

A high throughput methodology for measuring crystallisation activation energies of composition spread thin films

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Abstract—High-throughput parallel experimentation methods offer many advantages in the field of material science research compared to traditional methods of serial synthesis and experimentation. Such methods greatly reduce the time and costs for characterizing new substances, as well as improving the sampling density for investigating novel alloy compositions in an automated manner. We apply these experimental methods to characterize the technologically important crystallization temperature and optical modulation in phase change data storage materials, namely $\text{Ge}_2\text{Sb}_2\text{Te}_5$, with varying amounts of dopants.

This paper outlines an instrumentation design for measuring the reflectance change over temperature of composition spread materials. The experimental setup and procedures for analyzing the data are also discussed. Finally we show the preliminary results obtained from our prototype system as a proof-of-concept, and compare it to traditional serial measurement methods.

Keywords- high throughput; chalcogenides; phase change materials; composition spread, parallel experimentation

I. INTRODUCTION

A. Serial and Parallel Experimentation

The process of investigation and discovery of new substances or materials in research generally involves the experimental characterization of varying samples with the aim of establishing trends or optimizing for certain constraints. Many experimental procedures in these fields necessitates the repetitive measurements of discrete composition in the combinatorial space of parameters, such as the ratio of alloying elements in a material, or the properties of the medium in which a reaction occurs.

Traditional methods of obtaining such results involve the serial preparation and measurements of many different samples, one at a time, until a sufficient amount of data is collected. These methods are often time-consuming and require expensive resources to produce the samples.

Where feasible, more advanced methods employing parallel measurements can vastly improve the efficiency of these repeated experiments, as well as allowing for increased sampling density and thereby resolution of the data obtained. By preparing a single sample that exhibits a spread along a range of conditions, one can then perform the experiment and acquire results in a parallel fashion, effectively increasing the efficiency of materials characterization by orders of magnitude when compared to serial methods.

Indeed, in areas of chemistry and drug discovery where the underlying principles may not be fully understood, the process of combinatorial synthesis is well established, where a brute-force approach is taken towards creating as many molecules as possible with varying differences in makeup. These samples are then evaluated all together in the hope of finding trends that identify a suitable combination inputs.

B. Phase Change Materials

Here we shall focus on the field of material science research, in particular that of chalcogenide amorphous films that exhibit a variety of interesting properties related to changes in its structural state. The phase change is brought about by heating the material above its characteristic crystallization temperature, which causes the material to shift from the amorphous to the crystalline state, or by bringing the material briefly above its melting point and rapidly quenching it, which leads the atoms into a disordered amorphous state.

Chalcogenides can exhibit large differences between the optical and electrical properties of the two phases, and are capable of extremely fast transition between phases. This makes them of significant interest in many areas of technology, including optical storage devices, computer memory, artificial neural networks, or tuneable meta-materials, which allow the modulation of a material's properties. The ternary space comprising of the elements germanium, antimony and telluride (Ge-Sb-Te), possesses properties that make such alloys suitable for use in phase-change memory devices. In particular, much attention has been devoted to alloys that lie on the pseudo-binary line between GeTe and Sb_2Te_3 , which tend to be fast

switching, exhibit large optical and electrical contrast between phases, and are stable at room temperature.

However, advances need to be made for current phase-change materials to overcome the legacy of preexisting memory technologies such as FLASH. The materials should be further developed to withstand elevated operating temperatures without undesired switching or degradation over time, and the issue of resistance drift in the amorphous phase, which complicates the development of multi-bit storage cells needs be addressed. To address these limitations, research is being conducted on various dopants and compounds outside of the standard alloys, further expanding the possible compositional space available to study.

By developing the instrumentation and using parallel measurement methodologies as described above, we hope to greatly accelerate and facilitate research into the characterization of these new materials, and gain further insight into their properties.

Using a sputtering system, it is possible to deposit smooth compositional spreads of various source materials on a substrate. With the methodology discussed herein, these composition spread films can be analyzed as the sample is heated. Through automatic processing one can then obtain thousands of measurements of different compositions during heating. This is achieved by measuring the property as a function of position and temperature. This property map can then be correlated to the composition of the material.

In addition, this method lends itself well to the characterization of a material's crystallization activation energy; the energy barrier between its amorphous state and thermodynamically more stable crystalline phase. This property is especially important to determine the stability of the phase change memory in the RESET state (amorphous). By producing multiple samples with identical compositional spreads and heating them at different rates, we can derive the heating rate dependent peak crystallization temperature through Kissinger Analysis (see II.B for details), and obtain a correlation of a sample's activation energy with its composition.

II. METHODS

A. Data Collection

Our method, outlined here, utilizes the optical property of reflectance modulation in phase-change materials, which generally shows an increase when transitioning from the amorphous to the crystalline phase. Fig. 1 illustrates the components of our experimental setup, comprising of a stable light source, a camera, and a hotplate that is controlled centrally by a computer.

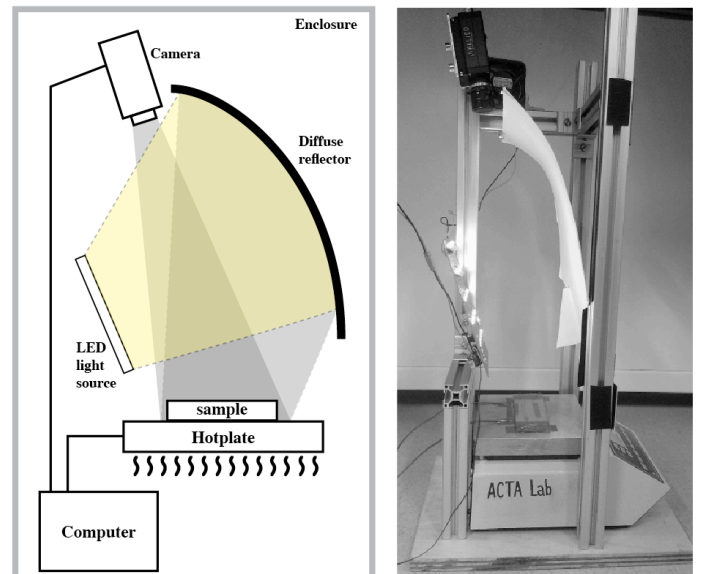


Figure 1. Diagram and photo of the instrument

The camera is mounted at a slight angle vertically above the imaging area, at a suitable focal distance (~ 400 mm) to minimize distortion and maintain a safe operating temperature. The sample reflects a uniformly lit image of the diffuse reflector into the camera, which records ~ 100 mm field of view and is sufficient to monitor a 100 mm silicon wafer. The LED light source is run in constant current mode to minimize intensity fluctuations during the course of the measurement. To further minimize disturbances in light intensity from the environment, the entire setup is enclosed in a black canvas material.

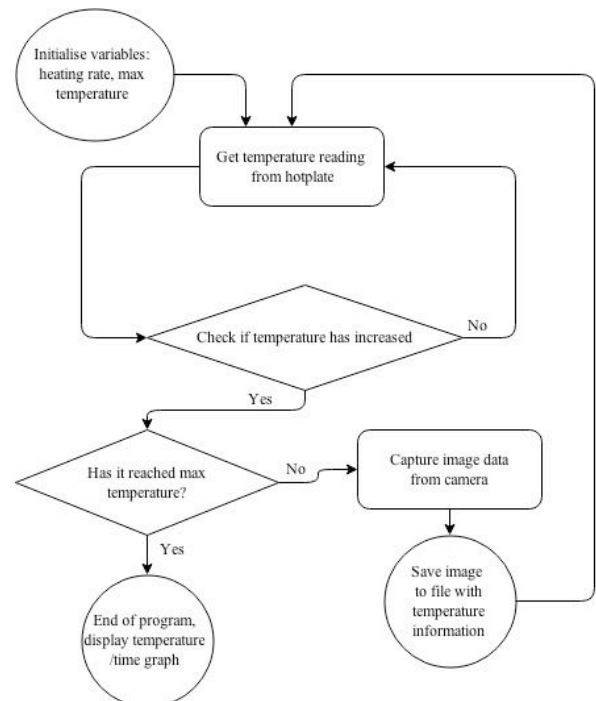


Figure 2. Flowchart of instrumentation control system

An automated system for data capture was developed using LabVIEW, allowing it to interface with the hotplate to record the temperature, and save images from the camera at each temperature increment. After initializing the heating rate and maximum temperature at the start of the experiment, the system will proceed automatically, and output a series of image files in a given directory, with the corresponding temperature reading of each image recorded in its file name. Fig. 2 depicts a graphical overview of this system.

At this point one can easily view the sequence of images in the format of an animation, which allows rough identification of the temperature and compositional ranges over which the phase transitions occur.

B. Data Processing

To analyze the experimental data, we implemented a batch image processing routine in Python, with the use of SciPy (PyLab) and PIL libraries, among others. The 12-bit grayscale images obtained from the camera are first converted into 2-dimensional arrays representing the pixel brightness value at each location. With successive arrays stacked in progression to form a 3D dataset, a cross section can be taken along the 'z-axis' of any given pixel location to obtain a plot of the reflectivity change over temperature at that point.

Due to the nature of phase-change materials, the resulting plots generally exhibit a sharp increase in pixel intensity (which correlates with reflectivity) within a narrow range of temperatures, and stays relatively constant elsewhere. We model this with a logistic function (1), which closely conforms to the data. Fig. 3 shows a typical plot of reflectivity vs. temperature obtained for a single pixel, with a best-fit logistic curve.

$$f(T) = \frac{a}{1 + e^{-k(T-T_0)}} + c \quad (1)$$

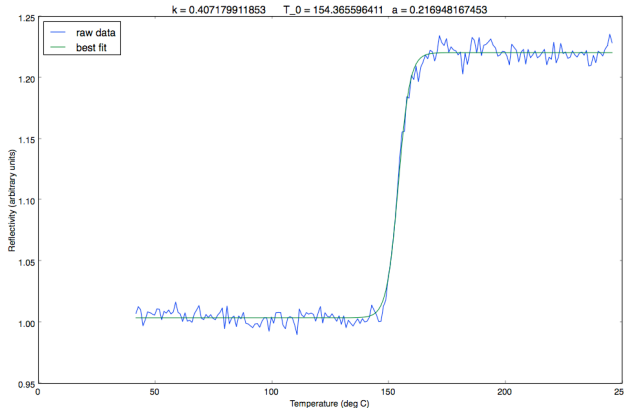


Figure 3. Reflectivity vs. temperature plot with logistic curve fitting

The coefficient T_0 obtained from the fitted function corresponds to the inflection point of the logistic curve, where its derivative is maximized. We then define the crystallization temperature for that particular pixel location as this temperature T_0 where maximum change in reflectivity occurs. Additionally, the processing routine normalizes each pixel intensity value to its relative ratio with respect to their initial value at the start of the experiment. The magnitude of change in reflectivity at each point can then be characterized by the coefficient a of the logistic function.

This analysis is then iterated over every pixel within the region of interest, returning a null value for areas where the function could not be fitted. The program can thus map out the crystallization temperature and reflectance shift magnitude of the sample as functions of position, which can be represented in the form of color maps or contour lines.

Several other processing steps were also taken to improve the quality of the analysis – firstly a certain amount of noise was observed in the images at the typical exposures of our experiments. This was modeled with a Gaussian white noise distribution, which can be largely removed by blurring areas of interest with weighted averages of neighboring pixels. To avoid undesirable softening of the edges between sample and the background surface, a median-weighted smoothing algorithm was used, which preserves edges while reducing the random variation of individual pixels. The smoothing radius can be optimized for each set of images depending on the noise present and desired resolution. In cases where the sample composition only varies along one direction, the extent of smoothing can also be set independently along each axis.

Additionally, the LED light source in our setup exhibited a significant decrease in its output brightness over the course of each experiment. We corrected for this effect by including a control sample in the image, such as a piece of silicon wafer, which remains at constant reflectivity throughout the range of temperatures. By analyzing the drift in brightness of this control region at different temperatures, the program adjusts the brightness of the entire image relative to initial conditions. This improves the accuracy of the subsequent characterization steps and reduces omission rates during curve fitting.

In order to measure the activation energy of a material's phase transition, we then repeat the entire process several times at different heating rates, with identical samples. This allows us to apply Kissinger analysis to the data, based on the Arrhenius equation, which describes the relation between the rate constant, k and activation energy, E_a . The phase transition is modeled with a first order reaction

$$\frac{d\alpha}{dt} = Ae^{-E_a/RT} \alpha \quad (2)$$

At the crystallization temperature of the material, the reaction rate is maximized, such that the derivative of $d\alpha/dt = 0$. Assuming a constant heating rate $\beta = dT/dt$, we obtain (3)

$$\frac{d^2\alpha}{dt^2} = \frac{\beta E_a}{RT_c^2} + Ae^{-E_a/RT} = 0 \quad (3)$$

The following relation (4) can then be derived:

$$\ln\left(\frac{\beta}{T_c^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_c} \quad (4)$$

Plotting the graph of $\ln(\beta/T_c)$ against $1/RT_c$ at different heating rates produces a linear relationship, where the activation energy, E_a , can be obtained from the gradient of the line.

The samples are tested and analyzed separately using Energy-dispersive X-ray Spectroscopy (EDX) to identify their atomic composition. In the case of composition-spread samples, we can interpolate between measurements taken at intervals throughout the sample. This allows us to correlate the maps of crystallization temperature, optical switching contrast and activation energy with the sample's atomic makeup and structure.

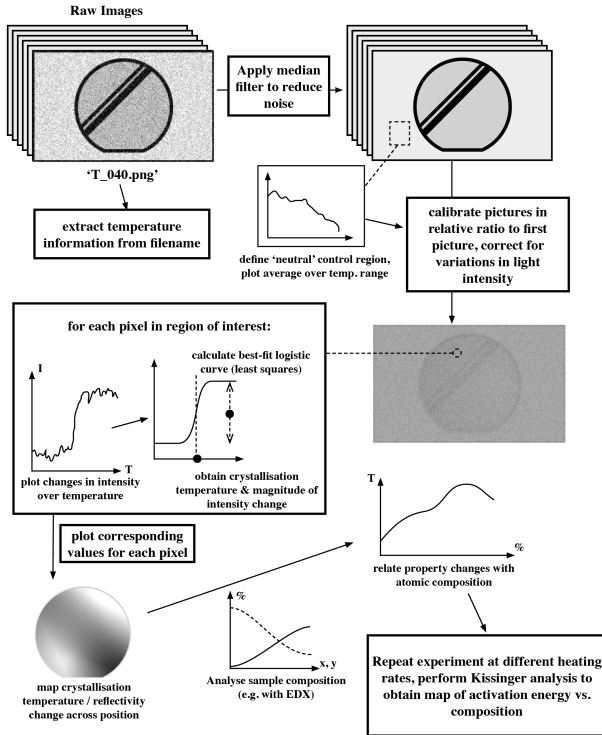


Figure 4. Analysis of data

C. Future improvements

To minimize the effect of temperature on the LED brightness, we can modify the setup to thermally insulate or actively cool the LED panel. In the data analysis stage, we made the assumption that the pixels' grayscale values are directly proportional to intensity of reflected light, without accounting for the nonlinear gamma curve of the camera. Although this is a second-order effect, further processing steps can be added to correct for this, allowing us to obtain more accurate values for the magnitude of optical reflectivity contrast between phases.

PRELIMINARY RESULTS

As a proof of concept, our setup was used to perform an experiment on a composition-spread sample of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ doped with varying amounts of silicon, produced by sputtering on aluminium foil substrate. A strip of the foil was cut along the sputtering axis and positioned such that the proportion of silicon would vary horizontally along the image. The strip was cut into halves and placed near the center of the hotplate to minimize effects due to temperature inconsistencies. Fig. 4 shows the image obtained by the camera at the beginning of the experiment.

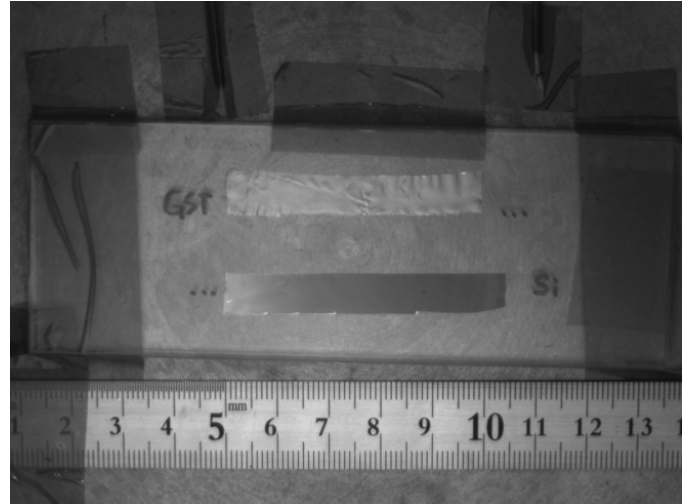


Figure 5. Image from camera at start of experiment

The experiment was run at a heating rate of 1°C per minute from 42°C to 246°C . The results were analyzed using the methods detailed above, with an applied median filter 5 pixels in the horizontal axis and 20 pixels in the vertical. This produced the following colour maps of crystallization temperature and optical contrast. (Fig. 6)

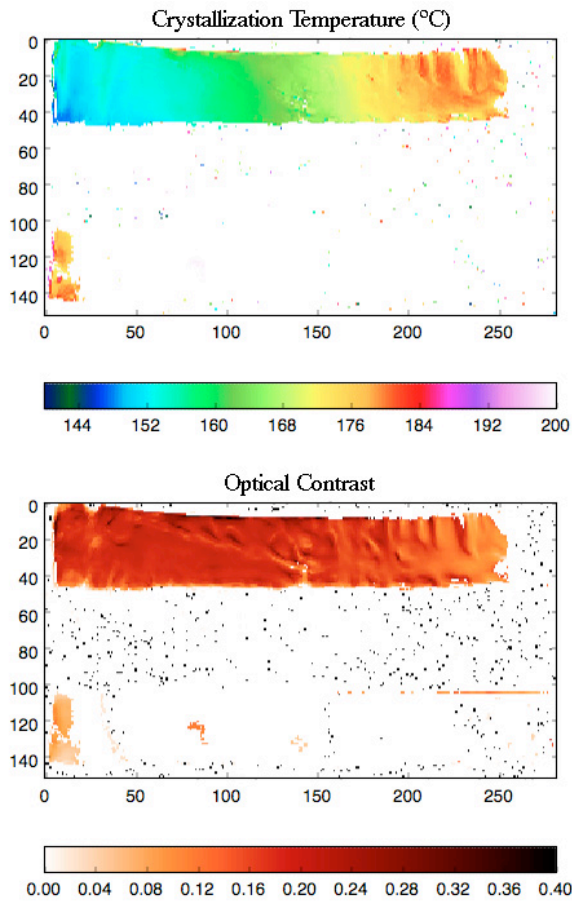


Figure 6. Colour maps

From these maps we can observe qualitatively that the crystallization temperature of silicon doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ increases with the atomic percentage of silicon, in the range of 145 to 190 °C, up till a certain point, after which it no longer exhibits phase change behavior. The optical switching contrast can also be observed to fade off towards this point. Fig. 7 shows the two halves of the sample overlaid over the original image and stitched together.

Several measurements with EDX were made at points along the main axis of the sample and interpolated to obtain the atomic composition as a function of location. This could then be plotted against other variables. Fig. 9 shows the plot of crystallization temperature against atomic percentage of Si.

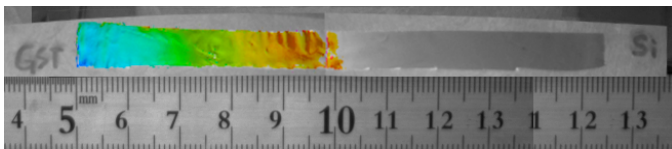


Figure 7. Stitched and overlaid map of crystallization temperature

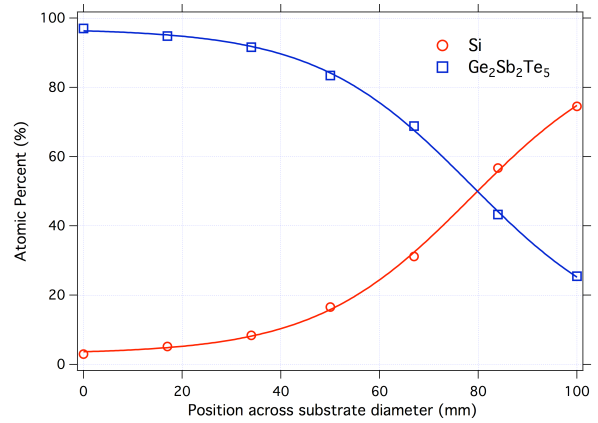


Figure 8. Atomic composition of sample, obtained from EDX

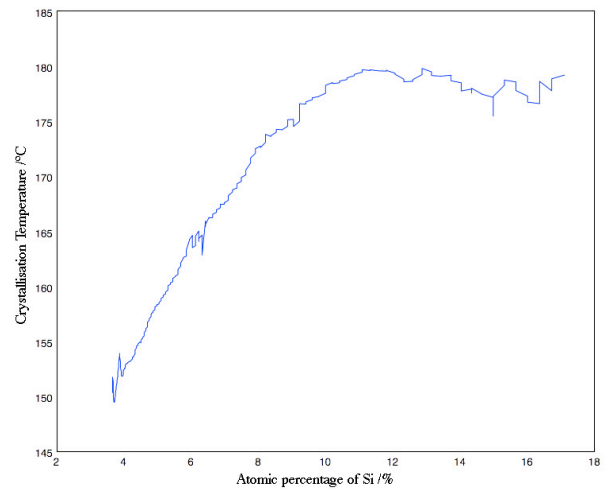


Figure 9.

This affords a broad overview of the behavior of the material, allowing us to identify the exact range (>17% Si) where the material exhibits phase change behavior without conducting multiple trials. Considering each pixel as an independent data point, altogether some 11,000 parallel measurements were made on this sample with a single run. Theoretically, this represents 4 orders of magnitude of increase in efficiency as well as cost savings compared to traditional serial methods of experimentation for similar amounts of data obtained.

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