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To cite this article: Bin Chen et al 2018 Nanotechnology 29 505706

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Dynamics of GeSbTe phase-change nanoparticles deposited on graphene

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Received 19 July 2018, revised 17 September 2018
Accepted for publication 25 September 2018
Published 12 October 2018

Abstract
Phase-change Ge2Sb2Te5 nanoparticles (NPs), that are promising for next-generation phase-change memory and other emerging optoelectronic applications, have been deposited on graphene support layers and analyzed using advanced transmission electron microscopy techniques allowing high quality atomic resolution imaging at accelerating voltages as low as 40 kV. The deposition results in about three times higher NP coverage on suspended graphene than on graphene containing an amorphous background support. We attribute this to the variation in surface energy of suspended and supported graphene, indicating that the former harvests NPs more effectively. Hydrocarbon contamination on the graphene profoundly enhances the mobility of the NP atoms and after prolonged (weeks) exposure to air resulted in more severe oxidation and spreading of NPs on the suspended graphene than on supported graphene because the network of hydrocarbons develops more extensively on the suspended rather than on the supported graphene. Due to this oxidation, GeOx shells are formed out of NPs having a uniform composition initially. The present work provides new insights into the structure and stability of phase-change NPs, graphene and their combinations.

Supplementary material for this article is available online

Keywords: GeSbTe, nanoparticles, graphene, transmission electron microscopy, energy dispersive x-ray spectroscopy

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

1. Introduction

Phase-change materials (PCMs) have attracted strong interest due to their great potential for applications in optical storage, electrical memory, photonic displays, etc [1–3]. They can be reversibly switched between their amorphous and crystalline phases within nanosecond time scale and nanometer length scale, while the significant optical and electrical contrasts between these two phases enable encoding and storing information by programing the PCMs between these two phases. The ever-increasing demand for information storage encourages pursuing storage media with stronger performances. One of the most promising paths is the down-scaling of the bit dimensions. Recently, several investigations of three-dimensionally scaled down PCM nanoparticles (NPs) have been presented, where GeTe and Ge2Sb2Te5 NPs have been successfully grown by chemical synthesis and physical deposition [4–8]. The weak size dependence in crystallization temperature ensures the long-time stability of the amorphous state and the wide operation window, as elucidated in our previous paper [6]. It was also demonstrated that the GST NPs, especially the GST NPs prepared with CH4 additional gas during deposition are a promising candidate for future phase-change memory, because they exhibited better data retention compared to the thin films and comparable crystallization speed in the switching regime [7].

Graphene has experienced intense investigations due to its unique mechanical, thermal and electron transport properties [9–11]. For instance, it has been demonstrated that the energy efficiency of the material in phase-change memory...
was enhanced by inserting graphene between the active GST and the bottom electrode heater [12]. In this device, graphene played a role as a thermal barrier and limited the atomic migration of PCM that also leads to improved endurance of the memory. In addition, there are numbers of investigations reporting that placing thin films or NPs on graphene not only influenced the thin films or NPs but also the electronic properties of graphene [13–19]. Some NPs could form 2D structures and have strong interactions with graphene [20, 21], which could lead to opening of the band gap of graphene and thereby greatly extends its potential in semiconductor applications.

On the other hand, the functionalization of graphene has attracted intensive studies [22]. Decorating graphene with NPs has applications in many fields, such as catalysis, sensors, supercapacitors, energy storage and the anode of Li-ion battery [23–26].

Despite the advantages it offers, sound understanding of the interaction between graphene and the GST NPs as well as the dynamics of NPs adsorption and oxidation are necessary before application of such systems. Although there have been comprehensive investigations on the metal oxide-graphene nanocomposite, the GST NPs grown by inert gas condensation are ‘clean’, i.e. without surrounding ligands that usually play an important role in surface activity. Due to this difference, the dynamics of NPs deposition and subsequent oxidation remain ambiguous. In this work we report the deposition of GST NPs on graphene and the subsequent interaction between the phase-change NPs and the graphene support. The dynamics of NPs attachment on the graphene and oxidation was unraveled by studying the NPs using state-of-the-art scanning transmission electron microscopy (STEM).

2. Experimental methods

2.1. Graphene preparation

Graphene was grown on oxygen rich copper foils by chemical vapor deposition. Briefly, the copper foil (Alfa Aesar, 99.8% purity) with a thickness of 25 μm was cleaned by soaking in acetic acid for 8 h, rinsed by water, before it was put into a quartz tube for growing the graphene. In order to eliminate the residual copper oxide on the copper surface, the quartz tube was filled with 0.1 mbar hydrogen (Messer, purity 5.0), and it was heated up to 1035 °C. To grow graphene, 0.2 mbar mixture of argon and methane (5%) was added into the quartz tube at 1035 °C for 2 h. Thereafter, the copper foil was cooled down to room temperature with all the gasses remaining.

After a high quality of monolayer graphene was confirmed by Raman measurement with He–Ne laser at 633 nm (see the supporting information (SI), figure S1 is available online at stacks.iop.org/NANO/29/505706/mmedia), graphene was transferred to Quantifoil R2/1 holey carbon (Electron Microscopy Sciences, Q225-AR1) TEM grids for the STEM characterization. Firstly, the TEM grids were placed on top of graphene on copper. Two drops of isopropanol (IPA) were deposited on the sample to enhance the bonding between graphene and the carbon membrane of the quantifoil TEM grids after the IPA evaporated. The sample was then annealed at 100 °C for 10 min to finally strengthen the contact between graphene and the TEM grids before the copper was etched away in (NH4)2S2O8 0.1 g ml−1 for 24 h. The TEM grids covered with graphene were eventually rinsed three times in demi-water to eliminate any remaining trace of the etchant.

2.2. GST NPs deposition

As described extensively in a previous paper [6], Ge2Sb2Te5 phase-change NPs with excellent size, crystallinity and composition control were grown by inert gas phase condensation based on magnetron sputtering in a home-modified NP system Nanogen50 from Mantis Deposition Ltd. The sample chamber was evacuated at a base pressure of 10−8 mbar. Ar (purity of 99.999%) was used as sputtering gas, while medium amount of CH4 was used as additional gas to initiate the nucleation process [6]. Low discharge current (0.105 A) was adopted to ensure the amorphous state of the NPs. The NPs were directly deposited on Au Quantifoil grids covered with transferred graphene at room temperature. The NP coverage was altered by changing the time and yield of the deposition process.

2.3. Characterization

The morphology of the as-deposited NPs was characterized using a JEOL 2010 at 200 kV within 1 h after sample deposition. The coverage is defined as the ratio of the NPs covered area over total area. The as-deposited amorphous NPs were crystallized by annealing them at a temperature of 180 °C for 10 min inside the JEOL 2010. The energy dispersive spectroscopy (EDS) elemental maps and high resolution STEM images were recorded using a JEOL (Accel) ARM 200 F (UHR pole piece) equipped with a single 100 mm2 (0.65 srad) EDX detector and FEI Themis Z equipped with SuperX EDX detectors (four 30 mm2 detectors providing 0.7 srad). High acceleration voltage (200 kV) was only utilized to record overview bright field TEM images of the GST NPs (in the JEOL 2010), but low acceleration voltages (40 and 60 kV) were used for all STEM work, i.e. for both HAADF imaging as well as for the EDS mapping, because high voltage (above 80 kV) can easily induce knock-on damage to the single layer graphene due to the collision of the beam electrons with the nucleus of the graphene target atoms [27, 28]. The EDS maps are based on the K-edge for O and the L-edges of Ge, Sb and Te. They were recorded with beam currents in the range 50–100 pA and convergence angles 20–30 mrad.

3. Results and discussion

The quality of the graphene support layer was characterized by selected area electron diffraction patterns (with an aperture...
diameter corresponding to 2.5 μm on the sample surface), as demonstrated in figure S2 of the SI. The line profile of the diffraction pattern in figure S2(a) indicates that the selected graphene support is a single layer [29], while the broad halo at 3.31 nm−1 infers the amorphous nature of the as-deposited GeSbTe NP. During the graphene transfer, it is possible for graphene to be teared and folded, which leads to the formation of bi-layer and multi-layer graphene locally as indicated in figure S2(b) of the SI. Here we intentionally chose the single layer graphene to image the GST NPs and the substrate.

The morphology of the NPs was characterized by bright field TEM images, as displayed in figure 1. The average diameter of the NPs is determined as 9.5 ± 1.1 nm. The substrate consists of two distinct parts on the TEM grids: (1) (suspended) graphene on holes or (2) graphene on carbon support films (hereafter named suspended graphene and supported graphene, respectively). Surprisingly the NPs attachment dynamics on the two different types of graphene diverge remarkably, generating distinctly different morphologies of the NPs. As can be observed clearly in figure 1(a), the coverage of the NPs on the suspended graphene (left side) is much higher than that on the supported graphene area (right side), although the used beam of NPs impinging on the sample is homogeneous on a much larger length scale. Figures 1(b), (c) show the overview image of the NPs on these two different areas that allow the quantification of the NPs coverage. It is found that the coverage on the suspended graphene is roughly three times higher than the one on the supported graphene for the same sample. In order to verify the
reproducibility of this difference, several samples with different coverages were prepared and characterized. As shown in figure 1(d), this difference in coverage is consistent for all of these samples with wide coverage range, from about 4% to 48% on the suspended graphene. Moreover, one can nicely observe in figure 1(a) that the coverage abruptly jumps to a high value at the vicinity of the carbon edge instead of a gradual change over some distance. Note that, although the NP coverage on the two types of graphene differs by a factor three, the NP size distributions are the same for both types of graphene as demonstrated in figure S3 of the SI.

If the difference in coverage has some electrostatic or mechanical, i.e. long-range, origin, then a gradient in coverage near the carbon edge would be expected. For instance, when the difference stems from the mechanical flexibility of the graphene on the hole that dissipates the kinetic energy of the GST NPs (usually ∼0.1 eV per atom [30]), a gradient in coverage close to the carbon edge should be observed since a gradient in flexibility also exists when the graphene is approaching the carbon edge. Although the energy per atom in the NP that is impinging on the graphene coated TEM grid is still close to the thermal energy (3kT per atom with k the Boltzmann constant and T the absolute temperature), still the speed with which the clusters approach the grid is on the order of hundred meters per second. This will impact the sticking of the NPs on the various types of surfaces. The non-gradient variation in coverage for the various surface types then drives us to consider a thermodynamic origin: the surface free energy. Due to the nature of high surface free energy for suspended graphene [31], more NPs are adsorbed on the surface in order to reduce the surface energy, leading to a much higher coverage of the GST NPs in comparison to the supported graphene surface where the surface energy is already lowered by the supporting carbon film. The other role of surface energy is adsorbing airborne hydrocarbon contamination on the surface in order to reduce the surface energy due to the long time exposure to air (∼3 weeks). The adsorption of hydrocarbon to reduce surface energy of graphite and graphene has been observed by water contact angle measurements [32, 33], and will also be shown in detail below based on high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images.

The GST NPs were also simultaneously deposited on a continuous carbon support film and their morphology was characterized as well. It is worth noting that the coverage on a holey carbon TEM grid (12.0%), where the NPs were directly deposited on, is comparable to the supported graphene support (12.2%), as shown in figure S4 of the SI. This phenomenon indicates that the surface free energy is dominated by this amorphous carbon support film at the carbon/graphene area. The surface free energy of fresh graphene grown on a copper substrate was determined as 53.0 mJ m⁻² for Owens–Wendt approach [33], slightly higher than the value of amorphous carbon films (49.3 mJ m⁻²) utilizing the same approach [34]. After adsorption of airborne hydrocarbon contamination after 24 h of air exposure, the surface free energy of graphene decreased to 37.5 mJ m⁻². Note that all the experimental data were derived on a Cu/Graphene surface and that (experimental) value for the surface energy of suspended graphene is lacking due to the huge challenge to measure it.

The above results suggest a promising application of graphene: harvesting NPs. The high surface energy of graphene also makes it possible to align the adsorbates onto it. Engineering graphene with NPs has several emerging applications. For instance, proteins were utilized to decorate the graphene oxide sheet with the aim of gluing metallic NPs (Au, Pd, Pt) on top of the surface [35]. Decorating graphene with metal oxide NPs, such as MnO₂ [36], CuO [37] and Fe₃O₄ [38], is of interest as anodes in Li-ion batteries. So here airborne hydrocarbon adsorbates also provide the capability of decorating the graphene and gluing NPs on the surface. Moreover, these hydrocarbon adsorbates are removable by heating graphene to ∼550 °C [32], enabling the reversible switch of the surface state of graphene.

It has been demonstrated in our previous work that the overall composition of the GST NPs are in good agreement with the nominal stoichiometry of Ge₅Sb₂Te₅ (Ge:Sb:Te = 22:22:56) [6], yet the elemental distribution within the NPs could not be determined due to instrumental limitations at that time. As shown in figure 2, high spatial resolution EDS elemental mapping of as-deposited amorphous NPs on graphene has been performed, with the corresponding morphology of the NPs demonstrated by the HAADF-STEM image, portraying the distribution of Ge, Sb and Te. The homogeneous distribution of the Ge, Sb and Te can be clearly observed in this figure. Moreover, no obvious oxidation (forming an outer shell) of (one of) these three elements can be detected in this mapping as confirmed by line profile of the combined mapping, inferring that the as-deposited GST NPs were not observably (<1 nm) oxidized after exposure to air for 1 day.

To investigate the oxidation dynamics of the NPs, we exposed the GST NPs to air for 3 weeks after crystalizing them by annealing in TEM at a temperature of 180 °C for 10 min [6]. Figure 3 shows the HAADF and bright field STEM images of NPs on graphene support film at different acceleration voltages (40 and 60 kV). Along the line of our previous results [6], the GST crystals exhibit a combination of rock-salt and trigonal structures, where the lattice parameter of the rock-salt structure is ∼1.8% expanded (with d₀₀₂ = 0.216 nm) in comparison to the lattice constant of GST films. While most of the NPs are in rock-salt phase, the trigonal phase was observed as well [39], as shown in figure S5 of the SI. The van der Waals gaps are visible for some of the crystallized NPs.

Due to the high surface energy of graphene/nanoparticle composite and exposure to air, the airborne hydrocarbon contamination is further absorbed on the surface, depicted as the ‘cloud’ in HAADF-STEM images (figures 3(a) and (c), in which low atomic number (Z) corresponds to low intensity) while it is obscured in the bright field images (figures 3(b) and (d)). Hence cautious have to be taken when interpreting the bright field images about hydrocarbon contaminations. The NPs are surrounded by the airborne hydrocarbon contamination. On one hand, the NPs prefer to land on the pre-
existed hydrocarbon adsorbates. On the other hand, owing to the high surface to volume ratio of the NPs (with diameter less than 10 nm), more airborne hydrocarbon is adsorbed by the NPs to reduce their surface energy, forming the encircling cloud-like structure. Yet it is impossible to distinguish the hydrocarbons adsorbed before or after NPs deposition.

At the edge of the NPs, large amount of atoms seem to distribute randomly instead of being bonded to the crystal. Then the hydrocarbon contamination plays a role as a highway for the migration of atoms, leading to the enrichment of atoms at the edge of the hydrocarbon, as indicated by the white arrows in figures 3(a) and (c). Figure 3 also demonstrates an acceleration voltage dependent mobility of these atoms. It is generally observed that more randomly distributed atoms assemble at the boundary of the hydrocarbon and the periphery of the NPs (green arrows in figures 3(a) and (c)) imaged at 60 kV in comparison to that recorded at 40 kV, indicating that the mobility of the heavy atoms correlates to the electron beam irradiation (see also figure S6). The real time video (SI 2) obtained by recording high resolution bright field images at each second shows the pop-up of heavy atoms induced by the electron beam at an acceleration voltage of 60 kV. It is highly possible that the Ge atoms migrate towards the outside of the NPs and forms a GeOx shell due to its highest sensitivity to oxygen among the Ge, Sb, Te elements.

In order to verify the species of the atoms that move towards the outside of the NPs and the edge of the hydrocarbon, EDS elemental mapping has been conducted for the NPs, as shown in figure 4. The Sb and Te atoms mostly remain within the NPs, while small amount of Te atoms move onto the hydrocarbon cloud. However, Ge atoms move towards the periphery of the NPs and form distinct oxide shells surrounding the NPs, which is further confirmed by the similar distribution of Ge and O atoms in figure 4. The line profile of the elemental maps for these four elements markedly portrays the identical distribution for Ge and O at the shell of the NPs. Figure S7 of the SI depicts more convincingly diffusion of Ge and Te atoms compared to Sb atoms on the hydrocarbon contamination. These results show the high sensitivity of the GST NPs (especially Ge) to the air exposure, inferring the necessity of a capping layer to protect the NPs. Also revealed by the above results is that Ge and Te atoms have a higher mobility on the hydrocarbon contamination than Sb.

In contrast, the NPs deposited on the supported graphene show a rather different morphology and oxidation dynamics after crystallization in comparison to the NPs on the suspended graphene, as elucidated in figure 5. Although hydrocarbon adsorbate can be hardly observed in both HAADF-STEM and bright field images, the adsorption still occurred. As can be inspected in figure S8 of the SI, some hydrocarbon...
contamination is observable in some HAADF-STEM images. There are two possible reasons for the less visible airborne hydrocarbon contamination in this type of area: (1) the surface energy of the graphene has been lowered by the carbon support film, so less hydrocarbons are absorbed; (2) the thick carbon support film (∼12 nm) strongly reduces the signal and thus visibility of the hydrocarbon contamination. Considering the phenomenon that GST NPs are attached to hydrocarbon contaminations, it is highly possible that the suspended graphene adsorbs more hydrocarbon in comparison to supported graphene due to higher surface energy, leading to higher coverage since the NPs can land on the hydrocarbon preferably.

The EDS elemental mapping of the GST NPs on the supported graphene shows relatively uniform distribution of Ge, Sb and Te atoms with GeO shells formed surrounding the NPs. Although the Ge atoms at the shell can be detected, more Ge atoms remain within the NPs compared to the NPs on suspended graphene, as demonstrated by line profile of these elemental maps. Also the less obvious oxidation shell indicates that the NPs on the carbon/graphene support are less heavily oxidized compared to the NPs on the suspended graphene. Because of the similar size of the NPs profiled in figures 4 and 5, a possible size effect on the oxidation can be excluded. Another information that the line profile delivers is that O atoms are present on the whole surface. The wide distribution of O atoms stems from the hydrocarbon and water adsorbed on the substrate.

Since acceleration voltage above 80 kV can easily induce knock-on defects to graphene [27], low acceleration voltage was used to image graphene in this work. The atomic structure was imaged with HAADF-STEM at 40 and 60 kV with a resolution where individual atoms in the graphene are still resolved, as depicted in figure 6. The STEM images show the C–C separation of 1.41 Å, that agrees well with the crystallography structure of graphene (where C–C separation is 1.42 Å) [40]. The signal-to-noise ratio can be improved by integrating multi frames. Figure S9 of the SI shows a 40 kV image after 21 frames intergration, portraying a sharper contrast. Defects could not be observed in large areas under the electron irradiation. Surprisingly, the electron beam induced etching, which is believed to happen for low acceleration voltage (20–100 kV) [27], was not observed in this work. As shown for example in figure S6, no holes could be

![Figure 3. High resolution STEM images of crystallized NPs on suspended graphene. (a) and (c) are the high angle angular dark field images recorded using 40 and 60 kV electron beams, respectively, while (b) and (d) are the corresponding bright field images.](image-url)
observed in the HAADF-STEM images, even near the hydrocarbon contamination sites, where the hole nucleates [27]. In addition, other types of interface-mediated reactions induced by the electron beam in our heterogeneous NP-gra- phene system, like for instance observed in many nanoparticle-carbon systems used in catalysis [41–43], were also not observed. This is probably related to the higher stability of graphene compared to some other allotropes of carbon (like amorphous carbon) in combination with the much lower accelerating voltage used here for generating the electron beam (40–60 kV here compared to the traditionally 200 or 300 kV).

From the above extensive analysis we can thus extract interesting new findings and discuss implications:

1. GeSbTe NPs when deposited using a homogeneous beam of NPs impinging on the graphene show a three times higher coverage on suspended graphene than on graphene that is in its back supported by an amorphous carbon film. We can deduce that this result does not have a mechanical or electrostatic origin and therefore most likely it is directly related to the difference in surface energy of suspended and supported graphene.

2. A network of hydrocarbons develops upon air exposure more extensively on the suspended than on the supported graphene. This is again a consequence of the initially higher surface energy of clean suspended graphene than of clean supported graphene. The graphene wants to reduce its surface energy and can do this by covering itself by hydrocarbons and this covering is stronger for the higher energy suspended graphene.

3. Hydrocarbons play an important role in enhancing the mobility of other adatoms on the graphene. Atoms of the GeSbTe NPs, in particular Te and Ge, distribute themselves over the hydrocarbons and move along the edge of the hydrocarbons with the still clean graphene parts. This also explains why the morphology with distinct individual NPs after deposition develops into a network of GeSbTe spread over the surface, because this spreading occurs over the network of hydrocarbons which also develops on the graphene after air exposure.

4. After prolonged (many weeks) exposure to air the GeSbTe NPs develop distinct oxide shells predominantly composed of Ge-oxide, which is expected because Ge has clearly higher affinity for oxygen than Sb or Te and also appears more mobile than Sb.

5. The oxide shell formation is more pronounced for the NPs on the suspended than on the supported graphene and this thus also probably relates to the higher mobility of Ge atoms on suspended graphene than on the supported graphene.

6. Using accelerating voltages as low as 60 and 40 kV still shows indications that the mobility of adatoms on the hydrocarbon contamination is enhanced by the exposure to the electron beam, because at 60 kV significantly more of such atoms are found on the edge of hydrocarbons with the still clean graphene than at 40 kV.

More follow-up work is required to put most of the above observations in a more quantitative perspective, but the present work already demonstrates that even at room temperature...
Figure 5. HAADF (a) and corresponding bright field (b) images of the GST NPs on the supported graphene recorded at an acceleration voltage of 40 kV. EDS elemental mapping of the same area is shown in (c).

Figure 6. Single frame HAADF-STEM images of suspended graphene at 60 kV (a) and 40 kV (b).
interesting atomic scale dynamics occur on various types of graphene surfaces.

4. Conclusions

Phase-change Ge$_2$Sb$_2$Te$_5$ NPs have been deposited on CVD grown graphene support layers transferred on Au Quantifoil. The coverage of NPs on the suspended graphene is about three times higher than that on the supported graphene. We attribute this distinct difference to the variation in surface energy, indicating that suspended graphene can be used to (more effectively) harvest NPs. Our observations of dynamics on the graphene support are strongly influenced by hydrocarbon contamination, which is effectively observed by HAADF-STEM images but not by bright field images. With uniform distributions for the Ge, Sb and Te atoms for the nascent Ge$_2$Sb$_2$Te$_5$ NPs, these particles are sensitive to air exposure, especially Ge atoms which tend to form after prolonged times clear GeO$_2$ shells. The NPs were oxidized more heavily and spread more extensively on the suspended graphene than on supported graphene, probably related to the higher coverage with hydrocarbons on the suspended than on the supported graphene. The high quality atomic structure of graphene has been well-resolved at accelerating voltages as low as 40 kV.

Acknowledgments

We gratefully acknowledge the China Scholarship Council for financial support (of BC). JEOL Ltd, in particular Eiji Okunishi, is gratefully acknowledged for recording the results depicted in figures 3–6 of the main paper and figures S5–S9 of the SI. FEI (Europe B V), in particular Anna Carlsson is gratefully acknowledged for recording the results depicted in figure 2.

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