Chapter 6

Dynamics of GeSbTe nanoparticles on graphene

Abstract

Phase change materials are currently widely used in data storage and are considered as promising candidate for phase change memory. The properties of phase-change nanoparticles have been investigated yet the understanding of their dynamics is lacking. In this chapter we deposited GeSbTe nanoparticles directly on graphene support and studied the landing dynamics of these nanoparticles on graphene. The nanoparticles prefer to land on suspended graphene support three times higher compared to graphene on carbon support. Also the oxidation dynamics of the GeSbTe nanoparticles was investigated. It is found that the Ge atoms migrate to the periphery of the nanoparticles after exposure to air for two weeks.
6.1 Introduction

Phase-change materials (PCMs) have attracted strong interest due to their high potential for applications in optical storage, electrical memory, photonic displays, etc.

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 the pursuing for storage media with stronger performances. One of the most promising paths is the down-scaling of the bit dimensions.

Recently many investigations of three-dimensionally scaled down PCMs (nanoparticles) have been presented, where GeTe and Ge$_2$Sb$_2$Te$_5$ nanoparticles have been successfully grown by chemical synthesis and physical deposition. 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.

Also demonstrated is that the GST NPs, especially the GST NPs prepared with CH$_4$ additional gas during deposition, exhibiting better data retention compared to the thin films and comparable crystallization speed in the switching regime, are a promising candidate for future phase change memory.

Graphene has experienced intense investigations due to its unique mechanical, thermal and electron transport properties. 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. In this device, graphene played a role as a thermal barrier and limited the atomic migration of PCM that also leads to the endurance of the memory. In addition, there are numbers of investigations reporting that placing thin films or nanoparticles on graphene not only influenced the thin films or nanoparticles but also the electronic properties of graphene. Some nanoparticles could form 2D structures and have strong interactions with graphene, which could lead to the 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. Decorating graphene with NPs has applications in many fields, such as catalysis, sensors, supercapacitors, energy storage and the anode of Li ion battery.

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 its applications. Although there have been comprehensive investigations on the metal oxide-graphene nanocomposite, the GST nanoparticles grown by inert gas condensation is “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 chapter we report we deposited GST NPs on graphene and studied the 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 morphology of the NPs.

6.2 Experimental methods

6.2.1 Graphene preparation

Graphene was grown on oxygen rich copper foils by chemical vapour deposition. Briefly, the copper foil (Alfa Aesar, 99.8%, #46365) with a thickness of 25 µm was cleaned by soaking in acetic acid for 8 hours, 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 hours. Thereafter, the copper foil was cooled down to room temperature with all the gases remained.

After a high quality of monolayer graphene was confirmed by Raman measurement with He-Ne laser at 633 nm, graphene was transferred to a quantifoil R2/1 holey carbon (Electron Microscopy Sciences, Q225-AR1) TEM grids for the STEM characterization. Firstly, the TEM grids was placed on top of graphene on copper. Two drops of isopropanol (IPA) were deposited on the sample to enhance the binding between graphene and the carbon membrane of the quantifoil TEM grids after the IPA evaporated. The sample, consequently, had been annealed at 100 °C for 10 minutes to finally strengthen the contact between graphene and the TEM grids before the copper was etched away in (NH₄)₂S₂O₈ 0.1g/ml for 24 hours. The TEM grids covered with graphene were eventually rinsed three times in demi-water to eliminate any remaining trace of the etchant.

6.2.2 GST NPs deposition

The Ge₂Sb₂Te₅ phase-change nanoparticles with excellent size, crystallinity and composition control were grown by inert gas phase condensation based on magnetron sputtering, as described in chapter 2. The main chamber (to collect the NPs) is evacuated to a pressure of 10⁻⁸ mbar. Amorphous GST NPs were directly synthesized by sputtering the GST target (purity of 99.99%), employing a low current (0.15 A) to avoid the formation of crystalline NPs. The Ar gas flow (purity 99.9999%) used for the two types of samples analyzed in the present work is 35 sccm. Medium
amount of CH₄ was used as additional gas to initiate the nucleation process. 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 coverage was altered by changing the time and yield of the deposition process.

6.2.3 Characterization

The morphology of the as-deposited NPs were characterized in JEOL 2010 at 200 kV within 1 hour 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 minutes inside the JEOL 2010. The energy dispersive spectroscopy elemental mapping and high resolution TEM images were performed in JEOL ARM 200F and FEI Themis Z. High acceleration voltage (200 kV) was utilized to record overview bright-field TEM images of the GST NPs, but low acceleration voltages (40 and 60 kV) were used to record HAADF-STEM images when graphene is involved since 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 atom.

6.3 Results and discussion

The quality of the graphene support layer was characterized by selected area electron diffraction (SAED) patterns (with an aperture diameter corresponding to 2.5 μm on the sample surface), as demonstrated in Figure 6.7 of the Appendix. The line profile of the diffractogram in Figure 6.7a indicates that the selected graphene support is a single layer, while the broad halo at 3.3 1/ nm infers the amorphous nature of the as-deposited GeSbTe nanoparticle (NPs). 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 6.7b. 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 shown in Figure 6.1. 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 graphene and carbon/graphene, respectively). Surprisingly the NPs attachment dynamics on the two different supports diverges remarkably, generating distinctly different morphologies of the NPs. As can be observed clearly in Figure 6.1a, the coverage of the NPs on the graphene (left side) is much higher than that on the carbon/graphene area (right side), although the NPs are directly attached to the graphene on both sides. Figure 6.1b-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 graphene support layer area is roughly three times higher than the one on the carbon/graphene support film 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 6.1d, this difference in coverage is consistent for all of these samples with wide coverage range, from about 4 to 48 % on the graphene support layer. Moreover, one can nicely observe in Figure 6.1a that the coverage directly jumps to a high value at the vicinity of the carbon edge instead of a gradual change over some distance.

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 \(^{29}\)), 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 graphene,\(^{30}\) 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 carbon/graphene surface where the surface energy is already lowered by the supported 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 (~2 weeks). The adsorption of hydrocarbon to reduce surface energy of graphite and graphene has been observed by water contact angle measurements.\(^{31, 32}\)

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 where the NPs were directly deposited on is comparable to the carbon/graphene support. 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,\(^{32}\) slightly higher than the value of amorphous carbon films (49.3 mJ/m\(^2\)) utilizing the same approach.\(^{33}\) After adsorption of airborne hydrocarbon contamination after 24 h of air exposure, the surface free energy of graphene
decreased to 37.5 mJ/m². Note that all the experimental data were derived on a Cu/Graphene surface, the surface energy of suspended graphene is lacking due to the huge challenge to measure it.

Figure 6.1 Morphology of Ge₂Sb₂Te₅ nanoparticles on graphene and carbon/graphene support. The NPs at the edge of carbon support film (indicated by the green dash curve) shows an abrupt increase of coverage (a). (b) and (c) display the morphology of GST NPs deposited on the graphene and carbon/graphene support films, respectively. This difference in coverage between suspended graphene and graphene on amorphous carbon is consistent with all the samples produced, as shown in (d).

The above results suggest a promising application of graphene: harvesting nanoparticles. The high surface energy of graphene also makes it possible to align the adsorbates onto it. Engineering
Dynamics of GeSbTe nanoparticles on graphene

...has several emerging applications. Decorating graphene with metal oxide nanoparticles, such as MnO$_2$, CuO$^{35}$ and Fe$_3$O$_4$, 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, this hydrocarbon adsorbates are removable by heating graphene to ~550 °C$^{31}$ 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 Ge$_2$Sb$_2$Te$_5$ (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 6.2, high spatial resolution energy dispersive spectroscopy (EDS) elemental mapping of as-deposited amorphous NPs on graphene has been performed, with the corresponding morphology of the NPs demonstrated by the high angle annular dark field - scanning transmission electron microscopy (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.

Figure 6.2 Energy dispersive spectroscopy (EDS) elemental mapping of amorphous GST NPs on graphene. The NPs were exposed to air for 1 day before performing this measurement.
To investigate the oxidation dynamics of the NPs, we exposed the GST NPs to air for 2 weeks after crystalizing them by annealing in TEM at a temperature of 180 °C for 10 minutes. Figure 6.3 shows the HAADF and bright field images of NPs on graphene support film at different acceleration voltages (40 and 60 kV). Along the line of our previous results, the GST crystals exhibit a combination of rock-salt and trigonal structures, where the lattice parameter of the rock-salt structure is ~1.8 % extended (with d(022)=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. The van der Waals gaps are visible for some of the crystalized 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 (Figure 6.3a and c), while it is obscured in the bright field images (Figure 6.3b and d). Hence cautions have to be taken on 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 nanoparticles (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 that whether the hydrocarbons were 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 then 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 Figure 6.3a and c. Figure 6.3 also demonstrates an acceleration voltage dependent mobility of these atoms. It is evident that more randomly distributed atoms assemble at the boundary of the hydrocarbon and the periphery of the NPs (green arrows in Figure 6.3a 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. The real time video 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.
Figure 6.3 High resolution TEM images of crystallized NPs on graphene support film. (a) and (c) are the high angle angular dark field images recorded using 40 and 60 kV electron beams, respectively, while (c) and (d) are the corresponding bright field images.

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 6.4. 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 6.4. 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 6.8 of the Appendix
depicts more evidently 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.

**Figure 6.4** Energy dispersive spectroscopy (EDS) elemental mapping and the corresponding line profiles of NPs exposed in air for two weeks.

In contrast, the NPs deposited on the carbon/graphene support film show a rather different morphology and oxidation dynamics after crystallization in comparison to the NPs on the graphene support, as elucidated in Figure 6.5. Although hydrocarbon adsorbate can be hardly observed in both HAADF-STEM and bright field images, the adsorption still occurred. Some hydrocarbon contamination is observable in some HAADF-STEM images. There are two possible reasons for the less visible airborne hydrocarbon contamination in this 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 graphene adsorbs more hydrocarbon in comparison to carbon/graphene due to higher surface energy, leading to higher coverage since the NPs can land on the hydrocarbon softly.
Similar to the GST NPs on the graphene support layer, the EDS elemental mapping shows uniform distribution of Ge, Sb and Te atoms with GeO$_x$ 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 graphene, as proved 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 graphene. Because of the similar size of the NPs profiled in Figure 6.4 and 6.5, a possible size effect on the oxidation can be excluded. Another information that can be derived from the line profile 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.

![Figure 6.5](image)

**Figure 6.5** HAADF (a) and bright field (b) images of the GST NPs on the carbon/graphene supporting film at acceleration voltage of 40 kV. EDS elemental mapping of this area is shown in (c), indicating that some limited oxidation occurred of the NPs on the carbon/graphene, but oxidation is definitely not as strong as for NPs on graphene with clearly developed GeO$_x$ shell (cf. Figure 6.4).

Since acceleration voltage above 80 kV can easily induce knock-on defects to graphene,$^{26}$ 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 6.6. The STEM image shows the C-C separation of 1.41 Å, in excellent line with the crystallography structure of graphene (where C-C separation is 1.42 Å).\textsuperscript{38} 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 to 100 kV),\textsuperscript{26} was not observed in this work. No holes could be observed in the HAADF-STEM images, even near the hydrocarbon contamination sites, where the hole nucleates.\textsuperscript{26} The signal-to-noise ratio can be improved by integrating multi frames. Figure 6.9 of the Appendix shows the processed image after 21 frames integration, portraying a sharper contrast.

![Single frame HAADF-STEM images of graphene at 40 and 60 kV.](image)

**Figure 6.6** Single frame HAADF-STEM images of graphene at 40 and 60 kV.

### 6.4 Conclusions

Phase-change Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} nanoparticles have been deposited on CVD grown graphene support layers transferred on Au quantifoil. The coverage of nanoparticles on the suspended graphene is about three times higher than that on the carbon/graphene support. We attributed this distinct difference to the variation in surface energy, indicating that graphene can be used to (more effectively) harvest nanoparticles. Our observations of dynamics on the graphene support is 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\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} nanoparticles, these particles are sensitive to air exposure, especially Ge atoms which tend to form after prolonged times clear GeO\textsubscript{x} shells. The NPs deposited
on graphene were oxidized more heavily than the NPs on carbon/graphene support. High quality atomic structure of graphene has been evidently resolved at accelerating voltages as low as 40 kV.
Appendix

Figure 6.7 Selected area electron diffraction pattern of graphene with (a) and without GST NPs (b). The line profile inserted in (a) indicates that the graphene in this area is single layer. The broad bright halo demonstrates the amorphous nature of the as-deposited GST NPs. The line profile in (b) shows the bilayer graphene.

Figure 6.8 The high angle annular dark field image and energy dispersive spectroscopy elemental mapping of GST NPs on graphene. The NPs were exposed to air for two weeks after crystallization in TEM. Results were obtained with an accelerating voltage of 40 kV.
Figure 6.9 40 kV HAADF-STEM image of graphene, where 21 frames were integrated. Line profiles taken show a C-C separation of 1.41 Å that matches well with the crystallography structure of graphene.
References


