Phase change materials, a model system to study nucleation processes

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ABSTRACT

Phase change materials form the basis of a new class of non-volatile memories that are poised to provide significant improvements over today’s devices. We show that phase change materials can also serve as model systems to investigate the fundamental science of solid phase nucleation. Nucleation theory is well established, but it is difficult to probe many of the predicted phenomena – in particular, the development of subcritical nuclei – on the nanometer scale. Our recent work (Lee et al., Science 326, 980 (2009)) combines a pump-probe laser technique, atomic force microscopy (AFM), and fluctuation transmission electron microscopy (FTEM) to test multiple predictions of nucleation theory. We observe (i) the stochastic nature of nucleation, (ii) the existence of an optimal temperature for nucleation, (iii) the temperature dependence of the size distribution of subcritical nuclei, and (iv) the effect of pre-existing subcritical nuclei on the nucleation rate. Different device designs and processing conditions result in different size distributions of nanoscale nuclei, which in turn affect the crystallization of phase change materials.

Key words: nuclei, nucleation, amorphous materials, fluctuation transmission electron microscopy

1. INTRODUCTION

Phase change materials form the basis of a new class of non-volatile memories that are poised to provide significant improvements over today’s devices. We show that phase change materials can also serve as model systems to investigate the fundamental science of solid phase nucleation. Nucleation theory is well established, but it is difficult to probe many of the predicted phenomena – in particular, the development of subcritical nuclei – on the nanometer scale. Our recent work (Lee et al., Science 326, 980 (2009)) combines a pump-probe laser technique, atomic force microscopy (AFM), and fluctuation transmission electron microscopy (FTEM) to test multiple predictions of nucleation theory. We observe (i) the stochastic nature of nucleation, (ii) the existence of an optimal temperature for nucleation, (iii) the temperature dependence of the size distribution of subcritical nuclei, and (iv) the effect of pre-existing subcritical nuclei on the nucleation rate. Different device designs and processing conditions result in different size distributions of nanoscale nuclei, which in turn affect the crystallization of phase change materials.

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directly sensitive to the different amount and size of nuclei [9]. This study also provides experimental illustrations for several important predictions of nucleation theory. In this article, we explain these theoretical predictions and show how they can be experimentally tested by the study of phase change materials.

Fig. 1 (a) Free energy change associated with the formation of a nucleus. Note that the total change of free energy reaches a maximum at a critical size; a nucleus becomes stable (e.g., it is more likely to grow than to shrink) after exceeding this critical size. (b) Schematic diagram showing the evolution of a nucleus. A subcritical nucleus generally tends to decay in size but there is a probability for it to grow by thermal fluctuation. (Also see Section 5 – it is generally easier to make a critical nucleus in a sample with pre-existing subcritical nuclei, than in a sample free of subcritical nuclei. In other words, the starting point is different.)

2. STOCHASTIC NATURE OF NUCLEATION

Nucleation is stochastic in nature, i.e., it is an event governed by probability. Each subcritical nucleus may decay or grow (Fig. 1b) with certain probabilities, therefore the time to make one supercritical nucleus is not always the same. This stochastic nature of nucleation is illustrated by our laser crystallization experiment [9]. In the experimental setup (Fig. 2a), a Gaussian pump laser induces a temperature field in a sample, which may crystallize or melt the irradiated area depending on the laser power. The crystallized part has a higher density, hence smaller thickness, which can be probed by atomic force microscopy (AFM). A special feature of the laser-crystallization of AIST is that crystallization starts almost always from a single spot: only one supercritical nucleus forms and grows until the entire irradiated area becomes crystalline, before any more supercritical nuclei appear and grow macroscopically (Fig. 2b). If the reflectivity is measured in-situ using a probe laser (Fig. 2c), it stays almost constant until a single supercritical nucleus appears, then rapidly increases (within ~ 1 µsec) as the nucleus grows in size. Here, note that this nucleation time, measured as the time between the onset of the pulse and the sharp increase in reflectivity, is indeed decided by chance (stochastic). The system “tries and tries” to make one supercritical nucleus, and it may succeed over a variable delay of tens of µsec (Fig. 2c). By repeating this process on different areas of one sample, we obtain the statistics of nucleation time (Fig. 2d). In this specific case, about 50% of nucleation occurs within 30 microseconds, so the average nucleation rate is about one per 30 microseconds. From a sample prepared in a different condition, the statistics of nucleation time can be very different (see Section 5). Note that, in most cases including another important phase change material Ge_{2}Sb_{2}Te_{5}, many supercritical nuclei appear and grow individually – it is difficult to clearly distinguish the nucleation time and growth time. Laser crystallization of AIST shown here is a rare case where we can separately measure the nucleation rate (one per tens of µsec) and growth rate (~ 2 m/sec) by monitoring individual nucleation events.
3. EXISTENCE OF OPTIMAL NUCLEATION TEMPERATURE

Nucleation theory predicts that nucleation rate becomes a maximum at a certain optimal temperature $T_0$. At low temperature, i.e., with large undercooling, the thermodynamic driving force for crystallization is large but the kinetic motion of atoms is slow. At high temperature, atomic motion is fast, but the driving force of crystallization is low; at the melting point, there is no driving force to crystallize. Therefore, the highest nucleation rate is achieved at an intermediate temperature $T_0$ where these two effects make a balance [2-4]. Our simulation suggests that the nucleation rate of AIST makes a maximum at ~ 260 °C [9] (Fig. 3). Note that Fig. 3 is drawn on a logarithmic scale; it shows a very sharp maximum on a linear scale. (Similar simulation was performed for GST, which also showed a sharp maximum [10].) The AFM experiment shown in Fig. 1b provides a demonstration of this optimal nucleation temperature $T_0$. It is clear that nucleation occurs not at the center, where the temperature is highest, but at an intermediate radius where the temperature is ~ 260 °C. If the pump laser is more intense, $T_0$ ~ 260 °C occurs at a larger radius from the center, so nucleation mostly occurs near this radius. Ref. [9] presents more examples taken at different values of laser power.

![Fig. 3 Simulated nucleation rate of AIST. Note that the nucleation rate maximizes at ~ 260 °C, where the thermodynamic driving force and kinetic rate make a balance.](image-url)
4. EVOLUTION OF THE SIZE DISTRIBUTION OF SUBCRITICAL NUCLEI

By continuous formation and decay of many subcritical nuclei, a size distribution of nuclei is achieved in the parent phase (amorphous phase in this case). This size distribution depends on temperature and time. For example, if 125 °C is given to a room-temperature sample for some time (similar to our “pre-annealing” conditions in a furnace), the initial distribution evolves to have more and larger subcritical nuclei [9]. How about melt-quenching? Essentially all nuclei are removed by melting; then, during the cooling time, new nuclei develop in the disordered matrix. If the cooling time is very long, it may crystallize. If this cooling time were zero, there would be no nuclei. In reality, melt-quenching of phase change materials involves a very short but finite cooling time. Therefore, it is expected that a melt-quenched amorphous state contains a size distribution of nuclei, which depends on the cooling time and the material properties.

Experimental demonstration of the predicted evolution of nanoscale nuclei was formidable before the use of fluctuation transmission electron microscopy (FTEM) [9]. Although sub-nanometer resolution can be given by high-resolution TEM (HRTEM), detecting nanoscale nuclei (smaller than ~ 3 nm) embedded in an amorphous background is not reliable because of statistical noise issues. It has been proved by theoretical simulation [11] that even completely random noise might generate some obviously ordered regions in an HRTEM image. This is a fundamental problem of TEM, which is projection of a 3-D object to a plane, regardless of resolution [12,13]. Since it is not reliable to detect individual nuclei, we employed FTEM which is a statistical technique. For FTEM, we take hundreds of nanodiffraction patterns, collect the intensities, and obtain the statistical variance (Fig. 4). It has been shown that the obtained variance arises from the existence of 3- and 4-body correlation functions, which makes FTEM sensitive to the nanoscale structural order above ~ 1 nm in an amorphous structure [14,15]. Conventional diffraction data are based on the 2-body correlation function, which is only sensitive to a structural order of ~ 1 nm or less (short-range order). More details of the theory and practice of FTEM are provided, for example, in Ref. [16].

Fig. 4 Procedure of FTEM in the nanodiffraction mode. $k$ is the magnitude of the scattering vector, which corresponds to the inverse of the interplanar spacing in a crystal. (Reproduced from the supplementary online material for Ref. [9] by permission of AAAS.)
As theoretically expected, our FTEM result indicates that there are more/larger nuclei in the apparently amorphous AIST samples that were either annealed in a furnace ("pre-annealed") or laser-irradiated ("primed") for a short time [9]. The same trend had been observed from pre-annealed amorphous GST [17,18]. In the case of melt-quenched AIST, FTEM indicated slightly less/smaller nuclei than in the as-deposited state [9]. It shows that the evolution of nuclei was not very significant during the cooling time from melt. On the other hand, researchers have expected that melt-quenched GST has more and larger nuclei [19,20] than as-deposited GST; this also agrees with our FTEM results to be published [21]. While generating supercritical nuclei in as-deposited AIST takes tens of microseconds, it takes only ~ 100 nsec in as-deposited GST. It suggests that the evolution of subcritical nuclei is much faster in GST. More and larger nuclei will develop in GST than in AIST during a cooling time, so the melt-quenched state GST will have a significant amount of quenched-in nuclei. In a data storage device, the cooling time depends on the specific device design. Therefore, different device designs result in different size distributions of nanoscale nuclei, which may affect the crystallization speed.

At present, FTEM does not give the exact concentration of nuclei or their size; further theoretical progress is needed to fully quantify the data. However, conventional techniques could not reliably distinguish the amorphous states from different thermal histories. FTEM clearly proves the structural difference in those amorphous states and provides experimental evidences of the predicted behaviors of subcritical nuclei embedded in an amorphous matrix.

5. EFFECT OF SUBCRITICAL NUCLEI ON NUCLEATION TIME

Nucleation time, hence crystallization time, can be significantly affected by pre-existing subcritical nuclei. As shown from the previous section, an amorphous sample may contain many subcritical nuclei that are effectively frozen at room temperature. When high temperature is induced by a laser or electric current pulse, many of the pre-existing nuclei will decay in size, but some of them may grow by thermal fluctuation (Fig. 1b). On the other hand, if a sample has no pre-existing nuclei, as assumed in most simulation studies, a critical nucleus should be constructed from a zero size (individual atoms or molecules). Therefore, in a sample with more and larger pre-existing subcritical nuclei, it will be statistically easier to generate a supercritical nucleus than in a nuclei-free sample. Our laser-crystallization experiment [9] demonstrates that the average nucleation time is indeed shorter for pre-annealed or laser-primed AIST samples, which have more/larger pre-existing nuclei as indicated by FTEM. Average nucleation time was slightly longer in the melt-quenched state of AIST than in the as-deposited state, also agreeing with the FTEM data. (We produced a melt-quenched spot by irradiating a very short laser pulse (80 nsec) on an as-deposited AIST sample, then used a low-power laser to induce nucleation within this melt-quenched spot, not from the outside area.)

6. CONCLUSION

Phase change materials serve as good models to explore nucleation theory, in addition to serving as the basis of data storage devices. We observe (i) the stochastic nature of nucleation, (ii) the existence of an optimal temperature for nucleation, (iii) the temperature dependence of the size distribution of subcritical nuclei, and (iv) the effect of pre-existing subcritical nuclei on the nucleation rate. In addition, by comparing FTEM data and laser crystallization data obtained from phase change materials, we show that FTEM is a valuable tool to detect nanoscale nuclei in amorphous solids. In a practical sense, the result suggests that different device designs and processing conditions result in different size distributions of nanoscale nuclei, which in turn affect the crystallization of phase change materials.

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Bong-Sub Lee received his Ph.D. in Materials Science and Engineering at the University of Illinois at Urbana-Champaign (UIUC), USA, and his M.S. and B.S. at Seoul National University, Korea. After his postdoctoral study at UIUC, he is currently working as a senior materials analysis engineer at Tessera Inc. located in San Jose, California, USA. He conducted visiting studies at IBM Almaden Research Center and continued close collaboration with IBM. He won the Presentation Award at European Phase Change and Ovonics Symposium (E*PCOS) in 2007, first-authored a research paper published in Science in 2009, and is serving on the organizing committee for the phase change materials symposium at 2011 Materials Research Society (MRS) Spring Meeting.