Influence of catalyst choices on transport behaviors of InAs NWs for high-performance nanoscale transistors†

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The influence of the catalyst materials on the electron transport behaviors of InAs nanowires (NWs) grown by a conventional vapor transport technique is investigated. Utilizing the NW field-effect transistor (FET) device structure, ~20% and ~80% of Au-catalyzed InAs NWs exhibit strong and weak gate dependence characteristics, respectively. In contrast, ~98% of Ni-catalyzed InAs NWs demonstrate a uniform n-type behavior with strong gate dependence, resulting in an average OFF current of ~10^{-10} A and a high I_{on}/I_{off} ratio of >10^4. The non-uniform device performance of Au-catalyzed NWs is mainly attributed to a non-stoichiometric composition of the NWs grown from a different segregation behavior as compared to the Ni case, which is further supported by the in situ TEM studies. These distinct electrical characteristics associated with different catalysts were further investigated by the first principles calculation. Moreover, top-gated and large-scale parallel-array FETs were fabricated with Ni-catalyzed NWs by contact printing and channel metallization techniques, which yield excellent electrical performance. The results shed light on the direct correlation of the device performance with the catalyst choice.

Introduction

In recent years, significant progress has been achieved in the assembly of semiconductor nanowires (NWs) for the large-area device integration while the essential demands toward commercialization of such NW-based devices still highly rely on the accomplishment of uniformly reliable and controllable NW physical properties. The NW growths, including vapor-liquid-solid (VLS) or vapor-solid-solid (VSS), were typically utilized to realize a precise control of the growth position and morphology. However, in situ doping of impurities through the metal catalyst into nanowires during the NW growth may alter intrinsic electrical properties of NWs. In particular, InAs NWs have been widely explored as the channel material for high performance transistors owing to their high electron mobility (~10,000 cm^2 V^{-1} s^{-1}) and ability to readily form a near-ohmic contact with metal electrodes due to a small band gap and an intrinsic surface charge behavior.1,2 The synthesis of InAs NWs has been achieved by a metal-organic chemical-vapor deposition (MOCVD) method, with which Au nanoparticles were commonly used as the growth catalyst. The growth has been carefully controlled with different V/III ratios between As and In not only to achieve the lowest density of crystal defects such as As-antisites and As interstitials but also to reduce the tapered morphology owing to an overcoating via an uncontrolled adatom diffusion.3–5

In addition to MOCVD, a simple way utilizing a conventional furnace to grow InAs NWs via InAs powders as the growth precursor has also been demonstrated successfully regardless of the control of the V/III ratio.6 Furthermore, the electrical transport of NWs has been evidently demonstrated as the diameter of InAs NWs <30 nm grown by the same approach.7 However, it is still unclear how the metal catalysts could influence the intrinsic electrical transport properties of III–V nanowires as well as the nanowire morphology. In this regard, we found a substantial influence on the morphology and electron transport behaviors of InAs NWs with different metal catalysts, which would provide valuable insights into controlling and achieving uniform physical properties of NWs for large-scale high-performance device applications.
Results and discussion

NWs were grown by using the previously reported vapor transport technique. Briefly, 1.5 nm-thick Ni or Au thin films were deposited by e-beam evaporation on Si/SiO₂ substrates. Subsequently, the samples were annealed at 800 °C to form the Ni or Au nanoparticles (NPs) with average diameters of ~30–50 nm. The growth furnace simply consists of two independently controlled temperature zones, namely the high temperature zone at 700–800 °C for the vaporization of InAs solid source and the low temperature zone at 400–550 °C for the growth of InAs NWs with 200 sccm hydrogen (H₂) gas as the carrier gas. The pressure was maintained at 1–0.8 Torr. The corresponding SEM images of Ni-catalyzed and Au-catalyzed InAs NWs are shown in Fig. 1(a) and (b), respectively, grown with the identical conditions of pressure, temperature, and time being 0.8 Torr, 520 °C, and 30 min, respectively. Clearly, the InAs NWs grown from Ni NPs as the catalyst have a long and straight morphology with an average length >15 μm whereas NWs with a shorter length of <6 μm and a distinct tapered morphology are observed using Au NPs as the catalysts. Insets show the magnified SEM images of tip regions for the two cases, for which catalysts at both samples are clearly seen, confirming a catalytic growth mechanism, namely, VLS/VSS. The crystal phase formation was also investigated by grazing incidence X-ray diffraction (GIXRD) as shown in Fig. 1(c) and (d) for Ni-catalyzed and Au-catalyzed InAs NWs, respectively. Peaks at 240, 420, and 500, corresponding to (111), (220), and (311) were indexed for both spectra, which match the phase of InAs. Extra peaks at (211) and (311) in Fig. 1(d) could be ascribed to a phase of Au₇In₃, which is originated from a solid reaction between In and Au catalyst during the NW growth.

Fig. 2(a) and (b) show the transmission electron microscopy (TEM) images of representative Ni- and Au-catalyzed InAs NWs, respectively. Obviously, the tapered morphology is observed for the Au-catalyzed InAs NW, which is most likely induced by an overcoating via the uncontrolled InAs adatom diffusion during the growth while no overcoating behavior is observed for the Ni-catalyzed InAs NWs. Fig. 2(c) and (d) show the high resolution TEM images taken from rectangular areas in Fig. 2(a) and (b), respectively, for which (111) planes were indexed with a plane spacing of 0.35 nm. Insets show the corresponding selected area diffraction patterns (SAD) processed with a fast Fourier transform (FFT). (e) and (f) show the elemental profiles for Ni-catalyzed and Au-catalyzed InAs NWs, for which the colors, light green, dark green, blue, and pink represent Au, Ni, In, and As, respectively.
In order to characterize how the catalytic materials influence the electrical properties of InAs NWs, field-effect transistors (FETs) were fabricated and characterized. The grown NWs were drop-cast on Si/SiO₂ substrates (50 nm, thermal oxide as the gate dielectric layer and heavily B doped Si as the global back gate), followed by the photolithography patterning of S/D electrodes via thermal evaporation of Ni (50 nm-thick) and lift-off processes. A 0.5 wt% HF treatment of ~5 s was applied to remove the native oxide prior to the metallization. The representative \( I_{DS} - V_{GS} \) curves at \( V_{DS} = 0.1, 0.3, \) and 0.5 V for Ni- and Au-catalyzed InAs NWs are shown in Fig. 3(a) and (b), respectively. Notably, the Ni-catalyzed InAs NW with the diameter of ~35 nm device exhibits clear n-type switching characteristics with strong gate modulation of conductance, yielding an OFF current of ~0.1 nA and an \( I_{ON}/I_{OFF} \) ratio of ~10⁴ at \( V_{DS} = 0.1 \) V and \( V_{GS} = -2 \) V while the Au-catalyzed InAs NW with the diameter of ~100 nm device shows a near metallic behavior with weak gate dependence, resulting in a much higher OFF current of ~10 μA and a smaller \( I_{ON}/I_{OFF} \) ratio of ~5 at \( V_{DS} = 0.1 \) V and \( V_{GS} = -4 \) V. To gain a better insight on the electrical uniformity of both Ni- and Au-catalyzed InAs NWs, more than 100 devices from Ni- and Au-catalyzed InAs NWs were fabricated. The statistical data of the \( I_{ON}/I_{OFF} \) ratios and the corresponding smallest OFF currents are shown in Fig. 3(c) and (d), respectively. Notably, utilizing Au as the growth catalyst, ~80% and ~20% of grown InAs NWs exhibit weak and strong gate modulation behaviors, respectively, for which a wide range of \( I_{ON}/I_{OFF} \) ratios (~1 to ~10⁴) and OFF currents (~10⁻⁵ to ~10⁻¹⁰ A) were observed. On the other hand, with the Ni catalysts, ~98% of grown InAs NWs exhibit strong gate modulation with the relatively uniform \( I_{ON}/I_{OFF} \) ratios (~10³ to ~10⁵) and low OFF currents (~10⁻⁸ to ~10⁻¹¹ A).

To shed light on how the catalyst can influence the growth of InAs NWs, in situ TEM observation of the solid reaction between the metal catalyst and InAs is imperative. Due to the difficulty in direct observation of InAs NW growth inside the TEM, we, therefore, chose a simple way by directly observing solid state reactions between Au or Ni films on InAs crystals. The TEM samples of Au/InAs and Ni/InAs samples were prepared via the focus ion beam (FIB) method on the TEM grids, followed by in situ heating of the samples inside a TEM with a heating stage (Gatan 652 double tilt heating holder) at a pressure below 10⁻⁶ Torr.¹¹,¹² Heater temperature was elevated to 300 °C with a step of 50 °C. To completely observe the solid state reaction, each annealing temperature was maintained for 20 min. The compositions were in situ monitored by energy dispersive X-ray spectroscopy (EDS) measurements. Fig. 4 shows the in situ TEM images of the solid state reactions between InAs and Ni or Au films in real-time. As depicted in Fig. 4(a1)–(a3) with annealing temperatures from 25 to 250 °C for the Au case, In and As atoms are both dissolved into Au thin films with atomic compositions of Au, In, and As being ~79 at%, ~17 at%, and ~4 at% at 150 °C and then were changed to ~57 at%, ~27 at%, and ~16 at% at 250 °C, respectively, as listed in Table 1. Interestingly, increasing concentrations of As atoms in the AuIn₃, metastable alloy at elevated temperature could be found. These results could infer that As atoms are most likely involved in the nanowire growth from Au catalysts.

![Fig. 3](image-url) **Fig. 3** \( I_{DS} - V_{GS} \) curves of InAs NWs FETs at \( V_{DS} = 0.1, 0.3 \) and 0.5 V grown from (a) Ni and (b) Au as catalysts. Statistical results of (c) \( I_{ON}/I_{OFF} \) ratios and (d) OFF currents extracted from 100 devices based on Ni-catalyzed and Au-catalyzed InAs NWs, respectively.

![Fig. 4](image-url) **Fig. 4** In situ TEM images of the solid state reaction between Au and InAs substrate at elevated annealing temperatures of (a1) 25 °C, (a2) 150 °C, and (a3) 250 °C. (a4) shows the TEM image of the sample after cooling down to 25 °C. In situ TEM images of the solid state reaction between Au and InAs substrate at elevated annealing temperatures of (b1) 25 °C, (b2) 150 °C, and (b3) 250 °C. (b4) shows the TEM image of the sample after cooling down to 25 °C.
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Table 1 In situ EDS results of solid state reactions between Au and InAs at different annealing temperatures

<table>
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<td>79</td>
<td>57</td>
<td>69</td>
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<td>In (at%)</td>
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<td>17</td>
<td>27</td>
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<td>As (at%)</td>
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catalyst, resulting in the formation of a metastable AuInAsx alloy during nanowire growth (Fig. 5(a1)–(a2)). In other words, the segregation of In and As atoms from the metastable AuInAsx catalyst would partially contribute to the growth of InAs NWs with a growth rate of ~3 nm s⁻¹, extracted from the SEM image at different growth times. In addition, the spherical shape of observed catalytic seeds after nanowire growth provides evidence of the molten catalyst in its liquid state, suggesting that Au-catalyzed InAs growth is carried out via the VLS mechanism. Simultaneously, an adatom diffusion process, namely noncatalytic radial deposition of InAs NWs, occurs, leading to a tapered morphology as shown in Fig. 5(a2)–(a3). It was reported that when the NW length (l) is shorter than the surface diffusion length on NW sidewalls (lNW), the overcoating due to In adatoms impinging on NW sidewalls continuously increases with time, leading to the superlinear growth rate, for which the growth of NW length exponentially increases with the time, namely VLS without any overcoating.15 After l > lNW for the longer growth time, the growth rate of NWs is turned from the superlinear into the linear modes so that the surface diffusion via the overcoating occurs.15 The effect of this surface diffusion (overcoating) is manifested via the changes of the NW diameter during the growth. By drawing a contrast profile along the axis of NWs, we are able to extract the lNW ~ 70 nm as shown in Fig. S1(a) (ESI†). Compared with Au-catalyzed InAs NWs, the growth of NWs from Ni NPs shows a long and straight morphology with a growth rate of ~9 nm s⁻¹, which is much faster than that of Au-catalyzed InAs NWs (~3 nm s⁻¹). The corresponding schematics illustrating the growth of Ni-catalyzed InAs NW is shown in Fig. 5(b1)–(b4). Initially, the Ni catalyst can alloy with In and As atoms to form the NiInAs alloy catalyst with high concentrations of In (~24 at%) and As (~25 at%) confirmed by EDS (Fig. 5(b1)–(b2)). Subsequently, the axial growth of NWs resulted from the segregation of In and As atoms out of the NiInAs catalyst can be achieved once the NiInAs alloy catalyst reaches a supersaturation condition, which is the typical catalytic growth mechanism (Fig. 5(b3)–(b4)). It is worth noting that straight Ni-catalyzed InAs NWs indicate no lateral growth of NWs, ruling out the adatom diffusion, namely overcoating on the surface of InAs NWs (Fig. S1b, ESI†). The absence of the InAs overcoating is mainly attributed to the fast growth rate suppressing the lateral growth. It has been observed that at the identical growth temperature, the growth rate from VLS is normally one order of magnitude faster than that of VSS for the same NW while the observed results are not suitable in our case due to different chemical compositions found in the catalysts for Ni- and Au-catalyzed InAs NWs.16 The slow growth of Au-catalyzed InAs NWs is because excess In atoms segregated out of the catalyst need more time to bond with As atoms coming from the adatom diffusion, which also triggers the lateral growth. However, the exclusive supply of In and As atoms from the NiInAs catalyst could result in the fast growth rate without the lateral growth, thereby yielding a less defective and stoichiometric NW.

In addition, the growth of III–V nanowires is known to be a mass-transport limited process where the smaller diameter nanowires will grow much faster and the growth rate shows
an exponential increase as the diameter of NW < ~60 nm. However, the growth rate does not change significantly when the diameter > ~60 nm. In the present research, the diameters of Au-catalyzed InAs NWs are typically over 60 nm, exhibiting the less dependence with diameter variation while a clear growth rate dependence with diameter variation can be observed for the Ni-catalyzed InAs NWs. The smaller the diameter of the Ni catalyst, the faster the growth rate of Ni-catalyzed InAs NWs. This is why the Ni-catalyzed InAs NWs have a much faster growth rate than that of Au-catalyzed InAs.

Moreover, the lateral growth or sidewall overcoating may induce intrinsic defects such as In interstitials or As vacancies, resulting in the unstable and non-uniform electrical properties of grown NWs. To further understand the influence of these defects on electrical properties, the first principle calculation was performed to assess the corresponding density of states and their effects on NW transport via a density functional theory (DFT) using the CASTEP (Cambridge serial total Energy package) module. Based on the EDS results, Ni- and Au-catalyzed InAs NWs with the atomic ratios of In to As being 1 to 1 and 1 to 0.625 due to As vacancies were taken into account in the calculation, respectively (for detailed simulation processes, please see the ESI†). Consequently, typical partial density of states (PDOS) for both Ni- and Au-catalyzed InAs NWs were constructed as shown in Fig. 6(a) and (b). Notably, a distinct overlap of As-4p and In-5p from −3.5 to 0.3 eV with a band gap of ~0.35 eV could be obtained for InAs without As vacancies while a change of overlap in the energy level could be observed after rebuilding of As-In covalent bonds from In-5s, In-5p, As-4p, and a few As-as to the unoccupied high energy levels across the Fermi level, resulting in n⁺ type semiconducting or even metallic-like properties after the formation of As vacancies. In addition, segregation of Au clusters on the surface of the NW or in the NW from the Au catalyst via the VLS or VSS mechanism may be another issue of the unstable electrical transport properties.18,19

In this case, the balanced stoichiometry of InAs NWs is important to achieve uniform and high-performance NW electronic device arrays. To shed light on the performance limits of Ni-catalyzed InAs NWs, top gate NW field effect transistors were fabricated with a 8 nm thick HfO2 dielectric layer deposited by an atomic layer deposition system (ALD) as depicted in the device schematic (Fig. 7a). Fig. 7(b) shows the Ids–Vds Results at Vds = 0.1, 0.3 and 0.5 V, respectively, and the inset illustrates the corresponding logarithm-scale plot. Specifically, the device exhibits an impressive OFF current (~10⁻¹⁰) at Vds = 0.1 V and an excellent Ion/Ioff ratio (~10⁶) with the sub-threshold swings of ~130–160 mV dec⁻¹ (more device measurements are shown in Fig. S2, ESI†). The very stable and electrically uniform InAs NWs grown from the Ni catalyst are suitable for large-scale array devices via a contact printing technique where the channel width of InAs NW arrays can be controlled with a nanowire density of ~5 NWs μm⁻¹.20 A linear behavior of ON current with the increase of the channel width could be obtained.21 The ON current could be further increased through the reduction of the channel length by the metallization process via formation of the metallic nanoelectrode, Ni,InAs, as shown in Fig. 7(c) (~3 μm and ~1.5 μm before and after metallization, respectively).13 The corresponding ON current as the function of channel widths before and after metallization is shown in Fig. 7(d) where the channel widths were changed from 5–36 μm with the fixed channel lengths (~3 μm and ~1.5 μm for before and after metallization, respectively). Obviously, ON-current of nanowire arrays increases linearly with the increasing channel width, yielding a slope of 19 μA μm⁻¹ while the slope can be increased to 32 μA μm⁻¹ after the reduction of channel length to ~1.5 μm via the metallization process. As a result, the highest ON-current of 1.1 mA at a channel width of 36 μm can be achieved (see ESI† Fig. S3). InAs NW parallel array devices demonstrated the importance of the catalyst choice in controlling the transport properties for large-scale device applications.

![Fig. 6](Image)

Partial density of state (PDOS) of (a) In₈As₈ (pure InAs) and (b) In₈As₅ (with three intrinsic As vacancies).

![Fig. 7](Image)

(a) Schematic of the top gate device based on a Ni-catalyzed InAs NW.
(b) The corresponding top gate Ids–Vgs curves. (c) Optical and SEM images of controlled channel length at a channel width of 36 μm after the metallization process. (d) The corresponding Ids as the function of channel widths before and after the metallization.
Conclusions

In conclusion, the influence of catalyst choice and its catalytic effects on transport behaviors of InAs NWs have been investigated. The results indicated that the tapered morphology of InAs NWs grown with Au NPs as the catalyst yields the unstable and non-uniform electrical properties where \(~80\%\) and \(~20\%\) of InAs NWs exhibit strong and weak gate dependence characteristics, respectively. On the other hand, straight morphology is observed for InAs NWs grown with Ni NPs, in which \(98\%\) of InAs NWs exhibit a very uniform n-type behavior with strong gate dependence, giving the impressive OFF current \((\sim 10^{-6} \text{ to } 10^{-10} \text{ A})\) with the maximum \(\frac{I_{\text{ON}}}{I_{\text{OFF}}} > 10^4\). The unstable and non-uniform electrical transport performance can be concluded from non-stoichiometric composition of InAs NWs due to the different segregation or NW growth schemes from the Au catalyst, which was supported by the in situ TEM observation. These distinct electrical characteristics associated with different catalysts were further investigated by the first principle calculation. Based on the electrically uniform and stable Ni-catalyzed InAs NWs, the excellent performance of top-gate InAs NW parallel array devices demonstrated the importance of the catalyst choice in controlling the transport properties for large-scale device applications.

Acknowledgements

The research was supported by the National Science Council through grant no. NSC 101-2218-E-007-009-MY3, NSC 101-2112-M-007-015-MY3, and NSC 98-2221-E-007-104-MY3, and by the General Research Fund of the Research Grants Council of Hong Kong SAR, China, under Project No. CityU 101111.

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