Planck constant, $c$ is speed of light, $T$ is the temperature. The FWHM of $E_2$ (high) were fitted [line in figure 3(f)] using the following relationship:

$$\Gamma(T) = \Gamma_0 \left[ 1 + \frac{2}{\exp \left( \frac{h\omega_0}{4\pi k_B T} \right) - 1} \right],$$

where $\Gamma_0$ is the FWHM of $E_2$ (high) at 0 K. As can be seen, the data fit these empirical relationships reasonably well.

4. Conclusions

In summary, we performed temperature dependence of Raman scattering based on the defect-free AlN nanorods. The almost strain-free AlN nanorods on MLG/4H-SiC were obtained by vdWE and no obvious grain boundaries, stacking fault or dislocations were observed. TEM studies had further presented that such nanorods were defect-free. Micro-Raman spectrum analysed along the growth axis of individual nanorod indicated a decreasing level of residual strain away from the interface. Both Raman shift and FWHM of $E_2$ (high) mode vary with temperature were found to follow with the empirical relationships of temperature effect of AlN.

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ORCID iDs

Xianjie Xiong @ https://orcid.org/0000-0002-1419-0824
Yu Xu @ https://orcid.org/0000-0002-1843-3248

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