

Seeded Crystallisation and Enhanced Phase-Change Materials

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Abstract

A crystalline chalcogenide interface is shown to reduce the temperature, duration and energy necessary to crystallise amorphous GeTe. By incorporating ultra-thin layers of crystalline Sb_2Te_3 into $\text{Ge}_2\text{Sb}_2\text{Te}_5$ similar improvements are observed thus providing a way to enhance the performance of phase change memory devices.

1 INTRODUCTION

$\text{Ge}_2\text{Sb}_2\text{Te}_5$ and related alloys along the GeTe- Sb_2Te_3 tie-line possess a number of remarkable traits that make them attractive memory materials: amorphous marks just a few 10s of nanometers in diameter are stable for years at elevated temperature but will, upon application of sufficient heat, change into a completely new atomic structure in a few nanoseconds leading to several orders of magnitude differences in electrical properties[1] and substantial changes in refractive index[2]. Furthermore, new results indicate an amorphisation processes which might not necessarily involve thermal melting[3].

GeSbTe materials seem the likely successor to silicon based non-volatile random access memory but the electrical current necessary to switch the material between the resonant, cubic and the covalent, amorphous states is high, the re-crystallisation, set, time is relatively long ~ 50 ns and, crucially, the write-erase endurance is limited to 10^6 cycles. It is therefore clear that in order for successful implementation of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ based PCRAM devices these obstacles must be overcome. To overcome these difficulties, the authors discuss the use of phase change metamaterials with the same average composition as $\text{Ge}_2\text{Sb}_2\text{Te}_5$ yet remarkably superior memory properties. The approach is based on repeated, thin (0.5nm) layers of Sb_2Te_3 and GeTe that effectively incorporate octahedral nucleation sites at the interface between the constituent layers.

2 EXPERIMENTS

The effect of a chalcogenide - GeTe interface on amorphous GeTe films was investigated by preparing GeTe films (10 nm thick) atop of quartz substrates with and without a crystalline chalcogenide buffer layer. The crystalline chalcogenide layer was created by depositing at elevated temperatures. Both samples were capped by 10 nm of TiN. This work was then extended further to create *metamaterials* composed of alternating layers of Sb_2Te_3 and GeTe. The structures were again deposited atop of a crystalline chalcogenide layer and capped by TiN. The optical transmission of the samples was measured as a function of temperature using a Linkham microscope furnace. The temperature was controlled to within 1°C . For each sample the transmission was measured using heating rates of $2^\circ\text{C}/\text{min}$, $5^\circ\text{C}/\text{min}$, $7.5^\circ\text{C}/\text{min}$ and $10^\circ\text{C}/\text{min}$. The crystallisation activation energy was analysed by the non-isothermal Kissinger method[4, 5]. The crystallisation time of the samples was measured using a pump-probe static tester which continuously monitors a 633 nm probe laser beam whilst a 650 nm pump laser beam is coincident on the sample at the centre of the probe. Both lasers were focussed through a lens with a numerical aperture of 0.65. The time resolution of the system is 1 ns. X-ray diffraction from the crystalline films were also collected between 10° and 80° and pole figures around specific peaks using a Phillips MRD system.

3 RESULTS & DISCUSSION

A substantial reduction in the crystallisation temperature and activation energy of GeTe is achieved by depositing atop of a crystalline chalcogenide buffer layer. Fig. 1(a) shows transmission of visible light through the samples as a function of temperature. The buffer layer reduced the crystallisation temperature of GeTe by 100°C resulting in a correlated reduction in the crystallisation activation energy from $4.35 \pm 0.38\text{eV}$ to $1.78 \pm 0.24\text{eV}$. The separate contributions of crystal nucleation and growth showed GeTe to have a *growth* activation energy of $1.77 \pm 0.14\text{eV}$ [6]. This suggests that the crystallisation process of GeTe films in contact with a crystalline buffer (shown in Fig. 1) is limited only by growth and the energy for nucleation is insignificant thus implying that either the interfacial atoms of the buffer act as nucleation sites; the growth of the GeTe crystal is seeded by the chalcogenide buffer.

Taking this approach one step further, Sb_2Te_3 crystalline films just 0.5 nm thick were layered between 0.5 nm films of GeTe to form a GeTe- Sb_2Te_3 metamaterial atop of the chalcogenide buffer. The static tester was used to write amorphous marks into the metamaterial samples. The crystallised fraction of material within these marks was

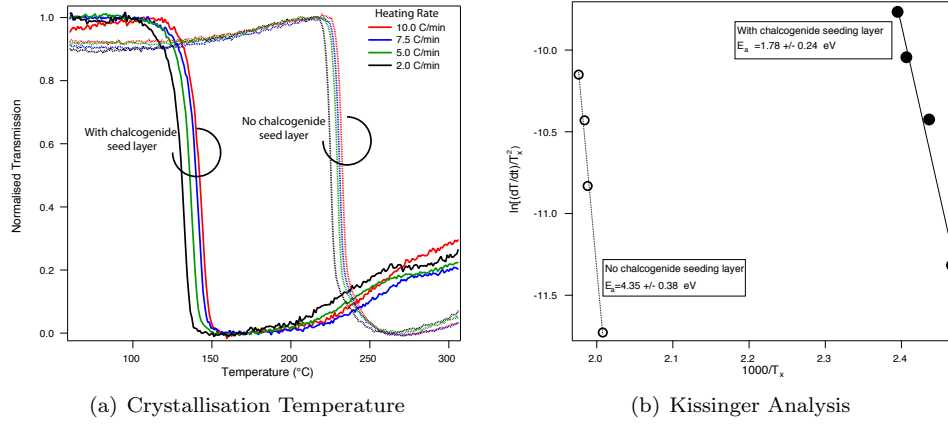


Figure 1: The (a) crystallisation temperatures and (b) associated Kissinger analysis of 10 nm thick as-deposited amorphous GeTe with and without a crystalline chalcogenide seeding layer.

then measured as a function of time by monitoring the intensity of the static tester’s probe beam during irradiation from the pump laser. For identical pulse conditions it was possible to fully crystallise the metamaterial in half the time required for the composite $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film. By increasing the pulse power, the entire depth of material could be crystallised in just 25 ns, see Fig. 2. Since multiple layers of crystalline Sb_2Te_3 nucleation seeds exist between very thin layers of GeTe in the metamaterial, no time is required for it to generate nucleation seeds and growth across the 0.5 nm GeTe layers can occur in a relatively short time. In contrast, the composite material has a low density of nucleation seeds hence additional time is required for crystallisation.

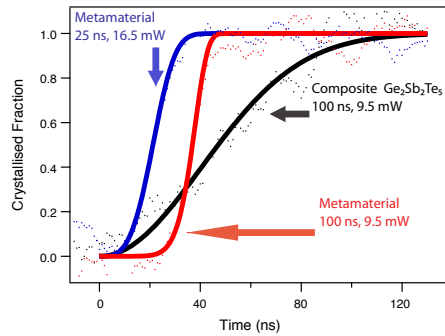


Figure 2: The fraction of re-crystallised amorphous mark as a function of time for the GeTe/ Sb_2Te_3 metamaterial and a composite $\text{Ge}_2\text{Sb}_2\text{Te}_5$ material. The laser pulse conditions are indicated.

4 CONCLUSION

The crystallisation process of GeTe is affected by the interface with a chalcogenide buffer layer resulting in a 100 °C reduction in crystallisation temperature and a drop in crystallisation activation energy from 4.35 eV to 1.78eV; a growth limited crystallisation process achieved. By growing thin layers of Sb_2Te_3 and GeTe atop of a chalcogenide buffer layer we have fabricated a metamaterial with the average composition $\text{Ge}_2\text{Sb}_2\text{Te}_5$ yet enhanced phase change properties resulting in a faster, more efficient memory material.

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