Synthesis of Polytypic Gallium Phosphide and Gallium Arsenide Nanowires and Their Application as Photodetectors

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ABSTRACT: One-dimensional semiconductor nanowires often contain polytypic structures, owing to the co-existence of different crystal phases. Therefore, understanding the properties of polytypic structures is of paramount importance for many promising applications in high-performance nanodevices. Herein, we synthesized nanowires of typical III–V semiconductors, namely, gallium phosphide and gallium arsenide by using the chemical vapor transport method. The growth directions ([111] and [211]) could be switched by changing the experimental conditions, such as H₂ gas flow; thus, various polytypic structures were produced simultaneously in a controlled manner. The nanobeam electron diffraction technique was employed to obtain strain mapping of the nanowires by visualizing the polytypic structures along the [111] direction. Micro-Raman spectra for individual nanowires were collected, confirming the presence of wurtzite phase in the polytypic nanowires. Further, we fabricated the photodetectors using the single nanowires, and the polytypic structures are shown to decrease the photosensitivity. Our systematic analysis provides important insight into the polytypic structures of nanowires.

INTRODUCTION

Nanowires (NWs) of wide-bandgap semiconductors have emerged as well-defined one-dimensional building blocks of next-generation nanodevices. Group III–V semiconductor NWs are among the most promising nanomaterials for many applications. The NWs often adopt the hexagonal phase, such as the wurtzite (WZ) phase, in contrast to the cubic zinc blende (ZB) phase of their bulk counterparts, and thus, they produce various polytypic structures. Many studies have reported that the electrical and mechanical properties of NWs are influenced by the stacking faults due to the two coexisting phases. Polytypic structures are often disadvantageous for electronic devices, because of the crystal defects that produce charge-trapping sites, and thus reduce the (photo)current. On the other hand, polytypic NWs exhibit complicated mechanical properties, which might come from the intrinsic difference between materials. Liao’s group reported that polytypic GaAs NWs have a larger elastic limit or a higher Young’s modulus than the WZ or ZB phase counterpart. In contrast, the Zhu group reported that the average Young’s modulus of obtuse-angle twin GaN NWs was greatly reduced compared to defect-free NWs. Therefore, controlled synthesis of polytypic structures and their characterization are important for assembling NWs in integrated circuits.

In this work, we synthesized polytypic gallium phosphide (GaP) and gallium arsenide (GaAs) NWs as well as the single-crystalline NWs. The growth directions ([111] and [211]) were controlled by the conditions of the chemical vapor transport, such as H₂ gas flow. Various typed polytypic structures were exclusively produced for the NWs grown along the [211] growth direction. We performed detailed structure analysis of the polytypic structures using HRTEM combined with strain mapping based on nanobeam electron diffraction (NBED). The NBED technique utilizes electron beam precession to generate spot diffraction patterns, thereby producing accurate strain maps with <2 nm spatial resolution and 0.02% accuracy. This technique enables the visualization of strain distribution along the individual crystal directions. To identify the polytypic structures, micro-Raman spectroscopy was employed, which is one of the most straightforward and widely used techniques for this purpose. Further, the effect of polytypic structures on the photodetectors was investigated, by fabricating and comparing the photosensitivity using single-crystalline and polytypic NWs.

RESULTS AND DISCUSSION

Experimental details are described in the Supporting Information. GaP and GaAs NWs were successfully synthesized, and peaks in their XRD patterns were all matched exactly to those of the ZB phase a = 5.450 Å (JCPDS card 32-0397) and a = 5.654 Å (JCPDS card 80-0016), respectively, as shown in Figure S1. The use of H₂ gas was critical for the high-yield...
growth of NWs, because otherwise the yield was very low. When the flow rate of H₂ gas was 10 sccm, the NWs grew along the [111] direction. A remarkable finding is that, when using a higher flow rate (50 sccm), the growth direction switched to [211]. The NWs with the [111] and [211] growth directions are simply referred to as [111] NWs and [211] NWs, respectively, and hereafter labeled as GaP-1 and GaAs-1 and GaP-2 and GaAs-2 NWs. The GaP-1 and GaP-2 NWs had similar diameters (average value: 150 nm), as shown by the diameter distribution in Figure S2. The average diameter of GaAs-1 and GaAs-2 is the same as 180 nm.

Figure 1a shows that the GaP NWs uniformly grew on the substrates with a high yield. The NWs have the length of 50–100 μm. Figure 1b corresponds to the HRTEM and FFT images of GaP-1, showing the defect-free single-crystalline ZB phase with the [111] growth direction. There are no obvious outer layers on the smooth and straight surface. The d-spacing between the neighboring (111) planes was \(d_{111} = 3.15 \text{ Å}\), in good agreement with that of bulk GaP (3.1460 Å).

As the H₂ flow rate increased, the polytypic GaP-2 NWs were grown instead. Figure 1c reveals that the [111] direction of the polytypic structures is perpendicular to the [211] ([422]) growth direction. The polytypic structures consisted of alternative ZB (marked as 3C) and WZ (marked as 2H) domains, as shown in the magnified view (inset). The sizes of the ZB domains varied, resulting in the lined ED spots along the [111] direction. The \(d_{422}\) value was the same as that of bulk GaP (1.1127 Å). Other polytypes were also found (see Figure S3).

Figure 1d shows that another NW contains 9R (Ramsdell notation) polytypic structures along the [111] direction, which is tilted to the [111] growth direction by 70.5°. The FFT image for the marked area shows three periodic spots dividing the distance between the two adjacent (111) plane reflections. The magnified FFT image was indexed using the rhombohedral (R)-phase [2110] zone axis. There are clearly three periodic spots between two adjacent (0009) \(_{R}\) [= (111)] planes along the [0001] direction.\(^{6,25}\) The SAED pattern for the NWs shown in Figure 1b–d is shown in Figure S4.

Figure 1e shows a 19.5° bent GaP NW, in which the growth direction switched from [211] (left segment) to [111] (right segment). The left segment has the polytypic structure perpendicular to the [211] growth direction, which is the same as that in Figure 1c. The right segment has the 70.5° tilted polytypic structure as seen in Figure 1d. Figure 1f shows the 19.5° bent GaP-2 NW, in which the growth direction changed from [211] to [111] toward the nanoparticle tip. The SAED pattern confirmed that the 70.5° tilted polytypic structures can be initiated from the perpendicular polytypic structures, followed by a change in the growth direction from [211] to [111]. The tilted polytypic structures were found as a minor portion (∼10%) compared to the perpendicular polytypic structures. Korgel’s group reported the lamella [111] twins in the kinked GaP NWs that changed the growth direction from [111] to [112].\(^{30}\) Dayeh et al. and Jeon et al. reported similar stacking faults for kinked Ge NWs and Si–Ge heterostructure NWs, with a 19.5° kink angle between the [111] and [211] growth directions.\(^{31,32}\)

On the other hand, the GaAs NWs were synthesized with a high yield on Au-deposited substrates (Figures 2a,b). Figure 2c reveals that GaAs-1 consisted of single-crystalline ZB phase with the [111] growth direction. When the H₂ flow rate (50 sccm) was higher than that (10 sccm) used for GaAs-1, GaAs-2 was preferentially grown. Figure 2d shows a bicrystalline ZB-phase GaAs-2, in which the twin structures are identified by the twin ED spots along the [111] direction, which is perpendicular to the [211] growth direction. The \(d_{111}\) and \(d_{422}\) values were 3.26 and 1.15 Å, respectively, which agree with those of bulk GaAs (3.2643 and 1.1541 Å). The SAED pattern for the NWs shown in Figure 2c,d is shown in Figure S4.

Figure 3a displays the HAADF STEM image and EDX elemental mapping for the terminal part of the GaP-1 NW, clearly revealing a round-shaped Au–Ga alloy nanoparticle tip. The EDX spectrum reveals that the atomic ratio is Au/Ga = 7:2 for the tip and Ga/P = 1:1 for the NW part. The concentration of P could not be exactly determined because of the overlapped P K-shell and Au M-shell peaks at approximately 2 keV. Therefore, the mapping of P element

Figure 1. (a) SEM image of high-density GaP NWs homogeneously grown on a substrate. HRTEM image reveals a uniform diameter of 150 nm. Lattice-resolved and the corresponding FFT images (zone axis = [011]) or SAED pattern for selected (b) GaP-1 and (c–f) GaP-2.

Figure 2. (a) SEM image of high-density GaAs NWs homogeneously grown on a substrate. (b) HRTEM image reveals the uniform diameter (180 nm) of the NWs. Lattice-resolved and corresponding FFT images (zone axis = [011]) of (c) GaAs-1 and (d) GaAs-2.
shows the distribution at the tip. The SAED pattern (at the zone axis of [0001]) for the tip part confirmed the hexagonal-phase Au$_7$Ga$_2$ (JCPDS card 24-0424, $P\bar{6}2m$, $a = 7.721$ Å, and $c = 8.751$ Å).

For bent GaP-2, the SAED pattern (zone axis = [131]) of the tip shows the orthorhombic-phase Au$_2$Ga (JCPDS card 29-0619, $a = 18.02$ Å, $b = 3.199$ Å, and $c = 6.999$ Å) (Figure 3b). The EDX mapping and line profile along the cross section of the nanoparticle tip reveal an atomic ratio of Au/Ga = 2:1, corresponding to a higher Ga composition than that of bent GaP-2 (Figure 3c). The SAED pattern at the [111] zone axis reveals the orthorhombic-phase Au$_7$Ga$_2$ (JCPDS card 07-0126, $Pbnm$, $a = 6.937$ Å, $b = 6.267$ Å, $c = 3.447$ Å).

Figure 3. (a) HAADF STEM image (scale bar = 100 nm), SAED pattern for the Au$_7$Ga$_2$ tip, EDX elemental mapping (using Au L-shell, Ga K-shell, P K-shell, and As K-shell), and EDX spectra of GaP-1, showing a composition of Au/Ga = 7:2 at the tip. HAADF STEM image, SAED pattern, EDX mapping, and EDX line profile (along the cross section of the tip) of (b) bent and (c) straight GaP-2, showing the compositions of Au/Ga = 2:1 and 1:1, respectively, for the Au$_7$Ga$_2$ and Au$_2$Ga tips.

Figure 4a displays the HAADF STEM image, SAED pattern, and EDX data of the GaAs-1. The catalyst–NW interface of GaAs-1 is parallel to the (111) planes of the NW. The EDX elemental mapping and EDX line profile reveal that the atomic ratio is Au/Ga = 7:2 for the tip. The SAED pattern at the zone axis of [0001] confirmed the hexagonal-phase Au$_7$Ga$_2$ nanoparticle. For GaAs-2, the EDX data reveal an atomic ratio of Au/Ga = 1:1, indicating a higher Ga composition than that of GaAs-1 (Figure 4b). The SAED pattern (zone axis = [112]) corresponds to the orthorhombic-phase AuGa nanoparticle.

On the basis of the EDX data of Au–Ga alloy tips, the growth of GaP and GaAs NWs would follow a vapor–liquid–solid growth mechanism using the Au nanoparticles. The H$_2$ flow facilitated the production of precursor vapors via the
reaction \(2\text{GaP}(s) \text{[or GaAs(s)]} + 3\text{H}_2(g) \rightarrow 2\text{Ga}(g) + 2\text{PH}_3(g) \text{(or AsH}_3)\) and promoted vapor transport. Then, the Ga vapors dissolved efficiently into the Au nanoparticles (forming the Au–Ga alloy) and precipitated by the reaction with \(\text{PH}_3\) (or \(\text{AsH}_3\)) at the triple-phase region (i.e., at the interface between the NW solid, the Au liquid droplet, and the gas phase), which induced the growth of single-crystalline [111] NWs (GaP-1 and GaAs-1). As the length of NWs increases, it becomes increasingly difficult to supply enough Ga and \(\text{PH}_3\) (or \(\text{AsH}_3\)) onto the alloy tip, and eventually the growth of NW stops.

As the \(\text{H}_2\) flow rate increases, the higher vapor pressure of precursors would increase the dissolution of Ga into the Au nanoparticles. Therefore, the Ga composition in the Au nanoparticles is larger in the [211] NWs (AuGa) than that in the single-crystalline [111] NWs (Au–Ga). We presume that, as the more Ga dissolved in the Au nanoparticles, the growth rate would increase. Then, the faster growth rate produces the [211] growth direction that is kinetically favorable. On the other hand, the [111] growth direction is thermodynamically favorable. The 19.5° kink at the termination part can be explained by the following model: as the vapor pressure of precursors decreases to slow down the growth rate, the growth direction turns from the kinetically favorable [211] to the thermodynamically favorable [111] direction. Therefore, the Ga composition in the Au nanoparticles depleted to form the Au–Ga alloy as the growth direction switched from [211] to [111].

Cheng et al. reported that the preferred orientations of SiC films are [111] and [110], respectively, in the lower and higher growth rate conditions, consistent with our model that the [111] growth direction is less kinetically favorable. 33 Extensive studies on cubic-phase Si NWs grown using a Au catalyst have reported that the growth direction can be switched from [111] to [211] by increasing the pressure of the precursor (e.g., \(\text{SiH}_4\), \(\text{Si}_2\text{H}_6\)). 34–37 A similar phenomenon was found in the present work. Glas et al. developed a nucleation-based model, in which high supersaturation at the triple-phase region induces the formation of the WZ phase along the [111] direction. This model was supported by many experimental results. 38 The production of the polytypic structures here can also be explained by high supersaturation, which is proven by the higher Ga concentration (50%, AuGa phase) at the Au tip (GaP-2 and GaAs-2).

Now, we examine the strain maps of GaP and GaAs NWs. The TEM image and NBED pattern of the NWs were recorded at the [011] zone axis. For the pure ZB-phase single-crystalline GaP-1 and GaAs-1, strain mapping shows no strains along any crystal direction. Figure 5a corresponds to the strain map of GaP-1 at the [111] growth direction. The strain map of GaP-2 at the [111] polytypic direction, which is oriented 70.5° away from the [111] growth direction, shows a lattice expansion of 1% in the region of polytypic structures (Figure 5b). As the orientation angle increases, the lattice expansion decreases to almost zero. Another strain mapping data of GaP-2 are shown in Figure 5c. The lattice expansion in the [111] direction, which is perpendicular to the [211] growth direction, reached a maximum of 1% in the region of polytypic structures. Figure 5d corresponds to the strain map of GaAs-2, showing that lattice expansion exists along the twinned boundaries in the [111] direction, which is perpendicular to the [211] growth direction.

The lattice constant of the WZ-phase GaP NWs has been measured as \(a = 3.8419\) Å and \(c = 6.3353\) Å, which differ from the values when the lattice parameters of ZB are geometrically converted into the WZ unit cell. 39 The lattice mismatch between the WZ phase (\(d_{002} = 3.1677\) Å) and the ZB phase (\(d_{111} = 3.1460\) Å) is ca. \(\Delta c = 0.69\%\). The lattice constant of the WZ-phase GaAs NWs was reported as \(a = 3.9845\) Å and \(c = 6.5701\) Å, 40 and the lattice mismatch with the ZB phase (\(d_{002} = 3.2851\) Å vs \(d_{111} = 3.2643\) Å) is \(\Delta c = 0.64\%\). The lattice expansion in the [111] polytypic direction would originate from the larger lattice parameter of the WZ phase than that of the ZB phase (\(\Delta c\)). It is emphasized that the strain mapping can be used to visualize the polytypic structures using the lattice mismatch between the different crystal phases.

Micro-Raman spectra were measured for the individual NWs using a 514.5 nm excitation source. In Figure 6a, the Raman spectra of GaP-1 and GaP-2 NWs both showed a transverse optical (TO) mode peak at 366 cm\(^{-1}\) and a longitudinal optical (LO) mode peak at 400 cm\(^{-1}\). GaP-2 showed the E\(_2\) mode peak at 324 cm\(^{-1}\). This is consistent with the previous reports on GaP NWs, where the E\(_2\) TO mode peak is shifted to lower frequencies due to the intrinsic strain in the NWs.

Figure 5. HRTEM image, NBED patterns (zone axis = [011]), and the corresponding strain maps of (a) GaP-1, (b,c) GaP-2, and (d) GaAs-2 along the [111] direction. In the NBED pattern, the [111] direction is marked, namely, the top one for GaP-1 and GaP-2 (growth direction = [111]) and the bottom one for GaP-2 and GaAs-2 (growth direction = [211]). Strain maps of lattice contraction (blue means a negative value) or expansion (red means a positive value), relative to a reference at the single-crystalline region of the NW (marked by white dots), where presumably no lattice deformation occurred, were taken in the [111] polytypic direction. The relative extent of expansion or contraction of the lattice (\(d\)) with respect to the reference \(d_0\), i.e., \((d - d_0)/d_0\). The scale bars indicate the range of the strain (±1%). The precision of the strain measurement was <0.03%, and the spatial resolution was 2 nm.
peak at a lower-frequency region of the TO band at 357 cm\(^{-1}\) (9 cm\(^{-1}\) red shift), originating from the WZ phase of the polytypic structures.\(^{41}\) GaP-1 showed the asymmetric shape of the TO band. The shoulder peak at 360 cm\(^{-1}\), red-shifted from the TO mode by 6 cm\(^{-1}\), would originate from a frequency-dependent damping oscillator as Bakker suggested.\(^{12}\) Measurement of polarization-dependent micro-Raman spectra confirmed the spectral features of each peak and the absence of hexagonal phase in GaP-1, as shown in Figure S5. Therefore, the significant intensity of the E\(^{2\ L}\) mode peak is definitely correlated with the polytypic structures of GaP-2 NWs.

The Raman spectra of GaAs-1 and GaAs-2 consisted of the TO and LO mode peaks at 269 and 288 cm\(^{-1}\), respectively (Figure 6b). It has been reported that the E\(^{2\ L}\) mode of GaAs at 255–256 cm\(^{-1}\) is red-shifted from the TO mode by approximately 10 cm\(^{-1}.\)\(^{43}\) No band was resolved below the frequency of the TO mode, probably owing to the negligible amount of hexagonal phase.

We fabricated a photodetector device by aligning the NWs between a prepatterned Ti/Au bottom electrode using a dielectrophoresis method and depositing a Pt top electrode using the FIB technique. Figure 7a shows the I–V curves of the photodetector device using single-crystalline GaP-1 and polytypic GaP-2, both under dark conditions and under 325 nm irradiation (3.8 eV) using a He–Cd laser (80 mW cm\(^{-2}\)). The SEM images show that the NW was aligned between the bottom and top electrodes with gaps of 2–2.5 μm, with Pt top electrode deposition using FIB (insets).

![Image 60x299 to 300x496]

**Figure 7.** (a) I–V characteristics of GaP NWs under 325 nm (80 mW cm\(^{-2}\)) irradiation and under dark conditions. (b) I–t curves at a bias voltage of 5 V under chopped irradiation. (c) I–V and (d) I–t curves (at a bias voltage of 2 V) of single GaAs NW under 365 nm (60 mW cm\(^{-2}\)) irradiation and under dark conditions. The SEM images show the single NW aligned between Ti/Au bottom electrodes with a 2–2.5 μm gap, with Pt top electrode deposition using FIB (insets).

Photodetectors were fabricated by aligning the NWs using different methods. Under chopped irradiation (3.8 eV) using a He–Cd laser (80 mW cm\(^{-2}\)), the photocurrent of GaP-1 and GaP-2 exhibits R = 1.7 × 10\(^2\) and 9.6 × 10\(^{-2}\) A W\(^{-1}\), respectively. Another quantity to characterize the performance of photodetector is its specific detectivity (D\(^*\)). In the case of small noise from dark current, D\(^*\) = R × (A/D\(_{0}\))\(^{1/2}\). The respective values are 2.4 × 10\(^{13}\) and 1.2 × 10\(^{10}\) Jones (= cm Hz\(^{1/2}\) W\(^{-1}\)), confirming that the GaP-1 is more suitable for the photodetectors than the GaP-2. We also measured the photocurrents for the other NWs, proving that all GaP-2 NWs exhibit at least 100 times less photocurrents than that of GaP-1 NWs (Figure S7). Therefore, we concluded that the GaP-1 is more suitable for the photodetectors than the GaP-2. The stacking faults of the polytypic structures could play as the trapping sites for the generation/transport of photocarriers and thus decrease the photocurrent. Therefore, the polytypic structures are indeed disadvantageous, which is consistent with previous works.\(^{9–18}\)

Figure 7c,d shows the I–V and I–t curves of the photodetector device fabricated using the GaAs NWs, respectively. The photocurrents from many NWs [under 365 nm irradiation (3.4 eV) using a LED (60 mW cm\(^{-2}\))] were all similar (ΔI = 1.7 μA at 2 V), being much higher than that of GaP NWs. The polytypic structure of GaAs-2 is negligible, so the photocurrents are nearly the same although the growth direction is different. The corresponding values of R and D\(^*\) are 4.6 × 10\(^3\) A W\(^{-1}\) and 4.5 × 10\(^{11}\) Jones, respectively. These values are comparable to the previous GaAs NW detectors by other groups.\(^{44–48}\) The photocurrent data of GaAs NWs support the result of GaP NWs, in which the polytypic structures play a major role in decreasing the photocurrent.

In dark conditions, the nonlinear I–V curve was ascribed to the Schottky barrier between the NW and Au contact. Under light irradiation, the I–V curve becomes more linear. This can be explained using the metal-induced gap states (MIGS\(\text{s}\)) model.\(^{49}\) The photogenerated holes shifted to the negative biased electrode are trapped in the MIGS\(\text{s}\). Because of the increased positive charge density in the depletion region, its Schottky barrier lowers and the space charge region shrinks. Then, the thermionic emission and the thermally assisted tunneling contribute in increasing the photocurrent for low applied voltage. We also fabricated the field effect transistors using the GaP-1 and GaAs-1 NWs, as shown in Figure S8. The measurement of gate effect revealed that both GaP and GaAs NWs are p-type semiconductors with carrier mobilities of 0.031 and 0.053 cm\(^2\) V\(^{-1}\) s\(^{-1}\), respectively. The Ho group reported that the surface oxide shell layer of GaAs NWs induces the acceptor-like interface trapping defects, which reduce the carrier concentrations in the NWs, leading to p-type conduction.\(^{50}\) Although the TEM images did not detect any distinctive shell layers, the low mobilities would be ascribed to the atomic oxide outer layers that inevitably formed under ambient conditions.

**CONCLUSIONS**

GaP and GaAs NWs were synthesized using the chemical vapor transport method. The ZB-phase NWs were grown in the [111] and [211] directions, respectively, under lower and higher H\(_2\) gas flow rates. The single-crystalline NWs were grown with the [111] growth direction. In contrast, the GaP [211] NWs exhibit a remarkable variety of polytypic structures, whereas the GaAs [211] NWs have a twinned structure. We propose that the [211] growth direction becomes kinetically
favored under higher vapor pressure of precursors (i.e., higher H₂ flow rates), supported by the higher Ga concentration in Au nanoparticles, Au-Ga₂ and AuGa, respectively, for the [111] and [211] growth directions. The production of the polytypic structures can also be explained by high supersaturation. The NBED technique was employed to obtain the strain maps of the NWs, which help visualize the distribution of polytypic structures. The single-crystalline GaP and GaAs NWs exhibit no strains. In contrast, all polytypic NWs exhibit lattice expansion along the [111] direction, because of the larger lattice parameter (a₀) of the WZ phase than that (d₁₁₁) of the ZB phase. Micro-Raman spectra of individual GaP NWs identified the polytypic structures from the WZ-phase E₁² peak. Further, we fabricated photodetectors using these NWs, and the results showed a significant decrease of photocurrents for the polytypic structures. The controlled synthesis, the characterization, and the photocurrent measurement here provide valuable insights into the polytypic structures of the NWs.

■ EXPERIMENTAL SECTION

GaP (99.999%, Alfa Aesar) or GaAs (99.999%, Alfa Aesar) powders (40–80 mg) and a 3 nm thick Au film deposited on a Si substrate were placed inside a quartz tube (2.5 cm diameter and 80 cm length) reactor. The substrate was positioned 10 cm away from the source powders. The temperature of the source zone was approximately 800 °C. The tube reactor was heated using an electrical furnace. Argon gas was continuously flowed at a rate of 200 sccm during the whole process. As the temperature reaches the set value, hydrogen gas was added for at a rate of 200 sccm during the whole process.

■ ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03548.

XRD data, diameter distribution, HRTEM images, SAED pattern, Raman data, photocurrents, and I−V data of FET devices (PDF)

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Notes

The authors declare no competing financial interest.

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