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Research Article

Scalability of Phase Change Materials in Nanostructure Template

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The scalability of In_2Se_3, one of the phase change materials, is investigated. By depositing the material onto a nanopatterned substrate, individual In_2Se_3 nanoclusters are confined in the nanosize pits with well-defined shape and dimension permitting the systematic study of the ultimate scaling limit of its use as a phase change memory element. In_2Se_3 of progressively smaller volume is heated inside a transmission electron microscope operating in diffraction mode. The volume at which the amorphous-crystalline transition can no longer be observed is taken as the ultimate scaling limit, which is approximately $5\,nm^3$ for In_2Se_3. The physics for the existence of scaling limit is discussed. Using phase change memory elements in memory hierarchy is believed to reduce its energy consumption because they consume zero leakage power in memory cells. Therefore, the phase change memory applications are of great importance in terms of energy saving.

1. Introduction

Chalcogenide phase change materials (PCM) are a family of materials with prominent contrast in conductivity between amorphous state (highly resistive) and crystalline state (highly conductive) [1]. When used as nonvolatile memory elements, crystalline-to-amorphous phase transition is conventionally accomplished by Joule heating from an electrical current pulse, during which the material is heated to above melting temperature followed by rapid quenching leaving the material being frozen in the amorphous state. The opposite amorphous-to-crystalline transition is achieved by heating to below melting temperature followed by a gradual lowering of the temperature leading to the formation of crystalline state [2–4]. Using phase change memory elements as nonvolatile memory in memory hierarchy is believed to reduce its energy consumption because they consume zero leakage power in memory cells. This advantage makes phase change memory element a perfect candidate in the memory industry due to its excellent performance in energy consumption. Driven by Moore's law [5], the system functionality increases rapidly in the same size package with decreasing device dimensions. A question crucial to the technology development of phase change random access memories (PcRAM) is the ultimate scaling limit. Despite the fact that the phase transition of some PCM in bulk form is well studied by dedicated groups [3, 6–8] and the fact that ultimate limit of phase change in $Ge_2Sb_2Te_5$ was reported [9], the size effects of In_2Se_3, another important candidate in the PCM family, have not been reported yet. Size effects start to play an important role as PCM devices scale further down to below 10 nm. Under these nanometer scale dimensions—(a) neither the crystallization temperature nor the melting temperature is the same as those of bulk and (b) crystalline state needs to

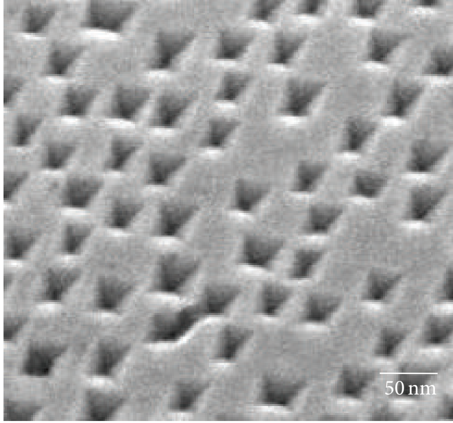

FIGURE 1: 35° tilt SEM image of nanopit substrate after KOH etching.

have long range order—the amorphous and crystalline states may not be thermodynamically distinguishable any more. Therefore, a concern may be raised as to whether PCM has a size limit; that is, the crystalline state becomes unstable when the volume is reduced to a certain value. In this work, the scalability and ultimate size limit of In_2Se_3 are investigated. By depositing In_2Se_3 onto a unique nanopit substrate, size effects of the nano-volume In_2Se_3 confined in individual nanopits can be studied. The underlying physics of the diminishing of crystalline state is discussed.

2. Experiment

The fabrication of nanopit substrate is achieved by anisotropic KOH etching of Si. Figure 1 shows the SEM image of the nanopit substrate. Detailed process flow has been reported previously [10]. The tip of the nanopit is atomically sharp with the radius of curvature being less than 1 nm [11]. Amorphous In_2Se_3 with different nominal thickness is deposited onto the nanopit substrate by sputtering, followed by SiO_2 capping layer to prevent the oxidation of In_2Se_3. Morphologies of the as-deposited films are examined by STEM. In order to determine the ultimate size limit, in situ heating TEM is used to observe the crystallization and melting behaviors of the nano-volume In_2Se_3.

3. Results and Discussions

3.1. Coverage of In_2Se_3 on Nanopit Substrate. Six different thicknesses (2, 3, 5, 8, 23, and 45 nm) of In_2Se_3 were deposited on the nanopitted substrate. STEM studies revealed that two types of morphologies exist depending on the nominal film thickness. In Figure 2(a), bare Si nanopit substrate is shown. The contrast of the bare pit image is mainly from mass-thickness contrast since Si is the only element in the sample [12]. Similarly, the contrast of Figure 2(c), showing the 45 nm nominal film thickness of In_2Se_3 on nanopit substrate, is also contributed from mass-thickness contrast only since In_2Se_3 covers the whole sample surface. The difference between the morphologies of the two images is the size of the open area in the pit region. Smaller opening area for the 45 nm sample results from that the In_2Se_3 fills in the pits, coating the entire substrate uniformly and forming a conformal film. The 23 nm (not shown) sample is also conformably coated as well, with similar morphology as in Figure 2(c). On the other hand, samples of 2, 3, 5, and 8 nm nominal film thickness are distinct from the conformal case. In Figure 2(b), the film coverage of the 2 nm sample is shown (the morphologies of the 3, 5, and 8 nm films are similar and are not shown here). We observed that there is lighter contrast from the pits region compared to the bare pit sample (Figure 2(a)). This indicates that the contrast is not only from mass-thickness contrast, but also from Z (atomic number) contrast. The higher the Z number of the material is, the more electrons get scattered at high angles into the High Angle Annular Dark Field (HAADF) detector [12]. Since In_2Se_3 is heavier than Si, it should give a brighter contrast. In this sample, the pit region is relatively darker compared to the surface, which suggests that In_2Se_3 did not fill up the pits. For films with very thin nominal thickness, due to different interfacial energies between In_2Se_3/Si(100) and In_2Se_3/Si(111), materials deposited into the pits are very likely to be confined in there forming nanoclusters instead of conformal films. A schematic of film coverage on pits is also shown in Figure 2.

3.2. Phase Transition. The initial phase of the as-deposited In_2Se_3 is amorphous; thus, the diffraction pattern of the sample is a combination of halo amorphous rings from In_2Se_3 and diffraction spots from the Si substrate. Phase transition temperature is determined by the observation of single crystalline diffraction spots or polycrystalline diffraction rings appearing from crystalline In_2Se_3 as the sample is in situ heated. The sample temperature is first heated to around 90°C, stabilized, and then annealed for 3 minutes. If no phase transition is observed in the time period, the sample temperature is then increased in 10°C increments. The process was repeated until phase transition is observed. Figure 3 shows the crystallization temperatures (T_x) of the samples with different nominal film thickness. An increase in crystallization temperature is observed as the nominal film thickness decreases. Such crystallization behavior is also observed from the thin films $Ge_2Sb_2Te_5$, GeSb, and Sb_2Te reported in another group's work [13]. For the sample with nominal thickness of 2 nm which translates to a volume of 5.3 nm^3, no crystallization was observed. Therefore, 5.3 nm^3 is believed to be the scaling limit of In_2Se_3. We speculate that the underlying physics of the scaling limit phenomenon is as follows. Thermodynamically, the driving force for crystallization is the reduction of the Gibbs free energy; that is, the amorphous phase is of higher energy which is at metastable state compared to the crystalline phase. However, for crystalline state In_2Se_3, the surface atoms are disordered or have higher energy than in the bulk due to the dangling bonds they have. This energy increase will be negligible for a bulk material with large volume. But with reducing volume or increasing surface to volume ratio, the higher energy of the surface atoms will become dominant in the total energy of the system. That means when the volume decreases to a certain value, which is the scaling limit, the disorderliness or the free energy of crystalline state is comparable to that of the amorphous state;

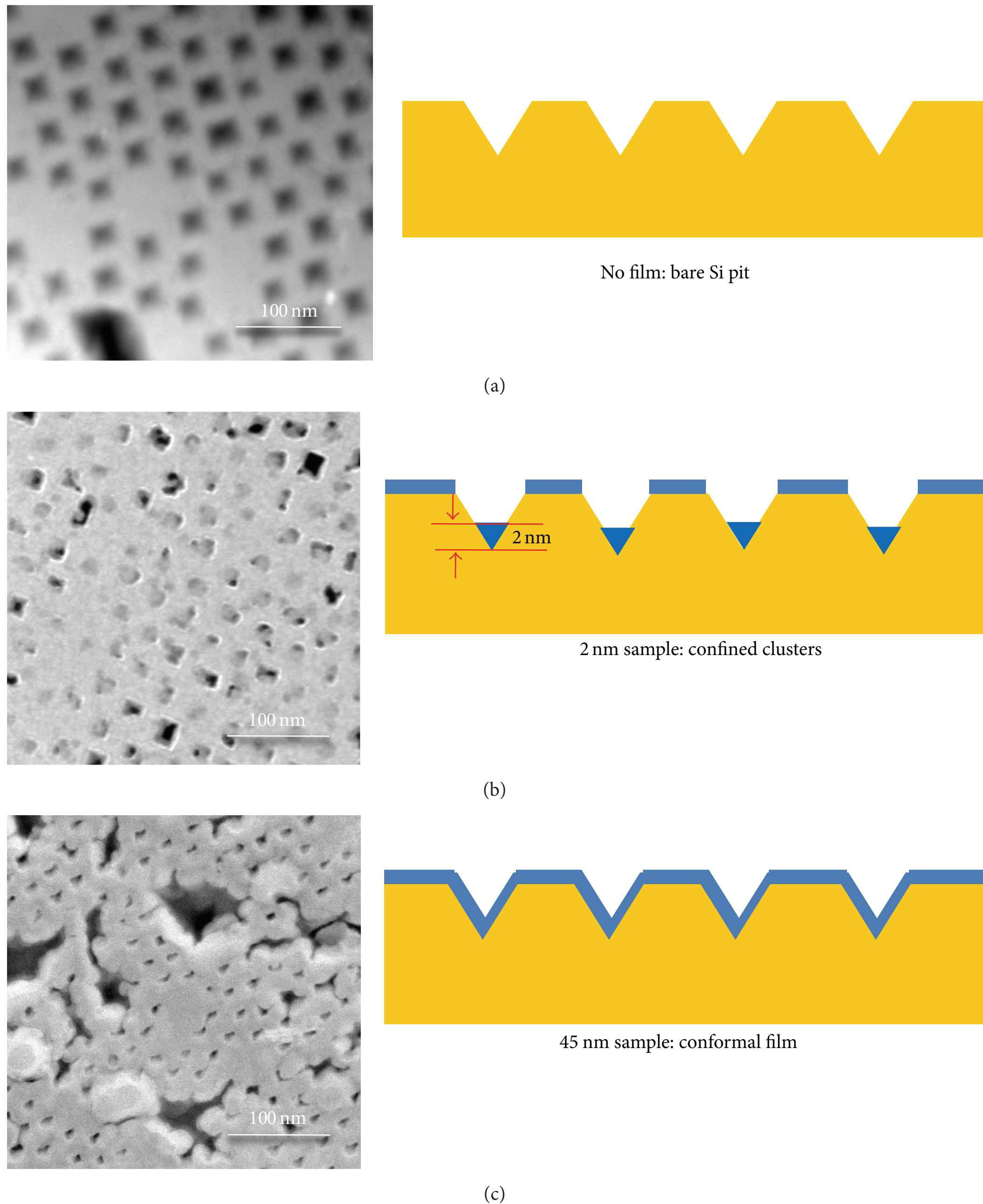

Figure 2: STEM images of (a) bare nanopit Si substrate and (b) 2 nm and (c) 45 nm In_2Se_3 deposited on Si nanopit substrate with cross section schematic of film coverage.

thus, the crystalline state diminishes. On the other hand, as we have already known from the working mechanism of In_2Se_3 phase transition, the crystallization temperature should be lower than the melting temperature. Therefore, the melting behavior of In_2Se_3 is also of interest as the crystallization temperature goes up with decreasing volume. The procedure for melting temperature measurement is similar to crystallization. The melting temperature is determined by the disappearance of polycrystalline diffraction rings. The sample is first heated to 280°C and then annealed for 3 minutes at the stabilized temperature. If no melting occurred, the sample temperature is increased by 10°C. This process is repeated until melting is observed. As seen from Figure 4, the melting temperature (T_m) decreases as the nominal film thickness decreases. As the volume of In_2Se_3 scales down, the melting temperature drops while the crystallization temperature rises. The T_m/T_x ratio has dropped from 2.8 in bulk to 1.7 at 5 nm size. The melting temperature of the 2 nm nominal thickness sample cannot be measured because there were no polycrystalline diffraction rings observed throughout the entire heating process. This indicates that the decrease of melting temperature is also a potential cause for the scaling limit of In_2Se_3.

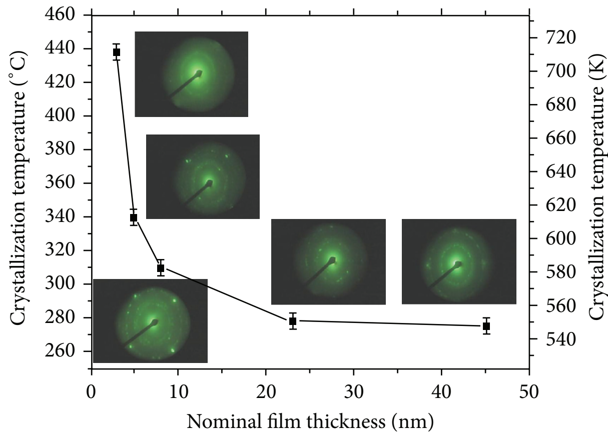

Figure 3: Crystallization temperature versus nominal film thickness of In_2Se_3 in nanopit substrate. Insets are diffraction pattern of the polycrystalline diffraction rings for each crystallization temperature.

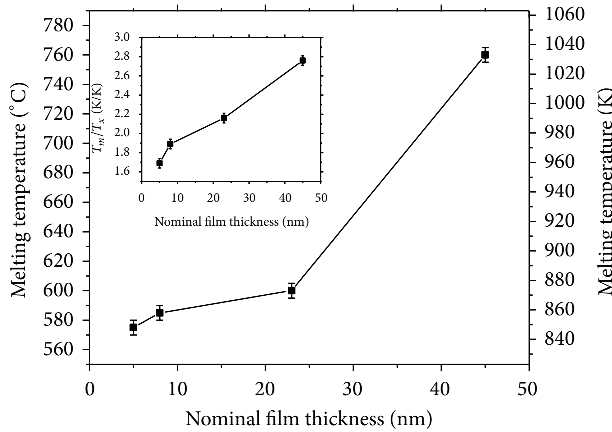

Figure 4: Melting temperature versus nominal film thickness of In_2Se_3 in nanopit substrate. Inset shows the ratio of T_m/T_x.

4. Conclusion

This study has shown that nanopit substrate is a unique pattern for nanosize PCM study. Film coverage on the nanopit substrate is not conformal when nominal film thickness of In_2Se_3 becomes very thin. 39% reduction of the ratio of T_m/T_x is measured with reducing volume of In_2Se_3, and it is a possible cause for the elimination of phase transition. At 2 nm nominal film thickness, no crystallization is observed, which suggests that the corresponding volume of $5.3\,\text{nm}^3$ is the scaling limit of In_2Se_3 concluded from this study. The diminishing of the crystalline state is believed to be due to the fact that the surface disorderliness dominates for small volume materials.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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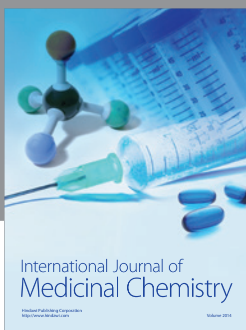
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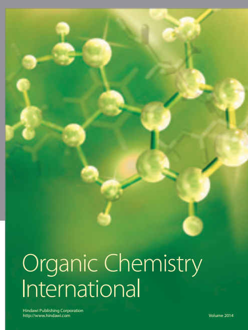
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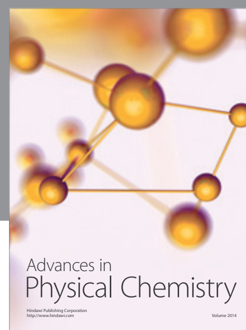
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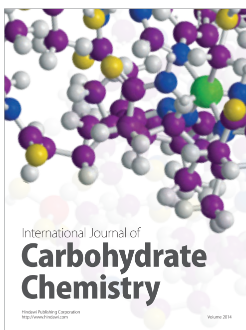
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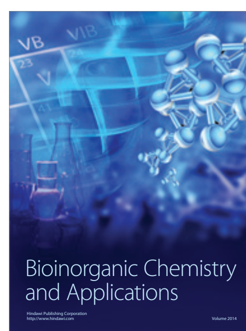
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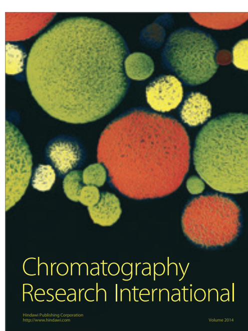
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