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Distinguishing mechanisms of morphological instabilities in phase change materials during switching

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ABSTRACT

The process of dewetting of a thin film from a solid substrate is important for its scientific and technological relevance, but can be difficult to observe experimentally. We report on an experimental method that may be used to investigate morphological changes, including dewetting, during laser heat treatment of alloys used for phase change memory devices. We have used nanosecond-scale time-resolved imaging to differentiate between competing thin film instabilities in GeTe, a chalcogenide-based phase change material. It is shown that in the absence of nucleated dewetting, thin films of phase change alloys may be unstable, but that nucleated dewetting can lead to a more disrupted final state of the thin film.

1. Introduction

The thermal stability of thin films and nanostructures is important for performance and reliability of materials for many applications, including memory based on phase change materials (PCMs). Chalcogenide-based PCMs, such as $Ge_2Sb_2Te_5$ and GeTe, are important for use in optical recording media and non-volatile resistance-based memory devices [1], which exploit the distinct optical and electrical properties of the amorphous and crystalline phases. For memory applications, switching between the amorphous and crystalline phases is achieved within a few nanoseconds by laser or Joule heating [1]. During crystallization the amorphous PCM may be heated well above its glass transition temperature and during amorphization the melting temperature of the crystalline PCM is exceeded [2,3]. Heating induces an increase in atomic mobility which enables rapid phase transformations, but which can also induce morphological changes adversely affecting device performance and reliability. Some studies [4–6] have addressed device reliability by observing changes in microstructure and nanostructure morphology during heat-induced phase switching. Morphology changes leading to void formation have been observed in electrically-switched GeTe nanowires [5]. Morphological defects have been observed in in-line PCM cells due to faceting of grains during crystallization of the amorphous phase [6]. Atomic force microscopy experiments show that during a full switching cycle (crystal to amorphous to crystalline) the topography of a PCM thin film may not return to its original shape [4].

Although morphology changes can have a dramatic effect on the performance of PCM devices [5,6], relatively few studies of the physical mechanisms underlying morphology changes and dewetting have been published about PCMs. This may be, in part, due to the short timescales (ns) under which these morphological changes occur in PCMs when rapidly heated by laser or Joule heating, making the relevant experimental measurements difficult to accomplish. The processes leading to hole formation in thin films of Te and Ge–Te alloys have been considered by Kivits et al. [7] in the context of intentional hole formation for optical data storage. They considered how gradients in surface tension and pressure induced by localized laser heating may lead to film thinning and rupture at the center of the laser-affected area and also considered the role of defects and pre-existing film defects in hole formation. The aforementioned mechanisms may play a role in the development of thickness variations and hole formation during laser amorphization and crystallization in thin films of $Ge_2Sb_2Te_5$ shown in Fig. 1. However, the patterns of the thickness variations in Fig. 1a and b and the more complex patterns of laser-induced thickness changes observed with in situ transmission electron microscopy (TEM) during laser crystallization of amorphous GeTe thin films [8] suggest that other types of thin film instabilities may be operational. Here we report on initial results using nanosecond time-resolved TEM to investigate the physical mechanisms causing thin film instabilities in PCM thin films during laser annealing.

Thin film instabilities and dewetting have been studied very extensively in other material systems [9–24], due to their importance in an

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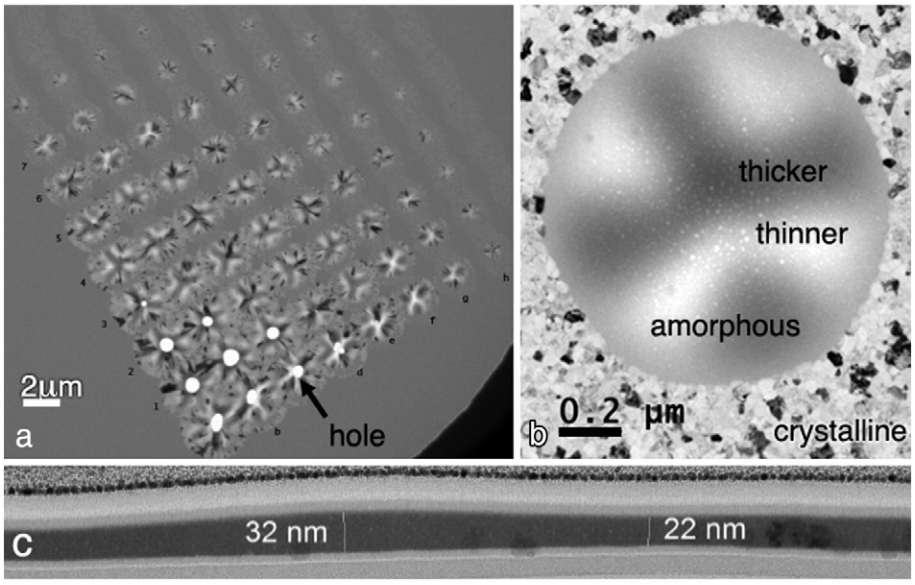

Fig. 1. Conventional ex situ TEM images of (a) laser-crystallized marks in an amorphous $Ge_2Sb_2Te_5$ thin film and (b) a laser-amorphized mark in a crystalline film. Within the amorphous mark, darker areas are thinner and lighter areas thicker. High-angle annular dark field scanning TEM of the area in (b) (not shown) and (c) TEM of a FIB cross section of a laser-amorphized area, similar to that shown in (b), confirm that the contrast changes in the amorphous region are due to thickness variations. Similar thickness variations occur within the crystalline marks and holes develop in the $Ge_2Sb_2Te_5$ with increased laser energy and pulse duration ((a), bottom).

enormous range of technologies (e.g. paints, coatings, electronics, dielectric layers, thermal barrier coatings). Instabilities and dewetting in liquid thin films can be initiated in several ways [9–11]. They may begin at pre-existing defects, such as pinholes, or may be nucleated [11] by a local variation in surface tension or film pressure which causes local thinning of the film. Instabilities can be induced by van der Waals interactions requiring no nucleation event [9,12]. It has been shown that in free-standing [9] or supported [12] very thin liquid films (<100 nm), thickness fluctuations above a critical wavelength, λ_c, will grow spontaneously due to the disjoining pressure arising from van der Waals interactions (below λ_c the film is still effectively stabilized by surface tension). The wavelength of the thickness fluctuation with the fastest growing amplitude, $\lambda_m = \sqrt{2}\lambda_c$, determines the characteristic length scale of the instabilities [9,12]. Instabilities caused by van der Waals interactions are sometimes called "spinodal" instabilities because the mathematical analysis is formally analogous to the analysis of the more familiar chemical spinodal decomposition [12]. Nucleated and spinodal dewetting may be simultaneously active as shown for liquid thin films of polymers [17], metals [13], and collagen solutions [18].

PCMs are generally embedded in a larger device or at least capped with a material that remains solid during the rapid heating used to induce the phase transformation, e.g. the ultrathin amorphous silicon nitride layer in Fig. 1c. The presence of a solid capping layer on the PCM introduces another layer of complexity. Capping layers change the physical interactions, such as interfacial energies and van der Waals interactions, and introduce new factors, such as mechanical properties and stress state, in the solid capping material [23,24]. The presence of a solid cap may suppress some instabilities [22,24] but, if subject to compressive stresses, may induce instabilities [19,21,24]. The need to better understand the complex physical mechanisms causing instabilities in nanostructured PCMs during switching motivates experimental observations of their development during laser heating in an effort to distinguish the different mechanisms of instability development.

We observe the development of morphological instabilities in situ, on the nanosecond scale, in capped GeTe films during laser heat treatment. GeTe is an important PCM, because its high crystallization temperature, T_x, relative to other commonly used PCMs [25,26] and rapid switching speed [26–28] make it attractive for random access memory applications. GeTe has been the subject of numerous theoretical and experimental studies including several examining the crystallization behavior of amorphous thin films during isothermal [29–31] and laser [2,3] heating and morphological changes have been seen during switching of GeTe nanowires [5]. Here we focus on GeTe, but we have observed similar instabilities in similarly prepared and treated $Ge_2Sb_2Te_5$ and GaSb thin films. In situ observations allow us to differentiate dewetting mechanisms that would be difficult to distinguish in post mortem analysis. The microstructural changes that occur during laser heating would be impossible to observe with most in situ imaging techniques because they occur on the nanosecond to microsecond time scale and on a nanometer length scale.

2. Experimental details

We use the dynamic TEM (DTEM), a pulsed photoemission TEM at Lawrence Livermore National Laboratory, to image the GeTe during the development of morphological instabilities. The DTEM achieves nanosecond-scale time-resolved imaging of irreversible processes in condensed phases with intense photo-emitted electron pulses. During a time-resolved experiment, a reaction is initiated in the specimen with a "pump" laser pulse. A pulse from another laser, which is timed against the pump laser pulse in an operator-defined delay, strikes the cathode inducing a burst of ~10^{10} photoemitted electrons, enough to form an image or diffraction pattern of a transient state of the material. The duration of the electron pulse passing through the reacting specimen defines the temporal resolution of the experiment. The DTEM has been used to study laser-induced crystallization in PCMs [3,8,32], rapidly-driven phase transformations in metals [33,34], and semiconductors [35], and has been used to verify that spinodal dewetting is the controlling physical mechanism in the dewetting of ultrathin liquid Ni films [36]. The design and operation of the DTEM have been described elsewhere [37].

Morphological instabilities were induced by laser-heating as-deposited amorphous films of 30 nm GeTe on a Si support with a 20 nm thick amorphous silicon nitride window (0.25 × 0.25 mm) and 8 nm silica capping layer. GeTe was deposited at room temperature using magnetron sputtering. A target with a nominal composition of Ge:Te = 50:50 at.% was used. Rutherford backscattering spectrometry revealed the film composition to be Ge 50.7 ± 2.0 at.% and Te 49.3 ± 2.0 at.%. The specimen was heated with a neodymium-doped yttrium aluminium garnet laser (1064 nm wavelength, 135 ± 5 μm $1/e^2$