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Investigation of Indium droplet assisted Nucleation of InAs Nanowires on Graphite

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Abstract

An investigation of the Indium (In) droplet assisted nucleation of InAs nanowires (NWs) on graphite based on the quasi-van-der-Waals epitaxy method is reported. The surface morphology of as-grown NWs was studied using FEI XL30 SFEG scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDX) used for composition determination. Clear evidence is presented to demonstrate that the uniaxial growth of the InAs NWs directly on the underlying graphitic substrate is driven by the Indium droplets which etch nanoholes in the graphitic substrate and promote the formation of InAs seed particles underneath the NWs facilitating their vertical directionality. A high yield of InAs NWs exclusively in the [111]/[0001] growth direction on graphite is attributed to the InAs seeding particle. This report not only provides a better understanding of the InAs NWs nucleation on graphite but also unravels a cost-effective technique for obtaining a high yield of vertically oriented NWs on graphite with enormous potential for applications in highly efficient and flexible nano devices.

Keywords: Indium Arsenide, Semiconductors, Nanostructures, growth, graphite

INTRODUCTION

The Monolithic integration of semiconductor nanowires (NWs) with graphene/graphitic substrates (GS) has triggered extensive research interest over the last few years to enable the exploitation of the excellent material properties of the former with the exceptional properties of graphene, the wonder material including high flexibility and mechanical robustness, excellent electrical properties, superb transparency and unique optical properties (Munshi and Weman, 2013; Yao *et al*., 2022) as well as low cost, scalability (De-Arco *et al*., 2010; Li *et al*., 2009) , relative abundance and ease in exfoliation (Pinki Yadav *et al*., 2022) for the development of novel, flexible and cost-effective, III-V/graphene functional hybrid heterostructures. Several Graphene/NWs hybrid devices have recently been demonstrated (Alper *et al*., 2013; Lee *et al*., 2011; Miao *et al*., 2012; Nalamati *et al*., 2020; Park *et al*., 2013; Peng *et al*., 2020).

Binary InAs NWs are particularly promising for applications in mid-infrared optoelectronic devices and high-speed electronics due to their narrow direct band gap, small electron

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effective mass and high electron mobility (Dimakis *et al*., 2011; Ihn and Song., 2007; Wallart *et al*., 2005). Stimulated by the enormous potential of III-V/graphene hybrid heterostructures, there has been an increasing research interest in the growth of InAs NWs on GS.

Over the last few years, the self-catalysed (Baboli *et al*., 2019; Hong *et al*., 2012; Hong and Fukui., 2011; Mohseni *et al*., 2013) and Au (Wallentin *et al*., 2014) catalysed growth of InAs NWs on GS by metal-organic chemical vapor deposition (MOCVD) have been demonstrated. The Indium (In) catalysed molecular beam epitaxy (MBE) growth of InAs on graphene (Kang et al., 2016) has also been reported. Meyer-Holdt *et al*. (2016) demonstrated the Ag-catalysed, MBE growth of InAs NWs on graphite flakes. InAs/InGaAs core/shell NWs has also been realized on graphene by Tchoe *et al*. (2015).

However, most of these research efforts have focused on basic NWs synthesis. Although the mechanism of InAs NWs growth on traditional III-V substrates is well-established, an understanding of the nucleation mechanism of InAs NWs on chemically inert, 2-dimensional GS by the noncovalent, quasi van der waals epitaxy (VDWE) growth is lacking and remains unclear. This study presents a detailed investigation of the nucleation mechanism of In-catalysed InAs NWs on graphite by VDWE.

METHODOLOGY

The Indium droplet – assisted, MBE growth of InAs NWs was performed on graphite substrates which were mechanically exfoliated from highly oriented pyrolytic graphite (HOPG) and transferred onto Si (111) substrates. The GS were quickly loaded into the MBE system (equipped with effusion cells for group III element sources, and cracker cells for As) and thermally outgassed (Kang et al., 2016). Prior to commencement of growth, In droplets were pre-deposited on the substrate after which the In source was switched off and the substrate temperature ramped up. Growth commenced with the opening of both In and As shutters simultaneously to allow for the introduction of growth species.

In order to gain detailed insight into the nucleation mechanism governing the VDWE growth of InAs NWs on the GS, the growth time was varied from 5-124 min while keeping the growth temperature, In and As fluxes fixed at 450°C, ~10^{-7} mbar and ~10^{-6} mbar respectively. For all growths, the In and As precursors were simultaneously opened and closed at the beginning and end of growth.

FEI XL30 SFEG scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDX) for composition determination was used for investigation of the surface morphology of as-grown NWs.

RESULTS AND DISCUSSIONS

The evolution of InAs NWs morphology for short growth durations provided an insight into the mechanism of NWs nucleation. The top and tilted-view scanning electron microscopy (SEM) images in Figures 1a & b respectively showed the initial nucleation phase of the NWs deposited for 5 minutes. As can be seen, the In droplets are cleaved to crystallites (Islands) in various directions, with some vertically aligned on top the crystallites (indicated with yellow circles in Figures 1a, hereafter identified as I) while others indicated with yellow arrows are either inclined or laterally attached to the crystallites, (aligned parallel to the graphitic substrate) and identified as II and III respectively in Figure 1b. In the first orientation (I), the In droplets are cleaved directly at the tip of the crystallites and well-aligned (as shown in the inset). This result is in good agreement with previous studies (Gomes *et al*., 2015; Robson *et* *al*., 2015; Woo *et al*., 2009) in which In droplets were observed on top of InAs island facilitating NWs nucleation.

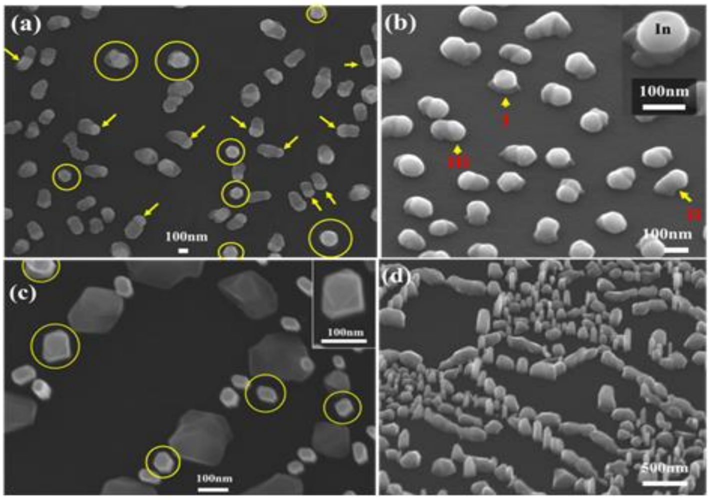

Figure 1: SEM images of InAs nanowires grown for 5 min. (a-b) and 10 min. (c-d).

It is expected that such a droplet would nucleate vertically well-aligned InAs NWs as illustrated in Figure 2I. On the other hand, droplets with orientations II and III are expected to either promote the growth of inclined or lateral NWs respectively (Figure 2II-III) or both favour the growth of larger crystallites. It can be seen that no droplet was deposited directly on the substrate rather the droplets are selectively nucleated on the crystallites which suggests that the VDWE growth of InAs NWs on graphite is mediated by 3D islands which is consistent with previous reports (Gomes *et al*., 2015; Woo *et al*., 2009). The presence of the In droplets which are clearly visible at the top of the NWs and magnified in the inset of Figure 1b suggests that the NWs nucleation and growth is catalysed by the In droplets.

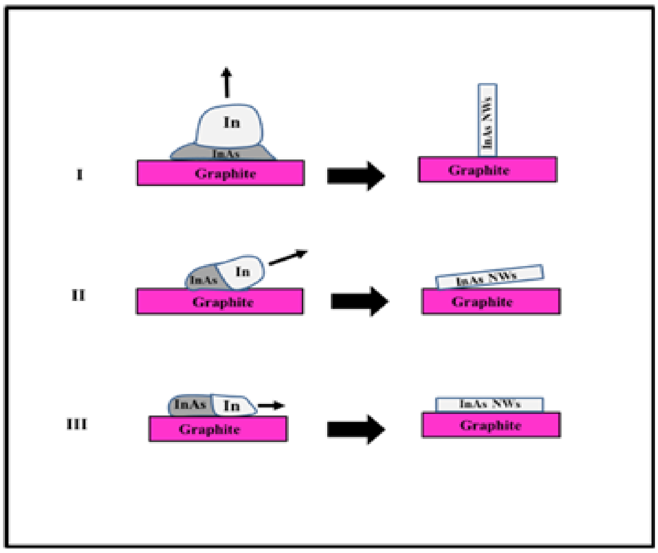

Figure 2: Schematic illustration of the deposition of In droplets on InAs islands

Slightly longer growth duration of 10 minutes (Figure 1c) also reveals the droplets formed directly on top of the crystallites. Interestingly, all the NWs are fully aligned with non-vertical or planar NWs absent (Figure 1d) which indicates that only vertically aligned, In droplets deposited directly on top of the crystallites (orientation I) successfully nucleated the free standing InAs NWs. This suggests that orientations II and III, with droplet cleaved to the crystallites in non-vertical directions favour the growth of large crystallites at the expense of NWs which suggests a critical contact angle of the liquid droplet is required to nucleate InAs NWs (Meyer-Holdt *et al*., 2016; Nebol'sin and Shchetinin, 2003). It is therefore not surprising that large and irregularly shaped crystallites are grown alongside the NWs (Figure 1c). This demonstrates that the In-droplets facilitated the nucleation of InAs NWs on graphite exclusively in the [111]/[0001] growth direction in the absence of non-vertical and/or planar NWs growth. The droplets collect the growth species from the vapour phase and subsequent supersaturation leads to the precipitation of InAs NWs, thus functioning as catalyst seeds for the promotion of NW nucleation (Potts *et al*., 2017).

For the 20 and 144 minutes NWs growth durations, the SEM images (Figures 3a & b respectively) showed the NWs are all vertically aligned. The hexagonal cross-section of the NWs (inset of Figure 3a) demonstrates that the side facets of the NWs exhibit the 6-fold symmetry characteristic of NWs growing along the ⟨111⟩ direction. No In-droplet is visible at the apex of the NWs owing to the highly As-rich conditions (As/In flux ratio ≥ 50) utilized for the growth which enabled the transformation of the In droplets into InAs NWs. Although, the In and As sources were opened and closed simultaneously at growth initiation and termination, the presence of excess As-flux (promoted by the longer growth duration) favoured the crystallization of the In-droplets to InAs NWs. It is well established that In readily reacts with the residual As present in the MBE growth chamber during post growth cooling, converting the liquid In into solid InAs (Biermanns *et al*., 2014; Gomes *et al*., 2015; Koblmüller *et al*., 2010; Mandl *et al*., 2010; Priante *et al*., 2013; Rieger *et al*., 2013). A close examination of the high magnification SEM image of the sample grown for 144 min (Figure 3c) shows the semblance of liquid In droplets at the NWs tip in the process of crystallizing into solid NWs. The existence of a post growth droplet combined with the observed rounded NW tips (Figure 3) provides clear evidence that the growth is guided by liquid In droplet which is in good agreement with Kang *et al*. (2016) who demonstrated that a round shape at the NWs tip is the remanence of the droplet after the shutters have been closed which is clearly different from flat tipped NWs (Dimakis *et al*., 2011) .

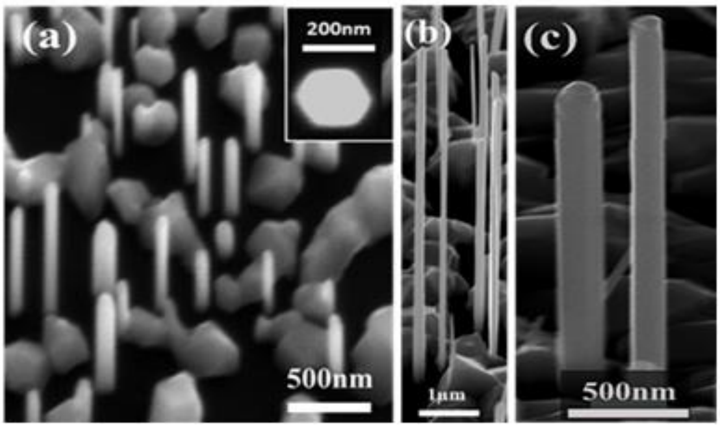

Figure 3: SEM images of InAs nanowires grown for (a) 20 min. (b) 144 min. (c) A high magnification image of the sample grown for 144 min.

Transmission electron microscope (TEM) investigation of the interface between the InAs NWs and graphitic substrate was conducted to better understand the nucleation of InAs NWs. The high magnification annular dark field (ADF) image corresponding to the interface between the NW and the graphite substrate (Figure 4a) reveals a "seed" material just beneath the NW protrudes into the graphitic substrate. It is believed that the pre-deposited In droplet dissolves the substrate locally to achieve equilibrium with it which suggests the uniaxial growth of the NW directly on the underlying graphite is driven by the droplet. This explains the earlier observation of NWs growth exclusively in the [111]/ [0001] growth direction. The composition of the seed was confirmed to be InAs by energy-dispersive X-ray spectroscopy (EDX) analysis (not shown). Finally, the dumbbells (Figure 4b) corresponding to the highlighted region of the seed material
(see blue rectangle) provided convincing evidence of its InAs composition.

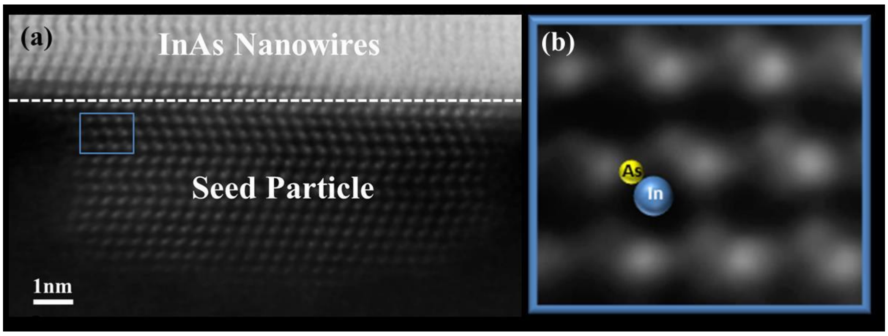

Figure 4: (a) High magnification annular dark field image of the interface between the InAs nanowire and the graphitic substrate showing the seed (b) dumbbell of the highlighted region.

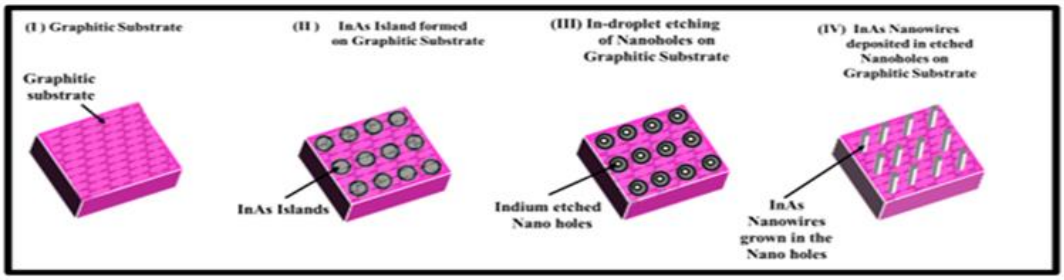

Figure 5: Schematic of the various steps involved in the fabrication of nanowires on graphitic substrates.

To better understand the mechanism of InAs NWs nucleation, we undertook a detailed investigation of the formation of the seed beneath the NW. As schematically illustrated in Figure 5, the first step involving the transfer of the graphitic substrate onto the Si (111) substrates (step I) is followed by the deposition of In droplets prior to commencement of NWs growth. Some of these droplets are soon transformed into InAs Islands (step II) in the As-rich environment of the MBE growth chamber, particularly at the initial stage of In droplet deposition. Driven by the lattice mismatch between InAs and graphite, the formation of these islands via the Volmer-Weber growth mechanism is believed to be due to its lower elastic energy. After the formation of the islands, In - droplet etching occurs through the islands onto the graphitic substrate as illustrated in step III (Figure 5). These droplets are eventually transformed to InAs underneath the NWs (seed particle) as described previously. This indicates that NWs nucleation started from the formation of In droplets in the nanoholes. The earlier observed exclusive growth of vertical NWs (Figures 1d and 3a) could therefore be attributed to the presence of the seed particle facilitated by the In etched nanoholes. This demonstrates that the In droplets are crucial for the droplet etching, formation of seed particle and facilitation of NWs growth. It can therefore be concluded that the absence of the seed particle is likely responsible for the nonappearance of non-vertical NWs. In the final stage (IV), InAs NWs are deposited in the nano holes while at the same time island growth is suppressed leading to their disappearance (Consonni *et al*., 2012, 2010; Dubrovskii *et al*., 2012b, 2012a). It is possible that the island undergoes a shape transformation to minimize their free energy resulting in the formation of NWs structures due to their lower surface energy (Dubrovskii *et al*., 2012b) as previously reported (Consonni *et al*., 2010; Gomes *et al*., 2015).

CONCLUSION

An investigation of the nucleation of Indium droplet assisted growth of InAs nanowires (NWs) on graphite is reported. It has been demonstrated that the uniaxial growth of the InAs NWs directly on the underlying graphitic substrate is driven by the Indium droplets which etch nanoholes in the graphitic substrate and promote the formation of InAs seed particles underneath the NWs facilitating their vertical directionality. This report unravels the mechanism of InAs NWs nucleation on graphite which is highly promising for applications in highly efficient and flexible nano devices.

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