

A high temperature orientated phase change material

Oxygen doped GeTe and its properties study

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Abstract—This paper discusses the amorphous-crystalline transition in oxygen doped GeTe, GeTeO, and analyses the data from the experiments. GeTeO is found to exhibit a relatively high crystallization temperature and high activation energy when compared with the well-studied Ge₂Sb₂Te₅ composition.

Phase change material; nanoelectronic; material science; Information Technology; semiconductor

I. INTRODUCTION

Phase change memory is one of the most promising technologies to enable the next generation of data storage. A good phase change material (PCM) is able to switch between crystalline and amorphous states quickly; typically the phase transition time is counted in nanoseconds. Furthermore, a good PCM must be thermodynamically stable at normal operating temperatures to prevent data loss [1].

A typical phase change memory cell structure is shown in Fig. 1, where SiO₂ acts as electrical and thermal insulating layer. The metal on top and bottom of PCM, such as Ti or W, act as the electrode of this memory unit. The active region of this memory cell is the PCM, which is the center of the structure.

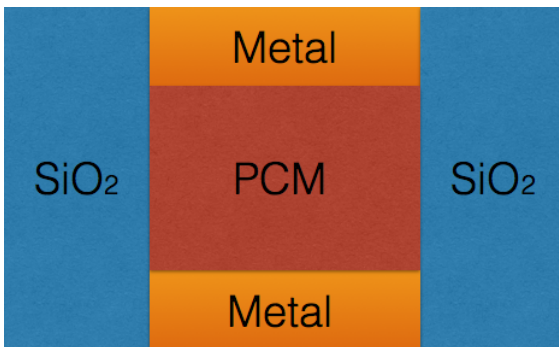


Figure 1. Schematic structure of phase change memory cell

The atomic structural representations of the amorphous and crystalline states are shown in figure 2, where atoms in the amorphous state are disordered while atoms in the crystalline state are highly organized. When the PCM changes its state from amorphous to crystalline, there is a substantial decrease in electrical resistivity of the material and a large increase in its optical reflection. Therefore the reading mechanism is able to

identify the phase of the material either from the resistivity or optical properties, which differentiate the data as 0 or 1.

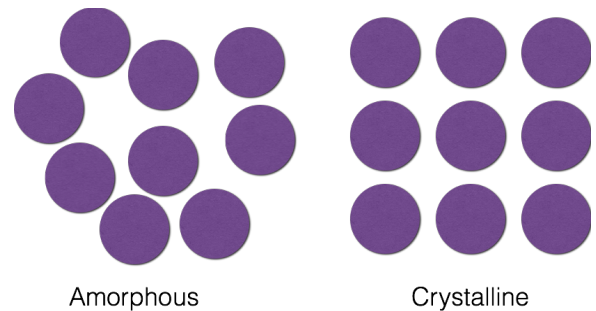


Figure 2. The geometric representations of the amorphous state and crystalline state atoms

The change of state from amorphous to crystalline is spontaneous but requires a certain amount of activation energy, E_a , to trigger this reaction. As shown in Fig. 3, the enthalpy of the material in the amorphous state is higher than that of the crystalline state. To increase the probability of the state transition happening, low activation energy is preferred for better energy efficiency, however reducing the activation decreases the stability of the material. Thus phase change data storage requirements are somewhat contradictory; at room temperature the material's state should be stable for years, whilst at elevated temperatures the material must be capable to crystallizing in Nano seconds. That is, the crystallization time must vary by approximately 16 orders of magnitude when the temperature of the PCM is raised from room temperature to its switching temperature.

Various PCMs are reported in the literature, Ge₂Sb₂Te₅ (GST) and GeTe are particularly well studied due to the low power rating, high data sustainability, long lifetime and fast phase changing speed. Doping specific elements such as N, Si or C with different concentrations could change the physical property of the PCM subtly, which is discussed by many others' work. In this case, we dope GeTe by different concentrations of oxygen and study how the crystallization temperature and activation energy change. This study is the first of its kind for GeTe compositions and is important because Ge and Te can both oxidize in air at high temperature. Thus we aim to study the phase transition properties of GeTe after exposure to oxygen during its manufacture. The study is crucial to determine whether oxygen impurities during the

manufacture of phase change materials will ultimately affect the memory device performance.

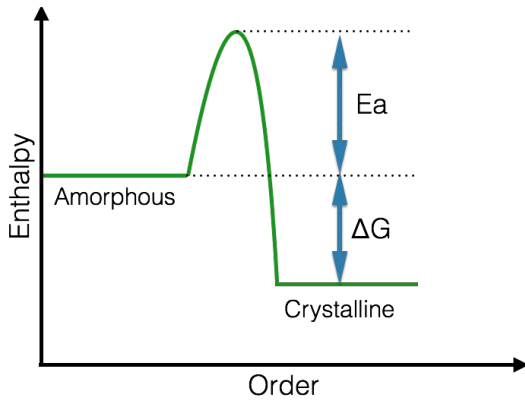


Figure 3. Change of free enthalpy of PCM from amorphous state to crystalline state

II. EXPERIMENTAL METHODS

A. Growth of the GeTeO films

The GeTeO films were prepared using sputtering system (see Fig. 4) in vacuum and room temperature. GeTe is sputtered from a composite GeTe target while the GeTeO thin film was grown in a mixture gas composed of Ar and O₂ on a glass substrate. A flow mass controller was used to change the Ar to O₂ ratio. The atomic proportions of GeTeO films were measured using Energy Dispersive X-ray (EDX) spectroscopy.

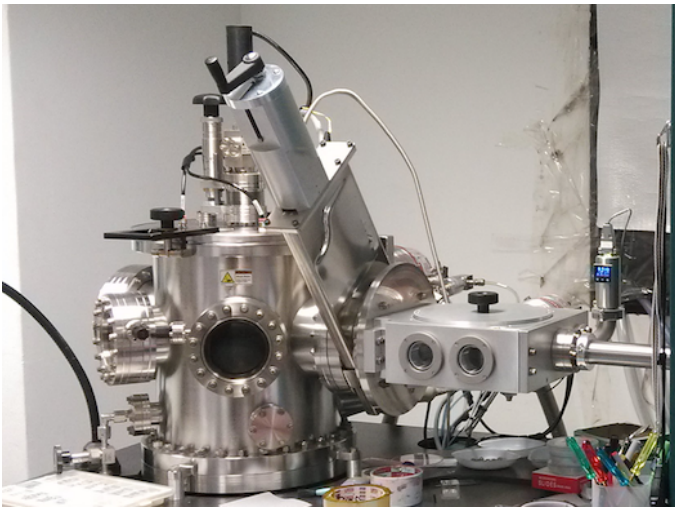


Figure 4. Sputtering System

B. Crystallization Temperature Measurement

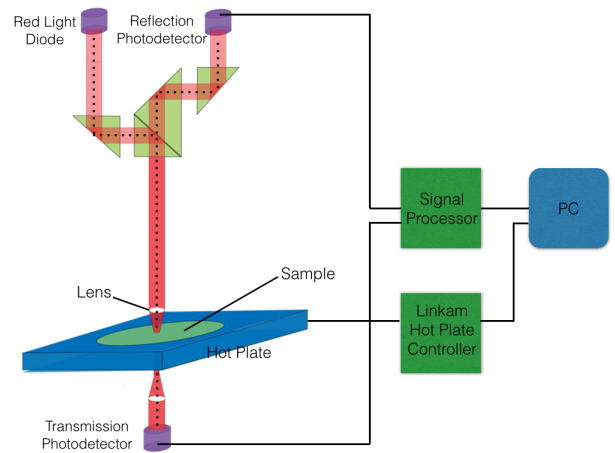


Figure 5. PCM Testing System

The set-up of the optical system used to measure the reflection and transmission change with respect to temperature is shown in Fig. 5. 633 nm laser radiation was introduced into an optical microscope and photo detectors were used to measure the reflected and transmitted laser beam intensities. The photo detector voltages were measured using an automated data acquisition analogue to digital converter. The reflected and transmitted laser intensities were measured while a computer controlled microscope furnace heated the PCM at constant rate from room temperature to 330 °C.

C. Error and precision

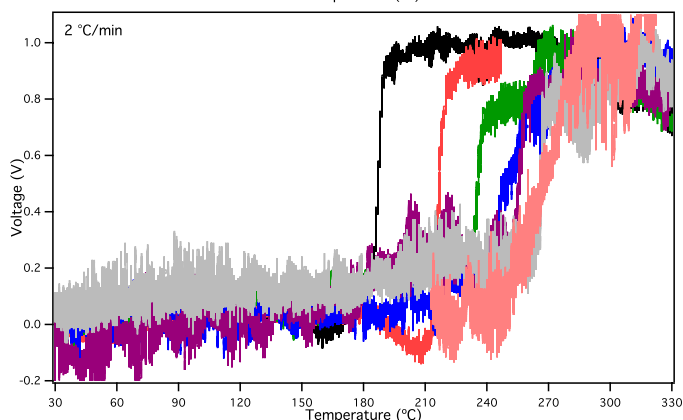
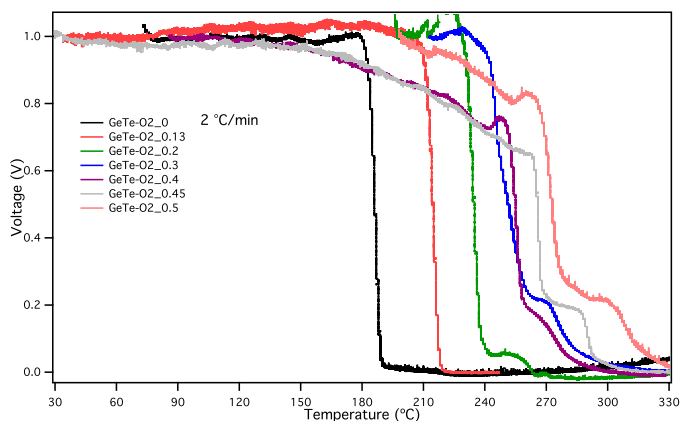
In the process of measuring the reflection and transmission light intensity with respect to temperature, the procedure may produce some error and affect the result of the experiment:

- To avoid the sample reacting with the content O₂ in the air, the hot plate chamber is filled with continuous flow of Argon gas, which is inactive.
- Due to the 8-bit-depth data acquisition card, the signal is not smooth. Therefore we fit a “hill equation” to the data, and differentiate it to find the temperature at which the crystallization rate is the maximum.

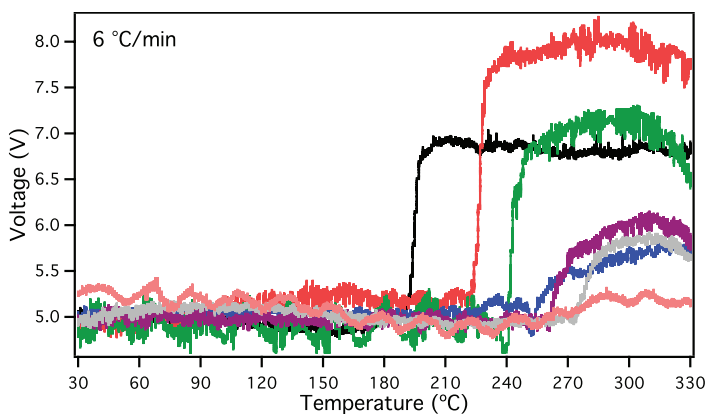
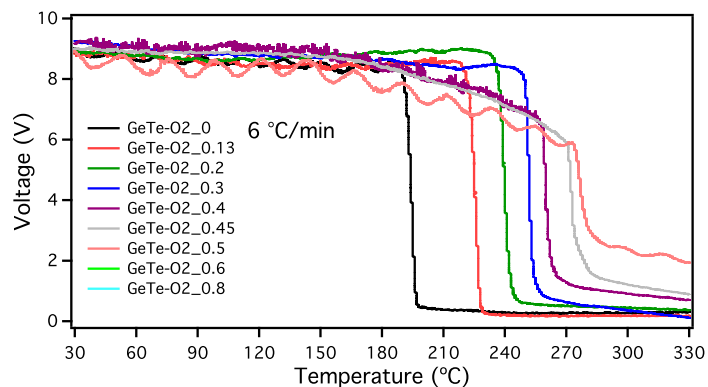
III. RESULTS AND ANALYSIS

A. Reflection/transmission voltage versus temperature

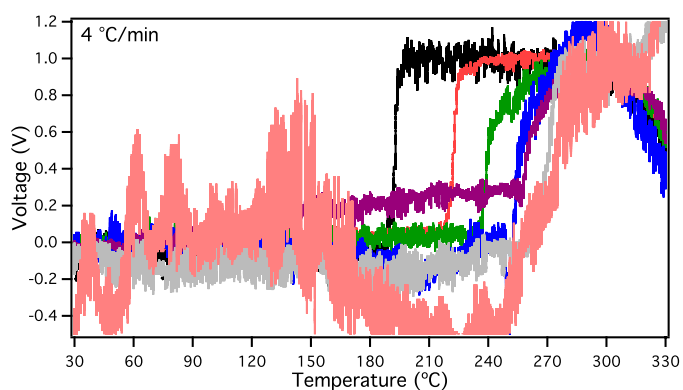
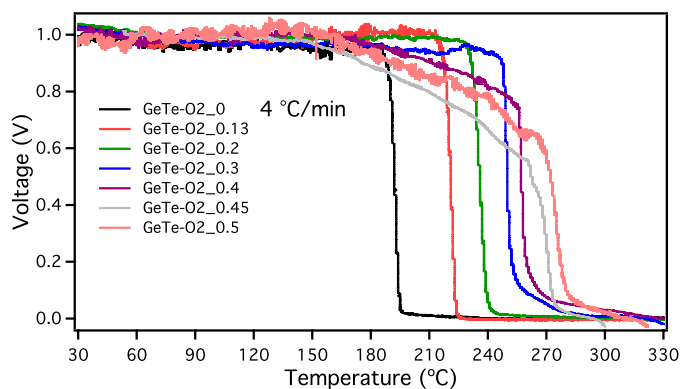
The following curves in Fig. 6 show the relation of the reflection/transmission light intensity with respect to temperature at a temperature ramp rate of 2 °C/min, 4 °C/min, 6 °C/min, 8 °C/min and 10 °C/min. The measured temperature range is from room temperature to 330 °C.



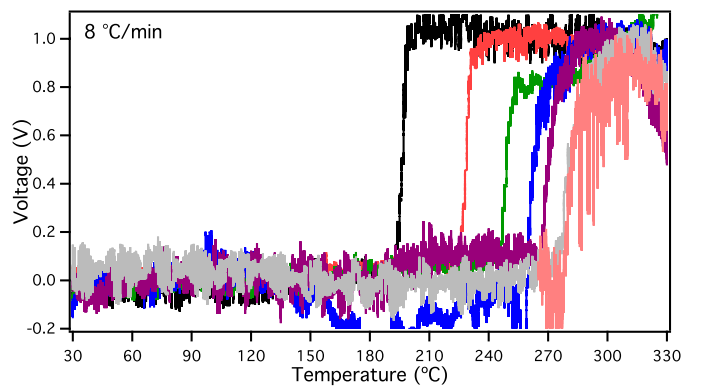
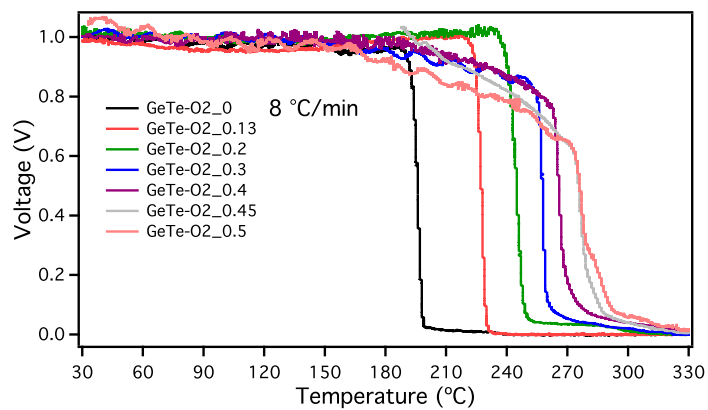
a) at temperature increasing rate 2 °C/min



c) at temperature increasing rate 6 °C/min



b) at temperature increasing rate 4 °C/min



d) at temperature increasing rate 8 °C/min

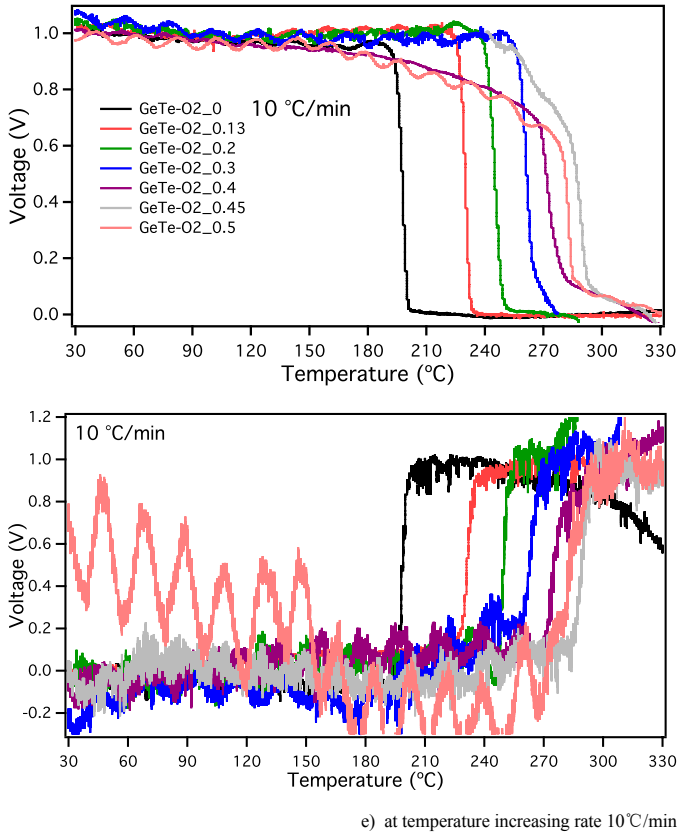


Figure 6. Reflection/transmission voltage vs. Time

B. The crystallization temperature of GeTeO

The plots of the crystallization temperature of the sample at different oxygen content are shown in Fig. 7. This data is derived from Fig. 6(a)-6(e). Note that the temperature where the reflection voltage has fastest increase or the transmission laser intensity has the fastest drop is considered the crystallization temperature.

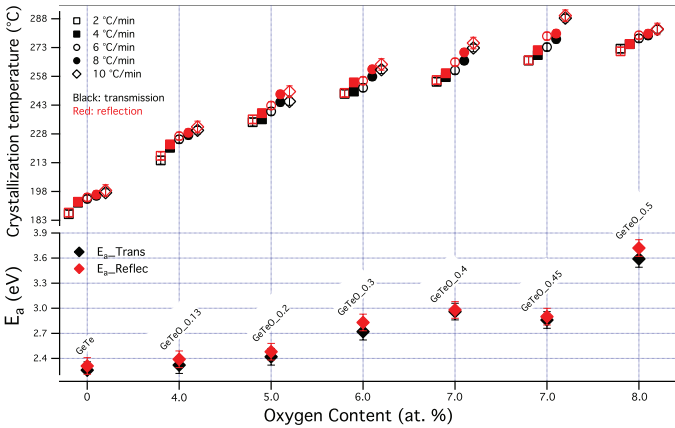


Figure 7. Crystallization temperature of GeTeO

C. Activation energy upon crystallization of GeTeO

The activation energy upon crystallization can be determined by Kissinger analysis, using equation (1) below. Where dT/dt is the heating rate, T_c is the crystallization temperature, E_a is the activation energy and k_b is Boltzmann's

constant. By plotting $\ln\left(\frac{dT/dt}{T_c}\right)$ against $\frac{1}{k_b T_c}$, we can get the E_a through the slope of the best-fit line in Fig. 8. The result of the activation energy is shown in Fig. 9, where y-axis is the activation energy in eV, and x-axis is the atomic percentage of oxygen content in the film [3].

$$\ln\left(\frac{dT/dt}{T_c}\right) = C + \frac{E_a}{k_b T_c} \quad (1)$$

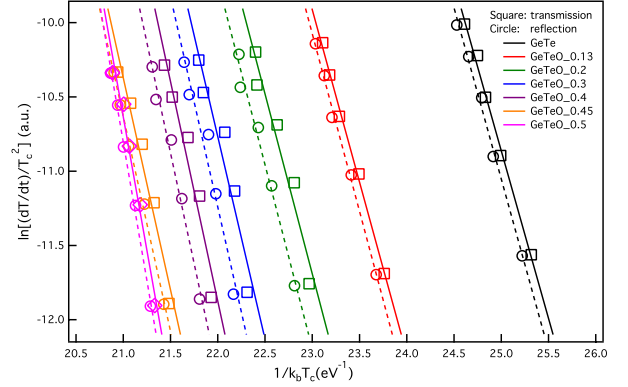


Figure 8. Kissinger Analysis of GeTeO

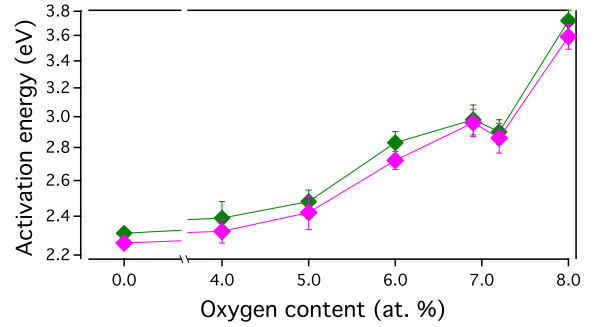


Figure 9. Activation energy upon crystallization as a function of oxygen concentration

IV. DISCUSSION

A. Oxygen causes increase of crystallization temperature and activation energy

As clearly shown in Fig. 7 and 9, there is an obvious increase in crystallization temperature and activation energy with oxygen incorporation. If one considers using GeTeO as the active material in a PCM device, following future development can be contemplated.

A higher crystallization temperature is an advantage since the GeTeO has more stable amorphous state and the crystallization will not happen at room temperature; however, the increase of activation energy is not good because that would cost more energy in switching the state of the material between amorphous and crystalline. Nevertheless, the GeTeO phase change material may be more suitable in some specific application such as permanent storage, e.g. archival data storage, or devices that are exposed to high temperature, e.g. space probe near to the sun.

B. Comparing GeTeO with Ge₂Sb₂Te₅

As stated in the introduction, Ge₂Sb₂Te₅ is one of the common PCMs. The crystallization temperature of Ge₂Sb₂Te₅ is around 150 °C and the activation energy upon crystallization is around 2.2 eV [4]. Comparing GeTeO with Ge₂Sb₂Te₅, GeTeO has much higher crystallization temperature and activation energy. Therefore we would expect it to show a higher resistance to spontaneous crystallization and loss of data.

C. Film becomes more transparent with higher Oxygen ratio and the phase change behavior stops

At the beginning state of the experiment, the thin films we prepared do not have phase change behavior and the film is almost transparent even if we increased the film thickness. After analyzing the problem, we tried decreasing the oxygen flow rate supplied to the sputtering system. The film became less transparent and the phase change behavior appeared. We suspect too much oxygen incorporation may react with Ge or Te atoms and the product has a similar crystal structure to SiO₂, which is also a poor phase change material.

V. CONCLUSION

Oxygen doped GeTe has higher crystallization temperature and activation energy than undoped GeTe films. Furthermore, the crystallization temperature and activation energy increase as the oxygen proportion increases. GeTeO has an advantage of high crystallization temperature, which makes the PCM stable at room temperature, however it uses more energy to make the phase change happen. The crystallization temperature and

activation energy are very sensitive to oxygen and when fabricating undoped GeTe devices care must be taken to minimize any oxygen impurities in the deposition system. On the other hand, deliberately doping GeTe with oxygen could have possible applications in archival data storage or memory devices for extreme environments, where the material needs to resist spontaneous crystallization.

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