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AlGa_{0.2}N nanowires grown on SiO₂/Si (100) using graphene as a buffer layer

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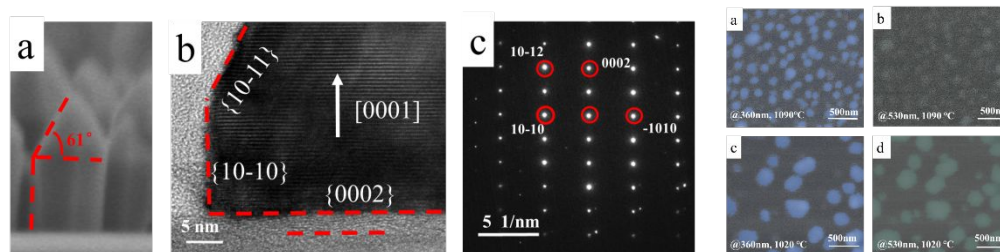
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III-nitride epitaxy is deeply dependent on the substrate and is difficult to grow on amorphous substrates because of the lattice-mismatch limits. In this paper, graphene is **employed** as a buffer layer to assist AlGa_{0.2}N nanowire growth on SiO₂/Si (100) substrate using metal-organic vapor phase epitaxy (MOVPE) technique. The **influence** of growth parameters such as reactor pressure, NH₃ flow and substrate temperature on the morphology of nanowires has been studied. In particular, it has been observed that AlGa_{0.2}N nanowires with hexagonal morphology can be achieved under lower reactor pressure and lower NH₃ flow, while **the tip morphology** can be **modified** with the substrate temperature during nanowire growth. The nanowires grown here are studied using **scanning and** transmission electron microscopy, photoluminescence and cathodoluminescence to characterize the structural and optical properties and demonstrate the high quality of grown nanowires. These findings provide a novel way to grow nanowires on any crystalline or amorphous substrates using graphene as a buffer layer, promising for future device applications.



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ABSTRACT

III-nitride epitaxy is deeply dependent on the substrate and is difficult to grow on amorphous substrates because of the lattice-mismatch limits. In this paper, graphene is **employed** as a buffer layer to assist AlGa_N nanowire growth on SiO₂/Si (100) substrate using metal-organic vapor phase epitaxy (MOVPE) technique. The **influence** of growth parameters such as reactor pressure, NH₃ flow and substrate temperature on the morphology of nanowires has been studied. In particular, it has been observed that AlGa_N nanowires with hexagonal morphology can be achieved under lower reactor pressure and lower NH₃ flow, while **the tip morphology** can be **modified** with the substrate temperature during nanowire growth. The nanowires grown here are studied using **scanning and** transmission electron microscopy, photoluminescence and cathodoluminescence to characterize the structural and optical properties and demonstrate the high quality of grown nanowires. These findings provide a novel way to grow nanowires on any crystalline or amorphous substrates using graphene as a buffer layer, promising for future device applications.

Key words: nanowire, AlGa_N, graphene, MOVPE, van der Waals epitaxy

INTRODUCTION

III-nitrides are wide band gap semiconductor materials commonly used in optoelectronic devices, such as light emitting diodes and laser diodes as well as in transistors for power electronics applications.¹⁻⁴ The cost of AlN/GaN native substrate is too high due to its complicated fabrication process,⁵ most III-nitrides based epitaxial layers are grown on non-native substrates such as sapphire, silicon carbide (SiC) and silicon (Si), which leads to the formation of many dislocations and eventually the reduction in the performance of the devices.⁶⁻⁸

Amorphous substrates have huge potential to be used in optoelectronic devices fabrication, especially in displays and flat light sources. However, the growth of III-nitrides on amorphous is challenging, for it is difficult to grow single crystals using traditional buffer layers, such as low temperature (LT) -AlN or LT-GaN, thus yielding the poor-quality epitaxial films and devices.^{9, 10} Recently, the epitaxy of GaN/AlN on SiO₂ has been demonstrated using graphene as a buffer layer.¹¹⁻¹⁴ Graphene is a two dimensional material with no dangling bonds on the surface.¹⁵ This makes graphene a good candidate for quasi van der Waals epitaxy, allowing the deposition of epitaxial layers with low density of dislocations caused by lattice mismatch.^{16, 17} In addition, carbon atoms in graphene are arranged in a hexagonal pattern, similar to the c-plane in GaN/AlN. So, the graphene can be used as a substrate with lower lattice mismatch for wurtzite GaN/AlN layers.

However, in the earlier reports, it is found that controlling the nucleation and the growth of GaN/AlN thin film on graphene is very difficult due to the absence of dangling bonds. Several methods have been tried to promote the nucleation, such as plasma treatment on graphene to create dangling bonds, and step structures.^{16, 18, 19} These methods are used mainly to expose the underlying substrate (sapphire, SiC) to help to control the orientation of the epitaxial layer, however this is not suitable for the growth on amorphous substrates. Another approach is using ZnO nanowalls on graphene whose lattice matches well with graphene, whereby good film and microdisk structures can be grown.^{11, 20-22} This method involves the growth of materials in two different reactors, which makes it more complex and expensive.

Compared to the thin film, it is easier to deposit nanowires with lower dislocation density on materials with large mismatch, since it can relax the strain in all directions.^{23, 24} Hence, nanowires are perfect candidates for device fabrication in small size. In addition, the growth conditions for the MOVPE epitaxy of GaN nanowires on other substrates like sapphire/GaN template are well established, which could be useful in

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4 optimizing the growth of AlGaN nanowires on graphene.

5 In this paper, we have attempted to grow AlGaN nanowires directly on SiO₂/Si
6 (100) substrate using graphene as a buffer layer. It is well known that the reactor
7 pressure, NH₃ flow, SiH₄ flow, and temperature influence the morphology of the
8 nanowires grown on **GaN template deposited on sapphire substrate**. Therefore, we
9 **perform** the experiments by changing the NH₃ flow and reactor pressure **systematically**
10 to obtain nanowires from nanopyramids and analyze the transformation process. After
11 that, the growth temperature is optimized to get a better nanowire morphology and
12 finally the **optical properties of nanowires are characterized by photoluminescence and**
13 **cathodoluminescence**.
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22 **EXPERIMENT**

23 Graphene was grown on Cu foils by chemical vapor deposition (CVD) and then
24 transferred on to SiO₂/Si(100) substrates using polymethyl methacrylate (PMMA) as a
25 release layer,²⁵ and then used for the growth of AlGaN nanowires by metal-organic
26 vapor phase epitaxy (MOVPE, Veeco p125 turbo-disc vertical flow reactor). Preceding
27 the growth of nanowires, hydrogen (H₂) was introduced in the reactor chamber at about
28 1060 °C with a flow of 1.5 slm for 5 minutes to clean the surface of the sample, followed
29 by ammonia (NH₃) nitridation at the same temperature with a flow of **1 slm for a**
30 **duration of 5 minutes. At the nucleation stage, AlGaN islands were grown for a duration**
31 **of 40-60 seconds**, with a trimethylgallium (TMGa) flow of 17.3 sccm and
32 trimethylaluminum (TMAI) flow of 30 sccm, respectively. For the AlGaN nanowires
33 growth, the TMGa and TMAI flows were 35 and 3.5 sccm, respectively, for a duration
34 of 25 minutes in all the samples grown in this study. H₂ was used as a carrier gas for all
35 the growths. During the growth process, the NH₃ flow, reactor pressure and substrate
36 temperature were changed to understand the growth mechanism of AlGaN nanowires
37 on graphene. It is worth noting that the SiH₄ flow was kept on in all the samples to
38 obtain one-dimensional nanowire structures. It was previously reported that the supply
39 of SiH₄ leads to the formation of a SiN_x passivation layer, **which mainly accumulates**
40 **on the nanowire sidewalls**, hindering the lateral growth and promoting the nanowire
41 growth in axial direction.²⁶
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54 The morphology of the nanowires was investigated using a Hitachi S4800
55 scanning electron microscope (SEM), the **acceleration voltage is 3 keV**, and the images
56 were acquired at a 45° angle between the sample surface and electron beam.
57 Photoluminescence (PL) spectra were acquired using a Jobin-Yvon HR800 system,
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with the temperature of about 300 K and excitation wavelength of 325 nm.

RESULT AND DISCUSSION

Effect of reactor pressure on nanowire growth

Firstly, several samples are grown at different reactor pressures between 75 and 300 Torr. For all the samples in this batch, the substrate temperature and NH_3 flow are set at 1090 °C and 15 sccm, respectively. **Figure 1** shows the SEM images of the nanostructures with growth pressures varied in the range from 300 Torr to 75 Torr.

Figure 1 shows the effect of reactor pressure on the morphology of nanocrystals, where the shape of the nanocrystals transformed from nanopyramids to nanowires by reducing the reactor pressure. **Figure 1a** shows the sample grown under a reactor pressure of 300 Torr, where the size of the nanopyramid is ~110 nm. By reducing the reactor pressure to 150 Torr, as revealed in **Figure 1b**, the nanopyramid becomes larger and the diameter increases to nearly 175 nm. It may be because that under lower pressure, the migration rate of Ga and Al atoms is enhanced to promote the coalescence of smaller nanopyramids. In addition, the growth orientation of the pyramids is quite uniform along the $\langle 0001 \rangle$ axis, and exhibit a tendency to grow higher. Finally, when the pressure is reduced to 75 Torr, nanowires appear with a well-defined hexagonal morphology, as shown in **Figure 1c**. Under higher reactor pressure, the decomposition rate of ammonia will increase, which enlarges the effective V/III ratio and shortens the mean free path of group III adatoms. In addition, it is well reported that the hydrogen atoms decomposed from the NH_3 passivate the sidewalls of the nanopyramids preventing any further growth of these pyramids.^{27, 28} So under low pressure, it may be important to determine the critical value of NH_3 , where hydrogen atoms do not passivate the nanopyramid sidewalls and allow the Ga and Al atoms to migrate over the interface energy and diffuse along the sidewalls, aiding the growth of longer nanowires.

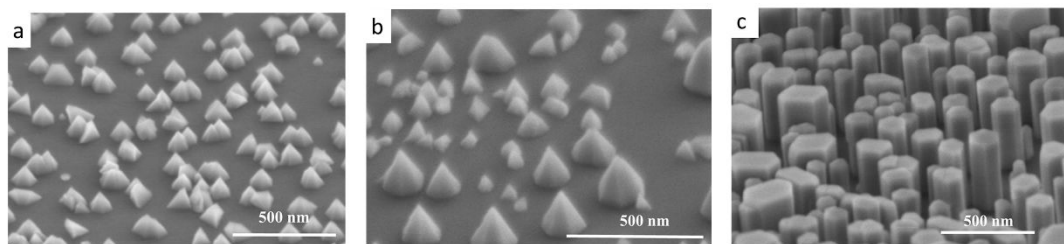


Figure 1. Tilted view SEM images of AlGaN grown on graphene/SiO₂/Si (100) substrate at a pressure of (a) 300 Torr (b) 150 Torr and (c) 75 Torr.

Effect of NH₃ flow on nanowire growth

To understand the influence of NH₃ flow on nanowire growth, it is varied between 15 and 100 sccm. For all these samples, the temperature and pressure are set at 1040 °C and 75 Torr, meanwhile TMGa and TMAI flows are set at 35 sccm and 3.5 sccm, respectively. Figure 2 shows the 45° tilted view SEM images of samples grown at different NH₃ flow rates.

The result shows that under higher NH₃ flow, nanopyramid structures with {1-101} sidewalls are formed, as shown in Figure 2a. The nanopyramid shape indicates that the growth rate of {1-101} planes are slow, which is caused by the hydrogen-passivation effect, and the hydrogen atoms generate from the decomposition of NH₃.^{27, 28} When the NH₃ flow is decreased to 25 sccm, as shown in Figure 2b, the growth rate of {1-101} planes increase leading to the formation of nanowires with the height of 289 nm. When the NH₃ flow is further reduced to 15 sccm, the nanowires become higher with a hexagonal morphology, and the height reaches 448nm, as shown in Figure 2c.

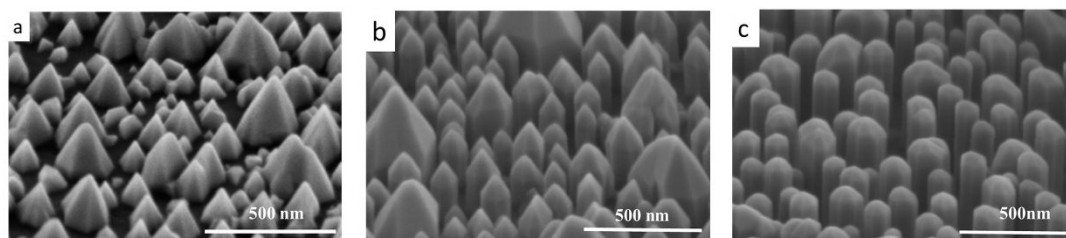


Figure 2. Tilted view SEM images of AlGaN grown on graphene/SiO₂/Si (100) substrate at a NH₃ flow of (a) 100 sccm (b) 25 sccm and (c) 15 sccm.

Effect of temperature on nanowire growth

Based on the results above, the growth parameters to obtain nanowires on graphene/SiO₂/Si (100) is known. Next, we further optimize the morphology of the nanowires by **systematically** changing the growth temperature. The NH₃ flow and the reactor pressure are set at 15 sccm and 75 Torr, respectively, and the TMGa and TMAI flows **are set** at 35 sccm and 3.5 sccm, respectively.

Figure 3 shows that nanowire growth is achieved at all three temperatures, with the main difference in the tip morphology. When the temperature is low (1020 °C), the tip of the nanowire is sharp and pyramid-shaped, as shown in **Figure 3a**, indicating that the growth rate on the {1-101} planes are smaller than that on the c-plane. When the growth temperature **reaches** 1040°C, the nanowire tip is still pyramid-like although it is not as sharp as before, as shown in **Figure 3b**, indicating an increased growth rate on {1-101} planes. When the temperature **comes up to** 1090°C, **a very flat nanowire tip is achieved**, as shown in **Figure 3c**, which means that the growth rate on the {1-101} planes have exceeded that on the c-plane. This may be due to that at higher temperature the atoms in the {1-101} planes get more energy to overcome the potential barrier, so that the growth rate increases rapidly. In this way, it is possible to control the tip morphology of the AlGaN nanowires to fit the demand of different applications.

It seems that nanowires grown under different temperatures lead to different polarity, (the shape of the tip can sometimes indicate the polarity of nanowires, a pyramidal morphology usually means Ga-polarity, whereas a flat tip is usually related to N-polarity),^{29, 30} KOH etching is introduced to examine the phenomenon, as it selectively etches N-polar surfaces.³¹ **Figure 4** reveals the results for nanowires grown at 1090°C and 1040°C. All nanowires are etched from the bottom (the interface of the nanowires and graphene, as shown in the red circle sites) leaving the tip surfaces unchanged. It is therefore concluded that nanowires under these conditions have Ga-polarity, no matter what the nanowire tip morphology looks like.³²

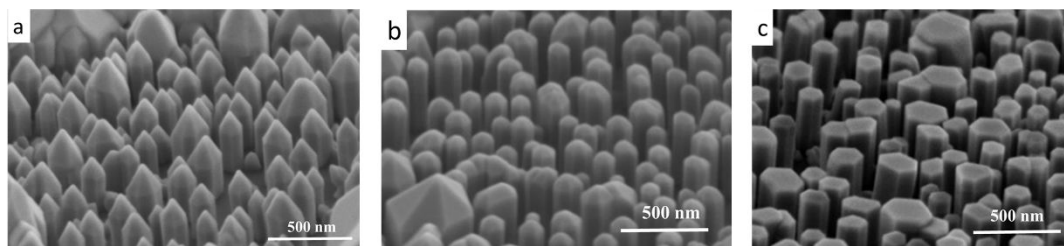


Figure 3. Tilted view SEM images of AlGaIn nanowires grown on graphene/SiO₂/Si (100) substrate at a temperature of (a) 1020°C (b) 1040°C (c) and 1090°C.

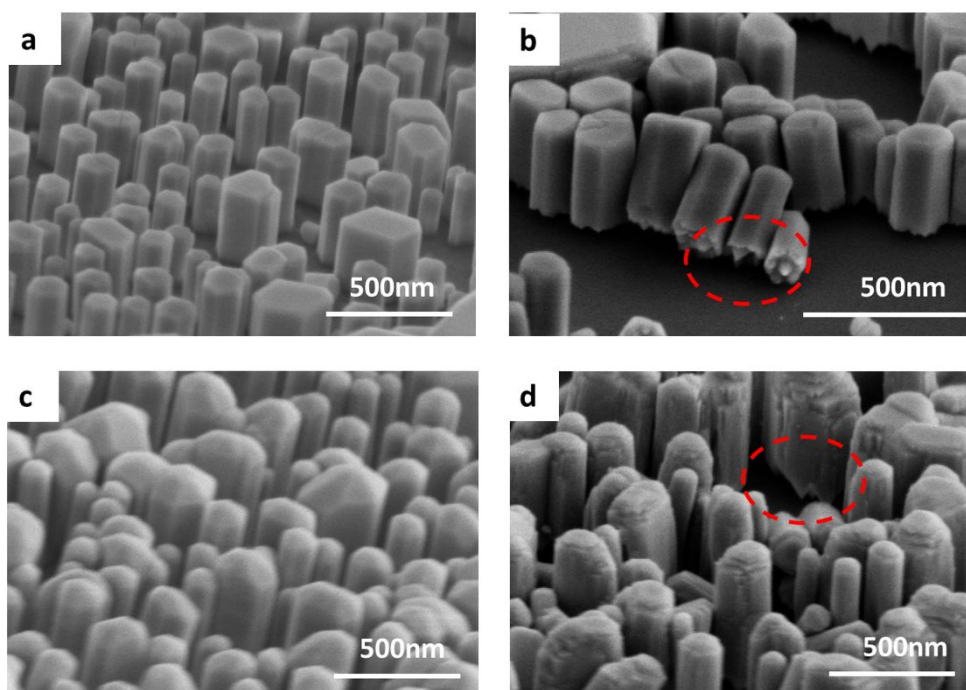


Figure 4. Tilted view SEM images of AlGaIn nanowires grown on graphene/SiO₂/Si (100) before and after KOH etching. (a) Nanowires grown at 1090°C before KOH etching, (b) nanowires grown at 1090°C after KOH etching, (c) nanowires grown at 1040°C before KOH etching and, (d) nanowires grown at 1040°C after KOH etching. The red circles show the etched sites of grown nanowires.

To summarize the optimized growth parameters, we can obtain good nanowire morphology by controlling the reactor pressure and the supply of reaction sources. At the first step, NH₃, TMGa, and TMAI are introduced at high gas flow rates of 1000 sccm, 17.3 sccm and 30 sccm, respectively, to promote the nucleation on graphene. Since the migration energy of Al on graphene is higher than Ga, this is beneficial for

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4 the formation of AlGa_N islands on graphene.^{33,34} After the formation of AlGa_N islands,
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6 the reactor pressure and NH₃ flow rates are reduced to aid the growth of nanowires. The
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8 low pressure provides the opportunity for metal atoms to migrate a longer distance, and
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10 the lower NH₃ flow rate is useful to weaken the hydrogen-passivation effect to promote
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12 the vertical growth of nanowires. Nanowires with good morphology can be achieved in
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14 this way where a Ga-polar nanowire tip-morphology can be controlled by the
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16 temperature.

17 18 19 **Structural and optical properties**

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21 **Figure 5a** shows the X-ray diffraction (XRD) spectra of the AlGa_N nanowires. **It**
22 **can be seen that** two diffraction peaks are observed at 34.52° and 72.84°, which is
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24 corresponded to wurtzite AlGa_N (0002) and (0004) planes, respectively. This reveals
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26 that the AlGa_N nanowires are of single crystal structure with c-axis orientation on the
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28 graphene substrate. The graphene is investigated by micro-Raman analysis before and
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30 after growth, as shown in **Figure 5b**. **Generally, graphene is identified by two peaks,**
31 **which are G-peak located at 1580cm⁻¹ and 2D-peak located at 2700cm⁻¹.** Before the
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33 nanowire growth, the unambiguous G-peak and 2D-peak is observed, without any
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35 defect peak at 1350 cm⁻¹, **which means the graphene is of excellent quality.** The
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37 $I_{2D}/I_G=0.47$, indicating that the graphene is multilayer.³⁵ After nanowire growth, the D-
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39 peak (~1350 cm⁻¹) of graphene increases, indicating that defects have been
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41 introduced in graphene.³⁶ This may be due to that graphene was partially etched/reacted
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43 by the H₂ and/or NH₃ during the nitridation and AlGa_N nanowire epitaxy process **at**
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45 **high substrate temperatures.**
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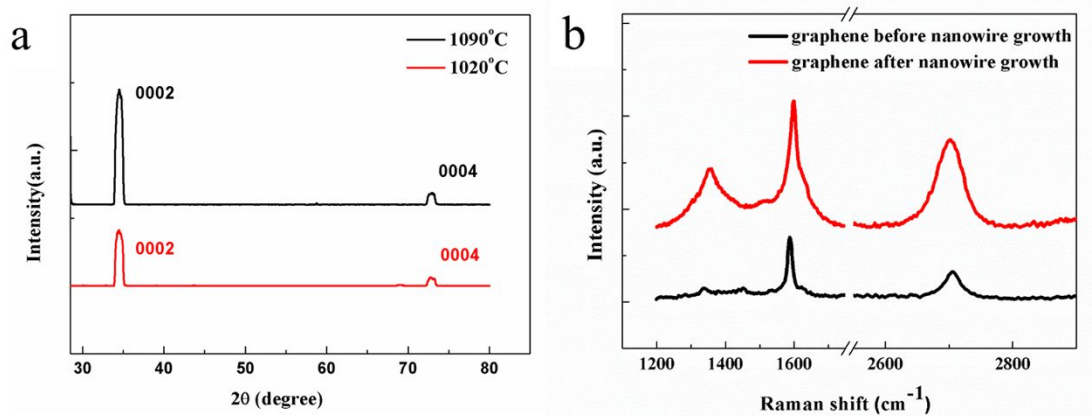


Figure 5. (a) XRD spectra of AlGaIn nanowires grown at 1090°C and 1020°C. (b) Micro-Raman spectra of graphene affected by the condition of nanowire growth.

The AlGaIn nanowires were further studied by TEM to investigate their structural properties. Figure 6a exhibits the SEM image of a nanowire, which is grown at 1020°C, under a NH₃ flow of 15 sccm and a reactor pressure of 75 Torr. Figure 6b displays the TEM image of this nanowire, showing that the nanowire has c-orientation without any dislocations. This is also confirmed by the SAED patterns in Figure 6d, which reveals that the grown nanowire is along <0001>direction and has a hexagonal wurtzite structure. The detailed graphene layer in the interface can be seen in Figure 6c with a multi-layer structure.

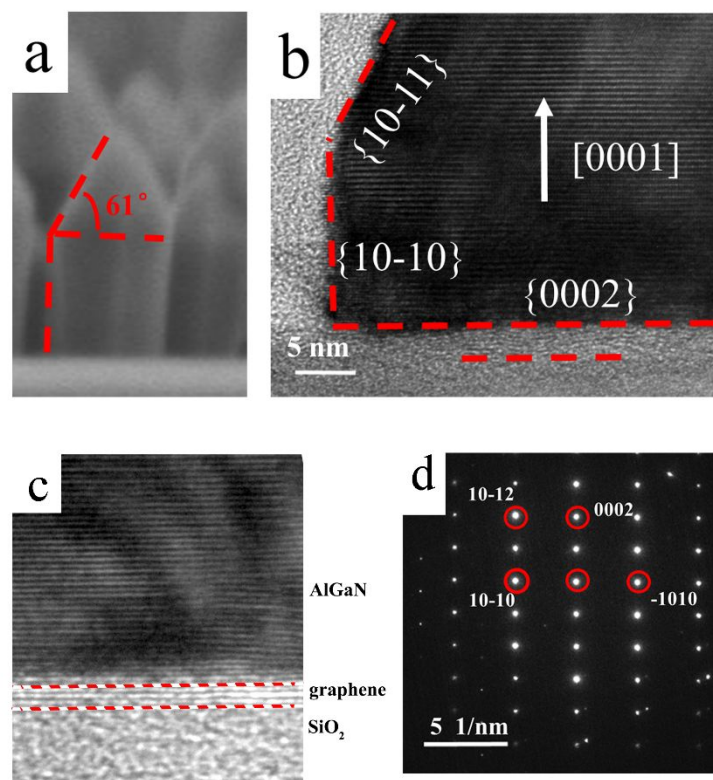


Figure 6. TEM characterization of AlGaN nanowires grown on graphene/SiO₂/Si (100). (a) SEM image of the nanowire. (b) Cross-sectional TEM image of the nanowire. (c) The detailed graphene structure. (d) Selective area electron diffraction (SAED) pattern from the same nanowire.

The room temperature photoluminescence (PL) is then characterized to compare the optical properties of nanowires grown at different temperatures, which is summarized in **Figure 7a**. There is a clear near-band-edge (NBE) emission at 359 nm and a broad yellow-luminescence (YL) at about 520-540 nm. The integrated intensity ratio of NBE/YL is ~ 0.005 at a growth temperature of 1020 °C, while it is ~ 0.29 at 1090 °C, indicating a better crystal quality at higher temperature. However, the graphene used in this study is multi-crystalline, and hence consists of grain boundaries, as well as wrinkles formed during the graphene growth and transfer. In addition, there are defects in the graphene layer formed by etching/reacting with the H₂ and NH₃ during the MOVPE growth as mentioned in the Raman analysis. These grain boundaries, wrinkles and defects not only promote the nanowire nucleation on the graphene surface but also lead to the coalescence of the crystals (shown in the **Figure 7b**). Since the migration

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4 rate of Ga and Al is lower at lower substrate temperature, the density of coalesced
5 structures with poor morphology is higher on wrinkles and grain boundaries, while the
6 nanowires with good morphology form only where graphene is free of wrinkles and
7 defects. At higher growth temperatures, the migration rate of Ga and Al is higher so
8 that nanowires can grow in larger densities at the expense of the islands. Therefore the
9 quality of the nanowires under this situation is higher.
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15 For $\text{Al}_x\text{Ga}_{(1-x)}\text{N}$ materials, the energy gap can be calculated as $E_g = (1-x) E_{g-\text{GaN}} +$
16 $x E_{g-\text{AlN}} - b \times (1-x)$, $b=1.0$ eV here. On the other hand, we can get E_g from the equation
17 $E_g=hc/\lambda$, then the Al content is obtained. In the paper, the TMAI flow is 3.5sccm, and
18 the TMGa flow is 35 sccm, the emission peak locates at 359nm when analyzed by the
19 PL results, which is calculated to be 1% of Al content. In order to directly observe the
20 incorporation of Al, we adopt EDX analysis in the sample, as shown in **Figure 7c**, the
21 Al peak can be seen clearly. Furthermore, we prepare the AlGaN nanowires with
22 various Al contents, the normalized PL spectra are shown in **Figure 7d**. For sample 1,
23 the TMGa flow is 35 sccm and TMAI flow is 11 sccm, the emission peak locates at
24 337nm, corresponding to the calculated Al content of 10%; while for sample 2, the
25 TMGa flow is kept the same, but the TMAI flow is 5 sccm, the emission peak locates
26 at 347nm, corresponding to the calculated Al content of 5%. It should be noted that the
27 TMAI flow used in this study is small, so it can be affected by the growth conditions
28 easily. Therefore, we do not observe a linear relation between the TMAI flow and Al
29 content in nanowires.
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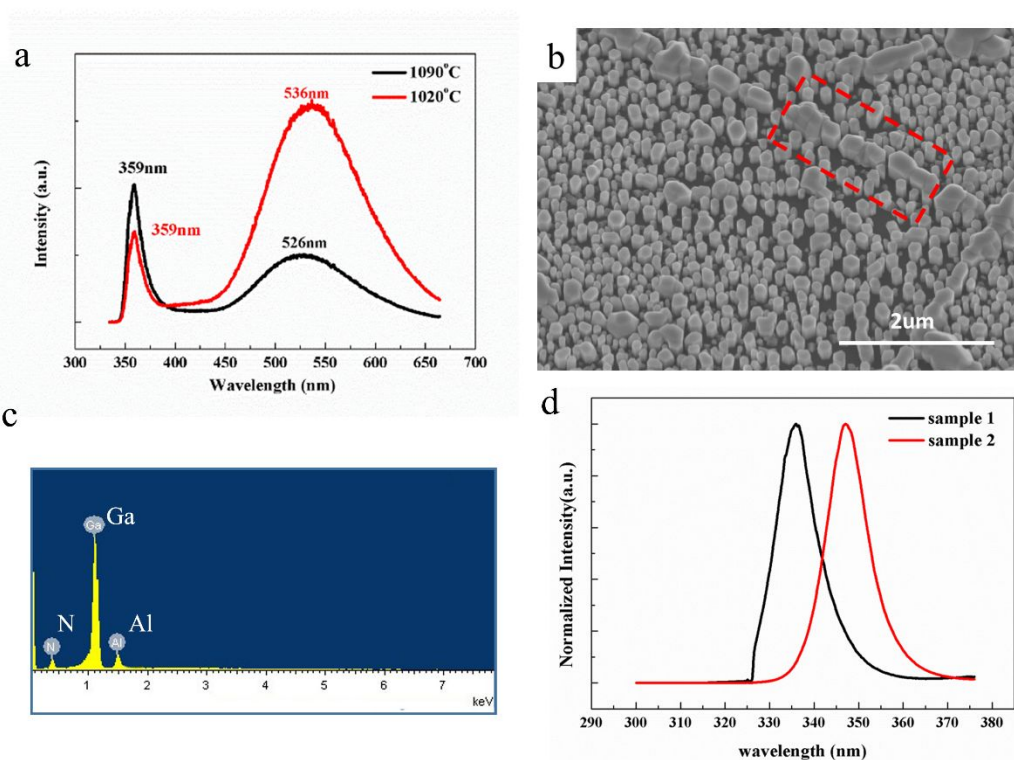


Figure 7. (a) PL spectra of nanowires grown at two different temperatures. (b) Large-scale SEM image of the nanowires, the red rectangle reveals the wrinkle and grain boundary areas. (c) The EDX analysis of the grown nanowire. (d) The PL spectra of nanowires with different Al content.

Combined SEM and spectral cathodoluminescence (CL) mapping is also carried out to compare the quality of individual nanowires. Only the nanowire areas are characterized, and two main emission wavelengths at 360 nm and 530 nm are used to analyze the growth quality, as shown in **Figure 8**. The nanowire is thinner and denser when the growth temperature is 1090°C, and there is only a weak emission at 530 nm. However, in the sample grown at 1020°C, the nanowire becomes larger in diameter with a larger spacing between each other and a strong CL emission at 530 nm. It is revealed that the quality of the nanowires grown under high temperature is better than that under lower temperature, probably due to a better crystallization on the graphene substrate.

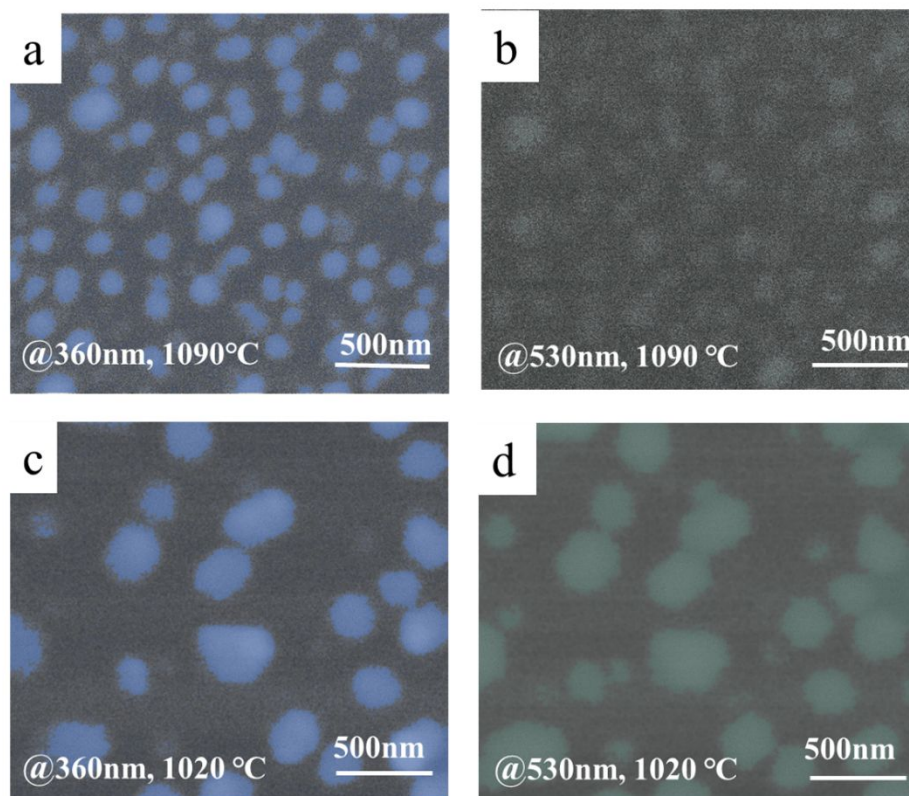


Figure 8. Spectral CL mapping images at different emission wavelengths and nanowire growth temperatures. (a) 360 nm, 1090°C. (b) 530 nm, 1090°C. (c) 360 nm, 1020°C. (d) 530 nm, 1020°C.

CONCLUSION

In this paper, we have described the transformation of III-nitride nanostructures on graphene/SiO₂/Si (100) substrates from nanopyramid to nanowire shape. It is found that a lower reactor pressure and lower NH₃ flow are critical to obtain nanowire growth. This is believed to be due to that under low pressure, the Ga and Al atoms have a higher migration rate and then have the opportunity to diffuse along the sidewalls of a nanopyramid to make it higher; when the NH₃ flow is very small, the hydrogen-passivation induced by NH₃ decomposition is weakened and the growth rate on {1-101} planes increase to form nanowires. In addition, we have shown the possibility to control the surface morphology of nanowires by changing the growth temperature. Structural and optical properties are also demonstrated to verify the high quality of

grown nanowires. These findings provide a feasible way to fabricate nano-devices on any crystalline or amorphous substrates layer in the future.

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Notes

The authors declare no competing financial interest.

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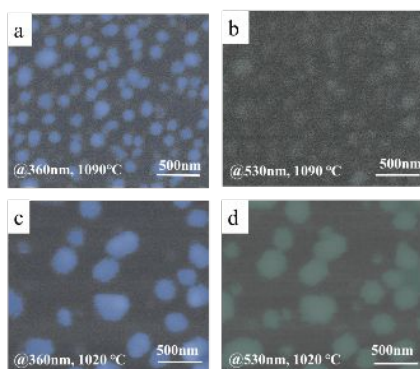
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For Table of Contents Use Only**AlGaIn nanowires grown on SiO₂/Si (100) using graphene as a buffer layer**

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Presented is CL mapping of nanowires grown under different temperatures. The nanowire is thinner and denser at a growth temperature of 1090 °C, with only a weak emission at 530 nm. However, in the sample grown at a substrate temperature of 1020 °C, the nanowire becomes larger in diameter with a larger spacing between each other, with a strong CL emission at 530 nm. This indicates that the quality of the nanowires grown under high temperature is better than that under lower temperature, probably due to a better crystallization on the graphene substrate.

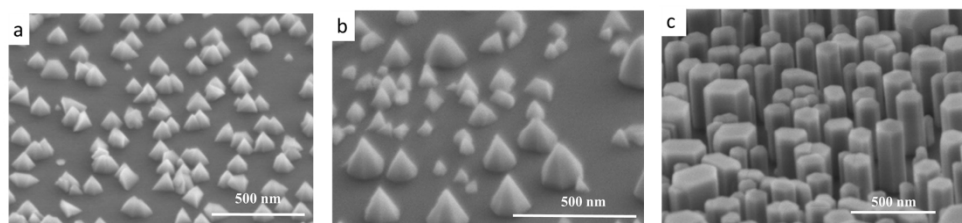


Figure 1. Tilted view SEM images of AlGaIn grown on graphene/SiO₂/Si (100) substrate at a pressure of (a) 300 Torr (b) 150 Torr and (c) 75 Torr.

1550x381mm (72 x 72 DPI)

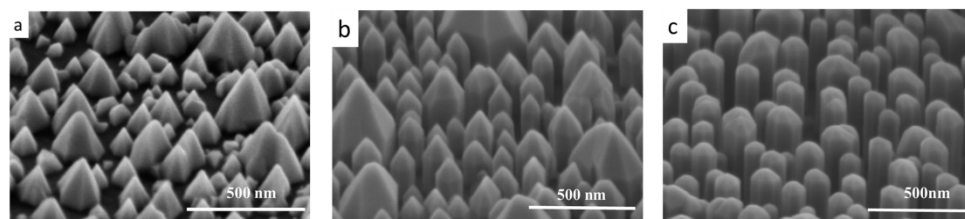


Figure 2. Tilted view SEM images of AlGaIn nanowires grown on graphene/SiO₂/Si (100) substrate at a NH₃ flow of (a) 100 sccm (b) 25 sccm and (c) 15 sccm.

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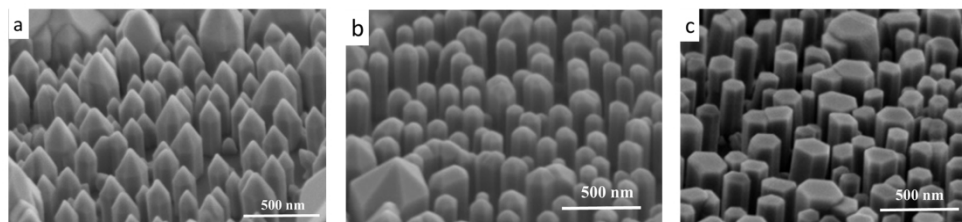


Figure 3. Tilted view SEM images of AlGaN nanowires grown on graphene/SiO₂/Si (100) substrate at a temperature of (a) 1020°C (b) 1040°C (c) and 1090°C.

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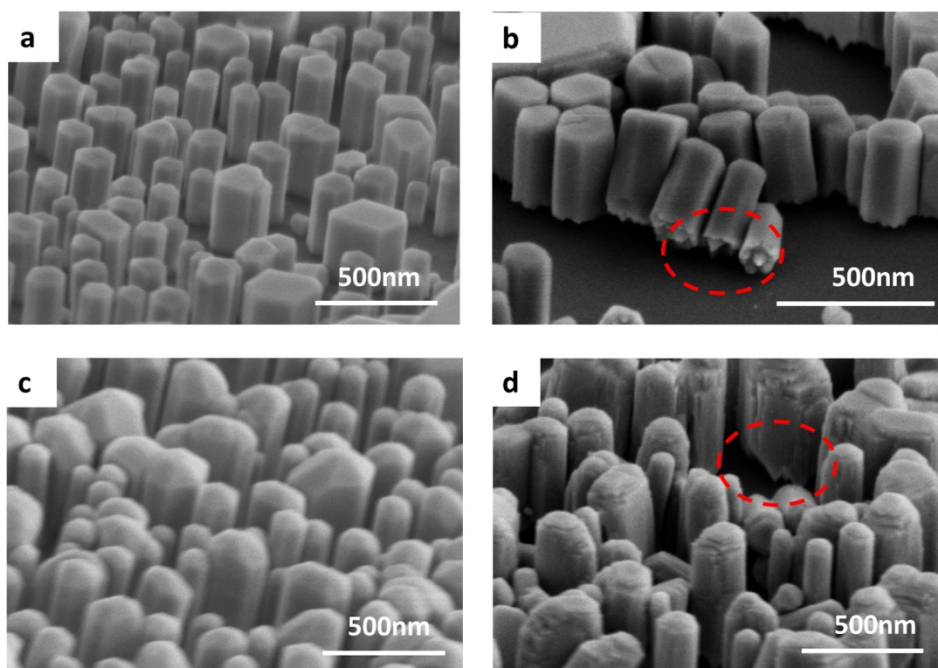


Figure 4. Tilted view SEM images of AlGaIn nanowires grown on graphene/SiO₂/Si (100) before and after KOH etching. (a) Nanowires grown at 1090°C before KOH etching, (b) nanowires grown at 1090°C after KOH etching, (c) nanowires grown at 1040°C before KOH etching and, (d) nanowires grown at 1040°C after KOH etching. The red circles show the etched sites of grown nanowires.

953x695mm (72 x 72 DPI)

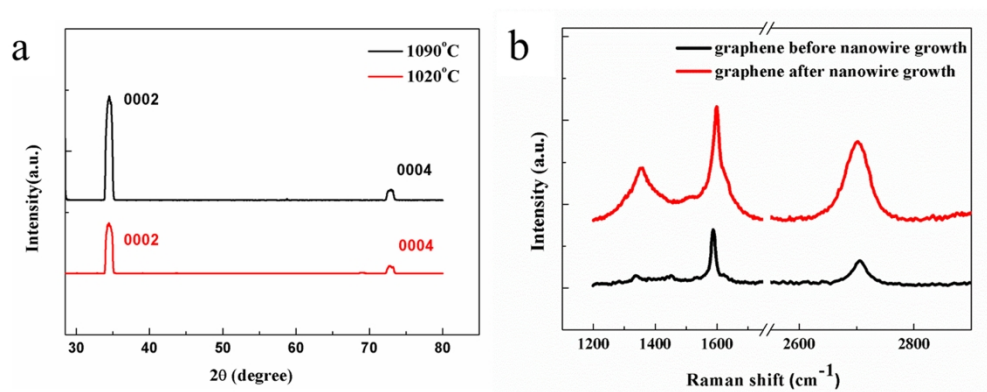


Figure 5. (a) XRD spectra of AlGaN nanowires grown at 1090°C and 1020°C. (b) Micro-Raman spectra of graphene affected by the condition of nanowire growth.

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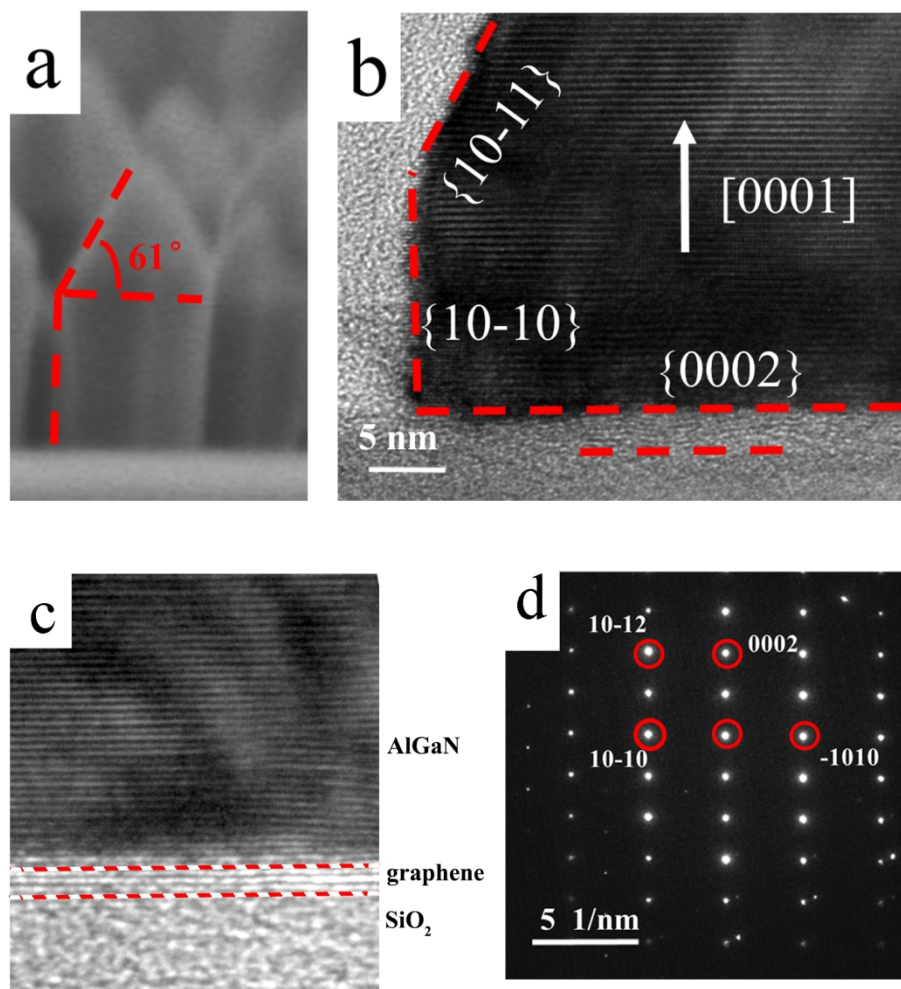


Figure 6. TEM characterization of AlGaN nanowires grown on graphene/SiO₂/Si (100). (a) SEM image of the nanowire. (b) Cross-sectional TEM image of the nanowire. (c) The detailed graphene structure. (d) Selective area electron diffraction (SAED) pattern from the same nanowire.

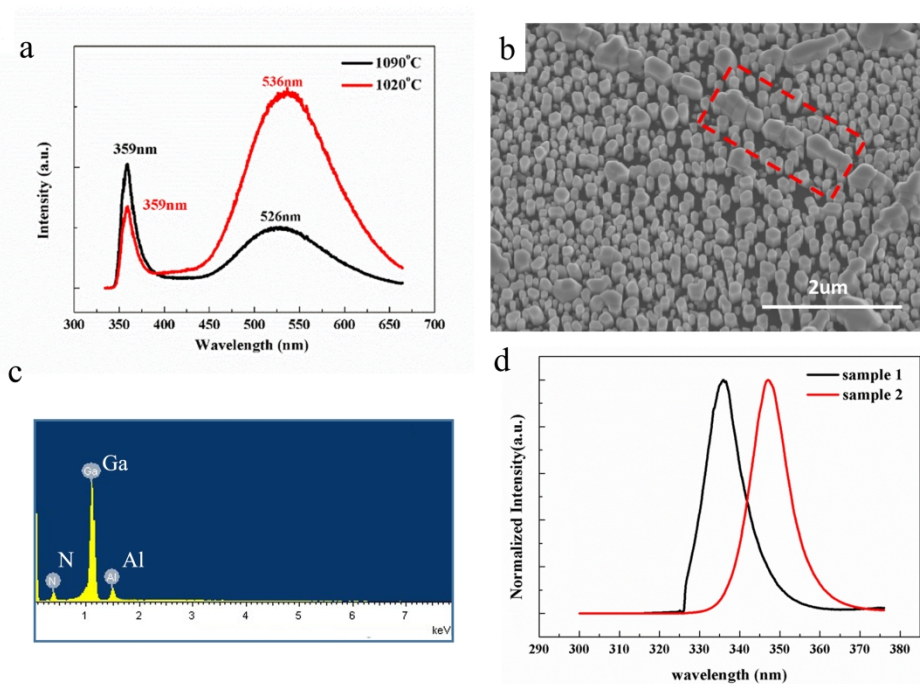


Figure 7. (a) PL spectra of nanowires grown at two different temperatures. (b) Large-scale SEM image of the nanowires, the red rectangle reveals the wrinkle and grain boundary areas. (c) The EDX analysis of the grown nanowire. (d) The PL spectra of nanowires with different Al content.

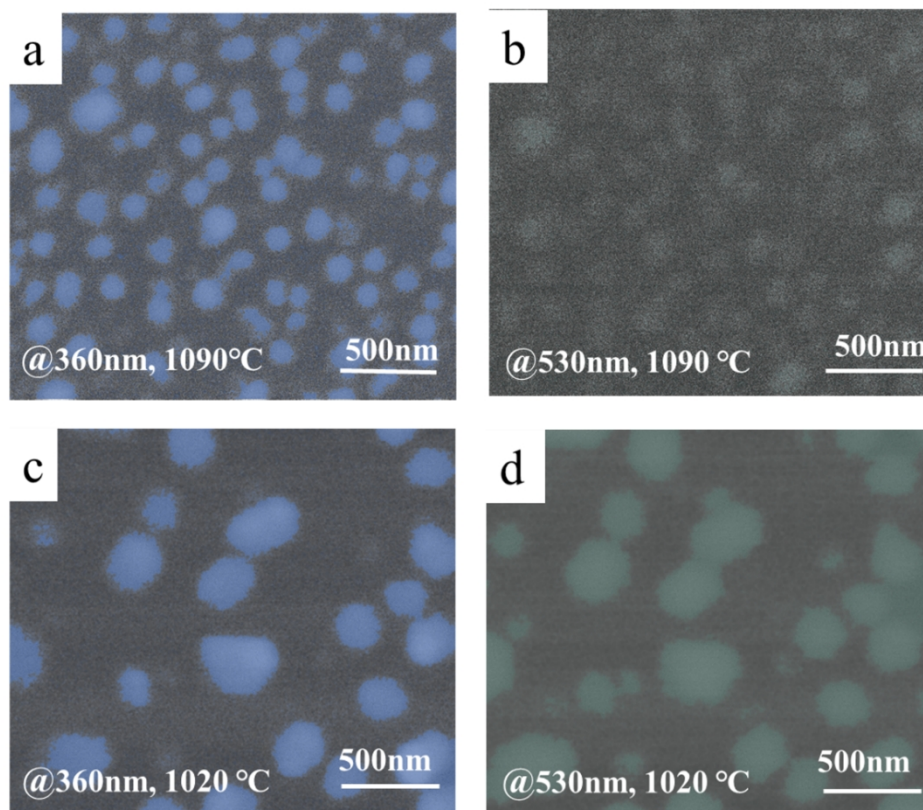


Figure 8. Spectral CL mapping images at different emission wavelengths and nanowire growth temperatures. (a) 360 nm, 1090°C. (b) 530 nm, 1090°C. (c) 360 nm, 1020°C. (d) 530 nm, 1020°C.

940x805mm (72 x 72 DPI)