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In situ dynamic TEM characterization of unsteady crystallization during laser processing of amorphous germanium

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ABSTRACT

The unsteady propagation mechanism for the crystallization of amorphous germanium (a-Ge) was studied with *in situ* movie-mode dynamic transmission electron microscopy (MM-DTEM). Short laser pulses were used to heat sputter-deposited a-Ge films and the resulting crystallization process was imaged with up to 16 sequential 50 ns long electron pulses separated by a controlled delay that was varied between 0.5 and 5 μs The unsteady crystallization in the radial, net-growth direction was observed to occur at a decreasing rate of ~1.5–0.2 m/s through a mechanism involving the formation of discrete ~1.1 μm wide bands that grew with velocities of 9–12 m/s perpendicular to the radial direction and along the perimeter of the crystallized area. The crystallization rate and resulting microstructure were consistent with a liquid-mediated growth mechanism, which suggests that locally the band front reaches the amorphous melting temperature of Ge. A mechanism based on the notion of a critical temperature is proposed to explain the unsteady, banded behavior.

1. Introduction

Pulsed laser processing is a widely used technique for crystallizing semiconductor thin films which are often deposited in the amorphous state [1–4]. As an alternative to annealing, the highly localized laser heating can protect nearby sensitive components and enables the use of temperature-sensitive substrates such as those used in flexible displays. Additionally, laser parameters can be tuned to control the resulting nano- and microstructure, which plays a large role in determining the properties of materials [5].

In some materials, the latent heat released from crystallization can lead to a self-sustaining propagation at rates >10 m/s in a process that has been referred to as “explosive crystallization” [6–8]. In Ge and Si, studies on the thermodynamics and kinetics of this process have shown that the high rates are produced by a liquid-mediated crystallization process whereby a thin liquid layer forms at the crystallization front. The liquid is nonequilibrium and highly transient, resulting from the amorphous phases of these materials having melting points that are ~20% less than that of the crystalline phases [9]. Crystallization of the liquid layer rapidly releases latent heat, which further sustains the propagation. Typically, this leads to long columnar grains that grow epitaxially out of the melt [8,10]. This process becomes more complex when the heat release is not sufficient for steady propagation, as in cases of thinner amorphous films and unheated substrates. Under these conditions, the propagation becomes unsteady and moves slower. It produces periodic microstructures that have been previously described as appearing like frozen waves in thicker films (>1 μm) and discrete bands in thinner films [11–13].

The differences in the resulting films from steady and unsteady growth are well illustrated in experiments involving pulsed laser heating with a Gaussian beam, an example of which is shown in Fig. 1. The crystallized area displays three distinct regions, which are labeled Zones I, II, and III. Zone I formed shortly (<50 ns) after the heating laser pulse in the center where the beam was most intense and the material reached above the amorphous melting temperature (~969 K) [9,14]. Since this melt was significantly undercooled relative to the crystalline phase melting temperature (1210 K), it underwent rapid homogenous nucleation of a high density of sites leading to the formation of very small grains (<100 nm). Zone II was formed from the fast and steady liquid-mediated crystallization discussed above and is made up of columnar grains that expand outward from Zone I at ~10 m/s [10,15]. Zone III resulted from unsteady growth which produces a characteristic periodic, banded structure [13].

In comparison to the other zones, the mechanism that controls

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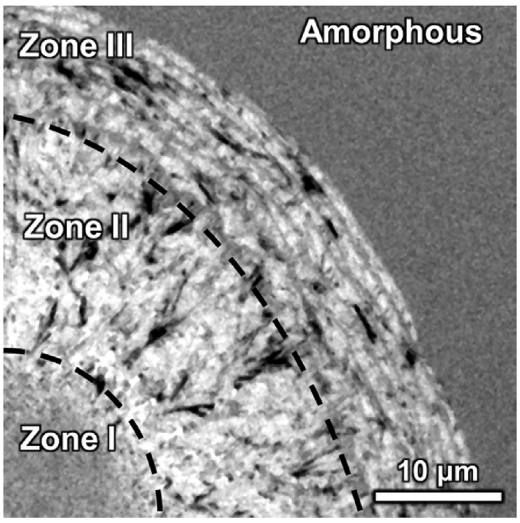

Fig. 1. A TEM micrograph showing the distinct regions that form as the result of spatially Gaussian pulsed laser heating of amorphous germanium.

the unsteady growth observed in Zone III is not well understood. Proposed explanations include, (1) periodically stuttering propagation as the front slows and speeds back up in regular intervals [12], (2) inward crystallization from a melt region with the width matching the period of the structure [11], and (3) a "zig-zag" propagation with fronts moving perpendicular to the net crystallization direction (i.e., the radial direction) [7,13]. This confusion exists, in part, because of the challenges inherent to directly observing this behavior at the relevant time and length scales. As the critical microstructure can range from several microns down to 50 nm or less, high spatial resolution, such as that achieved in a transmission electron microscope (TEM), is needed. However, the slow acquisition rate of TEM cameras and insufficient source brightness make it impossible to capture the rapid evolution of this crystallization process in traditional TEMs. To overcome these issues, the dynamic TEM (DTEM) at Lawrence Livermore National Laboratory (LLNL) uses laser pulses to induce photoemission in the cathode and produce short (20–50 ns) electron pulses with enough signal for each pulsed image to produce a highly temporally resolved image [16–20]. That image is timed with respect to a separate specimen drive laser pulse that is used to heat the specimen. The DTEM has been previously used to support a "zig-zag" style propagation mechanism for Zone III formation in Ge, with the discrete bands forming individually and growing perpendicular to the net propagation direction [13]. Extension of previous observations is made possible by the recently developed "movie-mode," where 9 or 16 individual electron image pulses are deflected onto different locations on the CCD camera, which is read out afterwards to produce a time-resolved sequence of images [16,17,21]. This technique has been previously used to characterize the liquid-mediated crystallization of amorphous Ge (a-Ge) that occurs in Zone II [10,15].

In this paper, we present an *in situ* investigation into the mechanism and kinetics of the unsteady crystallization of a-Ge in Zone III using movie-mode DTEM. Crystallization was observed to occur in discrete bands, ~1 μm wide, that grew at rates of 9–12 m/s perpendicular to the radial net propagation, which averaged only ~0.5 m/s. Multiple bands were found to spiral around the central crystallized region, with net outward growth occurring when a band would overpass another or a new band would nucleate. The resulting microstructure of each band was columnar in the band growth direction, while smaller "feathery" and nanocrystalline (<50 nm) grains separated each band. The similarities in morphology and growth rates between Zone II and the individual bands of Zone III suggest that they are both formed through liquid-mediated crystallization enabled by a front that reaches the amorphous melting temperature. Based on these observations, we propose a mechanism for Zone III that is dependent on material adjacent to the crystallized areas being preheated through thermal conduction to some critical temperature prior to the formation of the next band. The nature and value of this critical temperature was further explored with comparison to previous experimental results from the literature.

2. Experimental

Amorphous germanium (a-Ge) thin films were prepared with DC magnetron sputtering onto commercially available silicon nitride (SiN_x) TEM support films that were 20-nm thick with 0.5 × 0.5 mm electron transparent windows (Norcada Inc). Base pressure prior to deposition was $< 5 \times 10^{-7}$ Torr. A 99.999% pure germanium target with N-type doping of antimony (Kurt J. Lesker Company) was sputtered at 6 W under 3 mTorr of ultra-high purity argon. This process produced a deposition rate of ~1.05 nm/min as determined by depositing films on witness Si substrates and measuring thicknesses with a ZYGO NewView™ 7300 optical profilometer. Films of thicknesses ranging from 25 to 100 nm were produced.

The crystallization behavior of these films was characterized *in situ* using the movie-mode dynamic transmission electron microscope (MM-DTEM), the details of which can be found elsewhere [16,17,21]. In short, the MM-DTEM functions by using a UV laser to induce photoemission from a Ta cathode in a JEOL 2000FX TEM. The duration and separation of each pulse can be defined by the user and for these experiments the pulses were kept at 50 ns long, with delays between pulses ranging from 250 ns to 5 μs for a total of 9 or 16 pulses. Each pulse contains enough electrons (~10^9) to produce an image that is deflected to a different location on the CCD camera with all pulsed images read out at once after the experiment to compensate for the relatively slow refresh rate of the camera. These imaging pulses are timed with respect to a second laser which is used to heat the sample and induce crystallization. This laser (532 nm) has a Gaussian profile with $1/e^2$ diameter of 110 μm and a full width half maximum (FWHM) duration of 12 ns The total deposited energy per pulse was varied between 2 and 6 μJ. The laser hits the sample at a 45° angle which causes the elliptical crystallization spots observed. To avoid the potentially complicating effect of any preheating [22] or enhanced heat transport from the Si frame, each experiment was performed on a fresh area of the SiN_x substrate so that the beam would be at least 50 μm from any past experiments and the edge of the window. This typically enabled 9 experiments per TEM substrate. As well as imaging in pulsed mode, the DTEM can also operate as a traditional TEM in thermionic emission mode. This imaging mode allows for postmortem characterization with less noise and higher spatial resolution.

Precession electron diffraction orientation mapping was also performed on the crystallized specimens using the ASTAR system from NanoMEGAS on a Phillips CM300 TEM operating at 300 kV. The technique collects a diffraction pattern at each point in a map, which is indexed using automated software to provide the crystallographic orientation. The intensity of the central spot of each recorded diffraction pattern can also be used to construct a virtual bight field image. The freely available and open source MATLAB toolbox, MTEX, was used for analysis of the data and generation of the orientation maps [23].