Functionalization of nitrogen-doped carbon nanotubes with gallium to form Ga-CN$_x$-multi-wall carbon nanotube hybrid materials

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Abstract
In an effort to combine group III–V semiconductors with carbon nanotubes, a simple solution-based technique for gallium functionalization of nitrogen-doped multi-wall carbon nanotubes has been developed. With an aqueous solution of a gallium salt (GaI$_3$), it was possible to form covalent bonds between the Ga$^{3+}$ ion and the nitrogen atoms of the doped carbon nanotubes to form a gallium nitride–carbon nanotube hybrid at room temperature. This functionalization was evaluated by x-ray photoelectron spectroscopy, energy dispersive x-ray spectroscopy, Raman spectroscopy, scanning electron microscopy and transmission electron microscopy.

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(Some figures may appear in colour only in the online journal)

1. Introduction

Group IIIB nitrides, with the exception of boron nitride (BN), are some of the most important high energy direct bandgap semiconductors, with physical and chemical characteristics superior to silicon (Si), gallium arsenide (GaAs) and other group IIIB/group V compounds. Some examples of these characteristics are physical and chemical stability, high-temperature stability, and strong optoelectronic properties. Most of the group IIIB nitride compounds crystallize in the thermodynamically stable hexagonal wurtzite phase under ambient conditions. The group-III nitrides, gallium nitride (GaN), aluminum nitride (AlN) and indium nitride (InN), have bandgap energies of approximately 3.4 eV, 6.2 eV and 0.64 eV, respectively, in the wurtzite phase at room temperature [1–3]. These characteristics make the group IIIB nitrides promising semiconductor materials for applications such as light emitting diodes (LEDs), which
have been fabricated successfully with emission ranging from green to ultraviolet. These materials are also finding use in electronics that operate at high temperatures. Of these nitrides, gallium nitride (GaN) has generated the greatest amount of interest, with some researchers claiming that it is the most important semiconductor material since silicon. Despite the large number of investigations regarding optoelectronics, the development of GaN has not been solely centered on light emitter applications but also extends to other applications like high speed transistors, such as those used for wireless communications [4].

An area of great interest that has generated a significant number of diverse results is the synthesis of controlled nanostructures and the development of related nanotechnology. The applications of such nanostructures extend to almost all fields of scientific research and have found many industrial applications, representing a technological revolution. Nanostructured GaN has the possibility of increased efficiency and power compared to conventional bulk GaN, with numerous applications ranging from diodes to transistors. There have been several theoretical efforts since 1999 to establish the physical properties of single wall GaN nanotubes, despite the fact that such single wall GaN nanotubes have not been synthesized to date [5–12]. The structure and predicted properties of nanotubes of GaN have been one of the motivations for the development of methods to synthesize GaN nanostructures. However, these methods have not produced single wall GaN nanotubes, but rather nanowires and nanocylinders of GaN, that exhibit a wide variety of crystallinities, ranging from mono-crystalline material to amorphous [13–18]. These techniques have primarily employed a sacrificial template method to create GaN nanostructures, which involves removal of the template either during or after GaN deposition.

Carbon nanotubes have been used in combination with the processing of nanostructured gallium oxides and nitrides in several studies [15, 17, 19]. Previous works have employed these carbon nanotubes as templates, reaction substrates and even as reactants. One form of carbon nanotube that seems to be of obvious relevance in regard to GaN formation would be nitrogen-doped multi-wall carbon nanotubes (CNx-MWCNTs). These nanotubes have been extensively studied by researchers and have unique chemical, electrical and mechanical properties [20–24]. Considering the presence of covalently bonded nitrogen atoms in these carbon nanostructures, they are promising materials for possible combination with GaN. This combination can allow for direct covalent linkage between one of the most exciting allotropes of carbon (nanotubes) and what has been called the most important semiconductor since silicon, gallium nitride.

In this work CNx-MWCNTs are functionalized with gallium (Ga3+) by reacting with an aqueous solution of GaI3. Rather than using the carbon nanotubes as sacrificial templates or nanoscale reaction vessels [15, 17, 19, 25], this technique combines gallium with carbon nanotubes in a simple non-destructive manner, to yield a novel hybrid nanomaterial, gallium–nitrogen-doped MWCNTs (Ga-CNx-MWCNTs).

2. Experimental methods

2.1. Materials

Both pristine MWCNTs and CNx-MWCNTs were synthesized in-house via a floating catalyst aerosol-assisted chemical vapor deposition (AACVD) method, under atmospheric pressure conditions. The chemical precursors used were mixtures of 22 mg ml–1 of ferrocene in xylene at a growth temperature of 775 °C for pristine MWCNTs and a xylene (25 vol%)–acetonitrile (75 vol%) solution with ferrocene (22 mg ml–1) at a growth temperature of 850 °C for CNx-MWCNTs. For both pristine MWCNTs and CNx-MWCNTs, argon/hydrogen (15% balance) gas was used to carry the nebulized precursor at a flow rate of 1.00 standard liters per minute and a precursor feed rate of 0.4 ml min–1 through a 46 mm internal diameter quartz tube furnace where the MWCNT materials were deposited onto Si wafers and collected after synthesis. The total nitrogen content of the CNx-MWCNTs was estimated at approximately 2.0% ± 0.5% based on x-ray photoelectron spectroscopy.

Fresh aqueous solutions of gallium iodide (Ga(III)I3 99.999%, Aldrich) were prepared with deionized water at 0.1 wt% (2.2 mM) and used immediately to prevent undesirable hydrolysis reactions of the Ga3+ ions in solution. Ammonium hydroxide solution (27% in H2O, Aldrich) was used as delivered.

2.2. Sample preparation

CNx-MWCNTs and MWCNTs were added to aqueous GaI3 solutions at 0.05 wt% (10 mg per 20 ml solution) and then sonicated in a Branson® bath sonicator for 30 min at room temperature and pressure. It should be noted that the MWCNTs were significantly more hydrophobic than the CNx-MWCNTs and that significant agitation was required to submerge and partially disperse the MWCNTs in the aqueous solution. The resultant solutions were then allowed to sit at room temperature overnight. To prepare the samples for scanning electron microscope (SEM) observation, the nanotube material was removed from the supernatant solution of both the CNx-MWCNT and MWCNT samples, and washed thoroughly by combining with deionized water in a low molecular weight (3 kDa) cutoff centrifuge tube subjected to 9000 r.p.m. for 10 min. This procedure was repeated several times to ensure that any unreacted salts (e.g. GaI3) were removed along with the HI acid produced by the dissolution of GaI3 in water. Some samples were subsequently washed with ammonium hydroxide by adding 100 ml of concentrated ammonium hydroxide and heating the solution to 80 °C for 30 min, then washing thoroughly with deionized water. In all cases the samples were dried on polytetrafluoroethylene membranes, transferred to adhesive carbon microscopy tape and observed with scanning electron microscopy (Phillips UHRSEM FEI XL30 SFEG). The same techniques were employed to clean nanotube samples prior to being deposited onto a degeneratively doped silicon wafer for Raman and x-ray photoelectron spectroscopy, and
onto a carbon coated copper grid for transmission electron microscopy (JEOL 2100, field emission, 200 kV from a LaB₆ source). X-ray photoelectron spectroscopy (XPS) data collection and analysis was performed with PHI MultiPak 7 software (ULVAC-PHI, Inc.).

3. Results and discussion

The nitrogen atoms in CNₓ-MWCNTs typically reside in one of two common positions—substitutional or pyridinic. Other positions are possible for nitrogen, but the two mentioned are the key doping sites [21]. The substitutional nitrogen atoms form four bonds and carry a positive formal charge, and they effectively substitute the carbon atoms in the sp²-hybridized graphitic lattice of carbon nanotubes. The pyridinic nitrogen atoms form three bonds and maintain a lone pair with no formal charge as a result. These pyridinic nitrogen atoms form defects in the sp²-hybridized graphitic lattice, and the present work exploits these defect sites. The addition of Ga³⁺ ions to a solution of CNₓ-MWCNTs allows for the lone pairs of the pyridinic nitrogen atoms to form covalent bonds with the gallium atoms analogous to the bonds present in gallium nitride (GaN). While ideally these pyridinic nitrogen atoms would be in groups of three for optimal bonding with Ga³⁺ (as shown in figure 1), there also exist sites where 1, 2 and 4 (porphyrin-like sites) pyridinic nitrogen atoms are found together. The structure shown in figure 1 is the same basic structure suggested by Shang et al with spin-polarized density functional theory for the functionalization of CNₓ-MWCNTs by transition metals [26].

The presence of nitrogen creates disorder in the sp²-hybridized carbon structure, and it is possible that the addition of Ga atoms into these defect sites would restore some degree of order to the sp² lattice. This is supported by Raman spectroscopy (see supporting information available at stacks.iop.org/Nano/23/325601/mmedia), which showed that the ratio of the G-band (ordered graphitic carbon lattice) to the D-band (disordered carbon structure) increased after functionalization with Gal₃(aq).

3.1. X-ray photoelectron spectroscopy

The Ga–N bonding in the Ga-CNₓ-MWCNTs was examined by XPS (figure 2). All of the XPS data contain a large carbon peak that is characteristic of the sp²-hybridized graphitic carbon atoms that constitute the majority of carbon nanotubes (284.5 eV) [27, 28]. Since the carbon constitutes the bulk of the samples, this peak allows for the reliable calibration of the XPS data collected.

The key spectral regions shown in figure 2 are the gallium Ga 2p, nitrogen N 1s and gallium Ga 3d. The CNₓ-MWCNTs were evaluated in pristine ‘as-produced’ condition (1), after functionalization in Gal₃(aq) solution (2), and after a post-treatment washing with concentrated ammonium hydroxide at 80°C for 30 min (3). While the Ga 2p peaks (left) clearly suggest that gallium is present in the sample after functionalization, they also confirm that the majority of the gallium is washed away in the final post-treatment washing. This is also similar to what can be seen in the Ga 3d (right), where only a small shift of the original background from the CNₓ-MWCNTs (from 1 to 3) can be observed. To further understand the interaction of Ga³⁺ ions in solution, inspection of the XPS spectra with attention to the N 1s region is necessary. The presence of nitrogen in the CNₓ-MWCNTs is seen in a region centered about 400 eV (figure 3), which corresponds to the N 1s binding energies. Careful examination of the various peak locations reveals the changes that occur in the nitrogen bonding environment as a result of Ga³⁺ functionalization.

Carbon nitride (CNₓ) films studied in previous works exhibit nearly identical bonding character as their curved CNₓ-MWCNT cousins, and both show characteristic peaks for the N 1s around 398 and 401 eV, with the peak at about 401 eV typically being the strongest [28–31]. The peak at about 398 eV is generally attributed to pyridinic nitrogen (three covalent bonds and one lone pair) while the 401 eV is attributed to substitutional nitrogen (four covalent bonds and a formal positive charge). Unfortunately, this spectral region is also precisely the region where GaN has its major N 1s peaks, with XPS data showing peaks around 397 eV and electron energy loss spectroscopy showing 401 eV [32–34]. This presents a significant problem for the unambiguous identification of gallium atoms bound to nitrogen atoms in CNₓ-MWCNTs. One observation that supports the assertion that newly formed Ga–N bonds change the nitrogen bonding environment of the CNₓ-MWCNTs is the fact that the ratio between the peak at approximately 401 eV and the peak at approximately 398 eV changes noticeably between samples.
Figure 2. Selected regions of XPS profiles of: (1) as-produced CNₓ-MWCNTs, (2) Ga-CNₓ-MWCNTs, and (3) Ga-CNₓ-MWCNTs after ammonium hydroxide wash. These data was obtained using a mono Al Kα x-ray source with an energy of 1486.6 eV, power of 50.3 W and a 45° angle of incidence. The step size resolution was set at 0.1 eV.

Figure 3. Deconvolution with symmetrical Gaussian–Lorentzian curve fitting of the N 1s regions seen in figure 2, with: (1) as-produced CNₓ-MWCNTs, (2) Ga-CNₓ-MWCNTs, and (3) Ga-CNₓ-MWCNTs after ammonium hydroxide wash. The peak positions in eV are given next to the relevant images. Details of the curve fitting calculations can be found in the supporting information (available at stacks.iop.org/Nano/23/325601/mmedia).

1 and 3. If gallium–nitrogen bonding is present in these GaI₃ treated samples, it could be the cause of such peak ratio changes. The mild low-temperature reaction conditions used during the GaI₃(aq) functionalization process alone are unlikely to significantly change the bonding environment of the nitrogen atoms in the CNₓ-MWCNTs as observed, and therefore it seems very likely that the Ga³⁺ ions are responsible. Another key feature of the N 1s spectral region is the presence of a peak at approximately 405 eV in the functionalized samples. The CNₓ-MWCNTs starting material contains a broad peak centered at 404.0 eV which is typically assigned to pyrrolic nitrogen positions, while the final material (3) shows a much more pronounced peak at 405.2 eV. This higher binding energy peak has been typically attributed to azide-like nitrogen bonding, which is when nitrogen forms four bonds and has a formal positive charge [35]. Interestingly this four-coordinated nitrogen peak has also been identified as the high binding energy peak for both cubic and hexagonal GaN [36, 37]. Furthermore, this peak has shifted to significantly higher energy (+1.2 eV) from samples 1 to 3. This shift toward the reported 405 eV of c-GaN and h-GaN is indicative of the increase in the four-coordinated high energy binding character of the surface nitrogen atoms. To provide a counterpoint, some researchers have suggested that this peak around 405 eV can be attributed to diatomic molecular nitrogen encapsulated within the CNₓ-MWCNTs [38, 39]. It is the opinion of the authors of the present work that this assumption is not applicable in this case. It is highly unlikely that the character of such encapsulated N₂ would change both peak position and intensity as seen from sample 1 to 3. It is far more likely that surface interactions with the GaI₃(aq) solution have resulted in a change in the local bonding environment of surface nitrogens by the addition of gallium atoms to the pyridinic nitrogen positions as illustrated schematically in figure 1.

The presence of gallium in the samples was further evaluated with the observation of several peaks in figure 2, which are the gallium Ga 2p at both 1146 eV (2p₁/₂)
and 1119 eV (2p$_{3/2}$), and the Ga 3d$_{3/2}$ at approximately 20 eV [40, 41]. The Ga 2p peaks can be clearly observed for sample 2 in figure 2. After the ammonia wash these peaks are reduced considerably and only small downshifted peaks are observed. This behavior confirms that gallium is present in sample 2, and that the majority of this gallium is removed in the ammonia washing. The XPS estimation of the atomic percentage of gallium based on the Ga 3d peak in sample 2 was 1.0% ± 0.5%, and this would equate to as much as a 1:2 ratio of Ga:N, as the nitrogen content of the as-produced CN$_x$-MWCNTs was approximately 2% with carbon at 97.7% and oxygen at 0.3%. It is suspected that the large increase in the gallium signal is disproportionate to the small amount of gallium which would be functionalized at the pyridinic nitrogen sites on the CN$_x$-MWCNT surfaces. The explanation is that the strong gallium signals seen in sample 2 of figure 2 are the result of gallium oxide, anchored to the CN$_x$-MWCNTs by the bonding of gallium atoms to the pyridinic nitrogen atoms on the surface. It is known that Ga$_2$O$_3$ is soluble in alkali solutions such as ammonium hydroxide, while GaN is not [40, 41], and for this reason an alkali washing step was necessary. It was found that after an ammonia wash the Ga presence was approximately 0.2%, reducing the Ga:N ratio from 1:2 pre-wash to 1:10 post-wash. To further investigate the presence of gallium and gallium oxides in the CNT samples, energy dispersive x-ray spectroscopy (EDX) was combined with electron microscopy.

3.2. Scanning electron microscopy

Field emission SEM was carried out at 5–10 kV with an accelerating current of 12.0 µA. Imaging revealed that the MWCNT sample contained a large amount of what appeared to be nanoscale clusters or crystals, while the CN$_x$-MWCNTs showed no such nanoparticles. These nanoparticles are not soluble in water, as both samples had been thoroughly washed with an excess of deionized water after the Ga$_3$$_{(aq)}$ treatment. Any Ga$_3$ or other water soluble salts would have been removed in these washes. The SEM micrographs shown in figure 4 demonstrate the clear difference in the two CNT samples after reaction with Ga$_3$$_{(aq)}$.

Although both the MWCNTs and the CN$_x$-MWCNTs grow in a vertically aligned fashion (CVD synthesis), the MWCNTs were processed in a way that disrupts this alignment. The CN$_x$-MWCNTs were not subjected to post-synthesis processing. The composition of the particles found amongst the MWCNTs was evaluated by EDX, which showed strong gallium and oxygen signals (see supporting information available at stacks.iop.org/Nano/23/325601/mmedia), consistent with gallium oxide. The fact that these nanoparticles were not removed in the ammonia wash removes the possibility that they are Ga$_2$O$_3$ (gallium oxide), as this material is highly soluble in concentrated alkali solutions such as ammonium hydroxide [40].

3.3. Formation of GaOOH versus Ga$_2$O$_3$

When Ga$_3$ salt is dissolved in water, it results in Ga$^{3+}$ and I$^-$/ions in solution. The Ga$^{3+}$ ions interact with water resulting in three hydroxide groups surrounding the Ga$^{3+}$ to form gallium hydroxide (Ga(OH)$_3$), while the I$^-$ ions interact with H$^+$ ions to form iodic acid. If the Ga$^{3+}$ is left unreacted in water it will begin to undergo hydrolysis and form gallium oxide hydroxide (GaOOH). In the MWCNT solution, the Ga$^{3+}$ ions do not have a room temperature reaction pathway with the sp$^2$-hybridized carbon atoms in the MWCNTs, and instead form GaOOH as a precipitate through a metathesis reaction of Ga(OH)$_3$. This reaction, shown schematically in figure 5, removes hydroxide anions from solution and contributes to a lower final pH of the MWCNT solution. The initial pH of the MWCNT containing Ga$_3$ solution was pH = 3.40 and the observed final pH after 30 min of sonication at room temperature and sitting overnight was pH = 2.75.

The shapes and sizes of the precipitates (seen in figure 4 and supporting information available at stacks.iop.org/Nano/23/325601/mmedia) were consistent with previously reported GaOOH structures obtained from the hydrolysis of gallium salts [42–44]. The lack of GaOOH precipitates in the CN$_x$-MWCNT samples, along with the facile removal of the majority of gallium from the CN$_x$-MWCNTs with ammonium hydroxide, are strong evidence that Ga$_2$O$_3$ was formed rather than GaOOH. Ga$_2$O$_3$ is highly soluble in concentrated ammonia, while GaOOH is not soluble and routinely precipitated from solution with ammonia solutions [45]. This is due to a unique interaction of the Ga$_3$$_{(aq)}$ solution with the CN$_x$-MWCNTs. Gallium atoms bonding covalently with...
Figure 5. GaI3 forms Ga(OH)3 in solution which subsequently undergoes a metathesis reaction in aqueous media with acidic pH. This results in nanometer and micron scale precipitates of GaOOH and a lower solution pH.

Figure 6. Proposed reaction mechanism for the formation of nitrogen anchored Ga2O3 on the surfaces of the CNx-MWCNTs.

Figure 7. SEM–EDX study at 20 kV of both MWCNTs (left) and CNx-MWCNTs (right) as-produced (1), after exposure to GaI3(aq) (2), and after a post-functionalization ammonium hydroxide washing treatment (3). The carbon (C) and gallium (Ga) peaks are labeled, along with silicon (Si) peaks from the substrate used in (2).

3.4. Energy dispersive x-ray spectroscopy study of ammonia washing

EDX was performed within the SEM sample chamber. The EDX spectrum obtained from the MWCNTs and CNx-MWCNTs, as-produced (1), post-functionalization (2), and post-functionalization with an ammonium hydroxide wash (3) are shown in figure 7.

All of the spectra show the characteristic carbon Kα peak at approximately 0.277 keV. The EDX technique is rather insensitive to the presence of nitrogen, and accordingly this element was not observed for the CNx-MWCNTs. The data for both samples at stage 2 show significant gallium Lα peaks centered at approximately 1.098 keV, along with smaller oxygen Kα peaks at approximately 0.525 keV. Iron which exists as entrapped catalyst particles within the MWCNTs and CNx-MWCNTs [46] was also observed but is not shown. The gallium Lα peak remains in the MWCNT sample after the alkali wash (figure 7 (3, left)), while the gallium is significantly reduced for the CNx-MWCNT sample after the alkali wash (figure 7 (3, right)). This supports the assertion that the gallium present in the MWCNT sample is GaOOH and that the CNx-MWCNT sample contains Ga2O3 anchored by nitrogen atoms on the nanotube surface. While the Ga2O3
is removed by the ammonia wash, the Ga–N bonding is not affected.

3.5. Transmission electron microscopy (TEM)

Transmission electron microscopy was used to examine the CNT samples more closely and to identify the presence of the gallium oxide presumed to be in the CNx-MWCNT sample. Again, the two samples showed a clear difference. While the MWCNTs had no noticeable surface coating, the CNx-MWCNTs were covered in a conspicuous amorphous layer (figure 8). It should also be noted that the CNx-MWCNTs exhibit a common bamboo structure; this is due to the defects introduced to the graphitic lattice by the dopant nitrogen atoms.

This surface coating of amorphous Ga2O3 on the CNx-MWCNTs explains why no nanoparticles were observed in the CNx-MWCNT sample in the SEM studies. To confirm that the surface coating of the CNx-MWCNTs was a gallium compound, a scanning transmission electron microscope (STEM) equipped with an EDX detector was employed to examine the CNx-MWCNTs. The scans did confirm that the surface deposits observed on the CNx-MWCNTs was indeed a gallium compound (see supporting information available at stacks.iop.org/Nano/23/325601/mmedia).

Considering the surface layer of Ga2O3 present on the CNx-MWCNTs and the absence of such a layer on MWCNTs, it is clear that the presence of the dopant nitrogen atoms in the CNx-MWCNTs is directly involved in the formation of this layer.

4. Conclusions

In this work we have shown, for the first time, compelling evidence for the hybridization of CNx-MWCNTs with trivalent gallium ions in solution. This is an important first step toward merging these two fast growing technologies to create a new class of hybrid materials. Carbon nanotubes have the ability to act as electron carriers in the form of Ohmic contacts, which has been shown previously [47], and this could provide for GaN materials with lower electrical resistance. In addition to the possibility of improved current injection into the direct bandgap semiconductor GaN, the dissipation of thermal energy by CNx-MWCNTs acting as a heat-sink would also be favorable. This may potentially allow for lowered electrical resistance, lowered operating temperatures, and improved performance in high-temperature environments. Nitrogen-doped carbon nanotubes are thermally stable in air up to approximately 500°C or higher, while GaN is stable up to and beyond 1000°C, suggesting that these materials will perform well in harsh conditions. The consequences of the direct covalent bonding of gallium to nitrogen-doped carbon nanotubes is not fully understood.
understood at this time, and unique phenomena are likely to be observed in future works.

Future efforts will focus on elucidating the various properties of these Ga-CN$_x$-MWCNT hybrid materials, as well as attempting to grow GaN directly to the Ga-CN$_x$-MWCNT structures with molecular beam epitaxy and atomic layer deposition techniques. It may also be interesting to attempt to convert the Ga$_2$O$_3$ layer present on the Ga-CN$_x$-MWCNTs to GaN through the careful addition of NH$_3$ gas at elevated temperatures, leaving multiple layers of GaN on the surface of the Ga-CN$_x$-MWCNTs. Additionally, other group IIIB elements such as indium and aluminium will be explored as solution phase moieties for CN$_x$-MWCNT functionalization, and the possibility of using other carbon nanotube dopants such as phosphorus to create group-III phosphide like hybrid nanomaterials will be explored.

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References

[28] Beshkov G et al 1999 XPS spectra of thin CN$_x$ films prepared by chemical vapor deposition Diamond Relat. Mater. 8 591


[41] 1989 CRC Handbook of Chemistry and Physics (Boca Raton, FL: CRC Press)


