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In situ investigation of explosive crystallization in a-Ge: Experimental determination of the interface response function using dynamic transmission electron microscopy

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The crystallization of amorphous semiconductors is a strongly exothermic process. Once initiated the release of latent heat can be sufficient to drive a self-sustaining crystallization front through the material in a manner that has been described as explosive. Here, we perform a quantitative in situ study of explosive crystallization in amorphous germanium using dynamic transmission electron microscopy. Direct observations of the speed of the explosive crystallization front as it evolves along a laser-imprinted temperature gradient are used to experimentally determine the complete interface response function (i.e., the temperature-dependent front propagation speed) for this process, which reaches a peak of 16 m/s. Fitting to the Frenkel-Wilson kinetic law demonstrates that the diffusivity of the material locally/immediately in advance of the explosive crystallization front is inconsistent with those of a liquid phase. This result suggests a modification to the liquid-mediated mechanism commonly used to describe this process that replaces the phase change at the leading amorphous-liquid interface with a change in bonding character (from covalent to metallic) occurring in the hot amorphous material. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4894397]

I. INTRODUCTION

Germanium is a group IV semiconductor possessing the highest hole mobility of all known bulk semiconductors.1 It is used extensively in current electrical devices such as solar cells,2,3 infrared detectors,4,5 and high efficiency transistors.6,7 The economic motivation to shrink electrical devices and reduce power consumption has driven research in germanium thin film device fabrication and new processing techniques. Ongoing fundamental research focuses on topics such as laser processing of amorphous germanium (a-Ge) thin films for control over the final structure and properties,8–10 as well as the integration of germanium on silicon.11,12

Control over the laser-induced amorphous to crystalline phase transition in thin a-Ge films is crucial for its implementation in electronic and optoelectronic devices. Potentially it can also be used for processing other relevant materials systems. This process can lead to a complex set of crystalline morphologies, with crystallization processes evolving on nano- to microsecond time scales that can result in intricate nano- to microstructural patterns.13–15 The details of the resultant microstructures depend on the crystallization mechanism, the heating geometry, and a variety of possible morphological instabilities through a subtle interplay of kinetics and thermodynamics. An in-depth understanding of the mechanisms for this transformation should lead to better control over the properties of crystalline films, a critical step for improved device performance.

Pertinent to the crystallization dynamics and morphological instabilities is the latent heat released at the crystallization front, which is significant; the latent heat, L, for the amorphous-crystalline (a-c) transformation divided by the specific heat capacity, $C_p$, is $L/C_p \sim 420$ K in Ge.16,17 Over certain film/substrate temperature ranges this release of energy can be sufficient to fuel a self-sustained crystallization front. Since the process is accompanied by heat, sound, and light emission it has been termed explosive crystallization,18 a phenomenon common to amorphous semiconductors and some metals.

There are several distinct modes of explosive crystallization described in the literature.19,20 These modes can be grouped into two broad classes; those in which the crystallization front involves a direct c-a interface (explosive solid phase crystallization, ESPC) and those that involve a metastable liquid layer between the two phases mediating the a-c transformation (explosive liquid phase crystallization, ELPC). In the ELPC case the two interfaces, a crystal-liquid (c-l) interface and a liquid-amorphous (l-a) interface, are thought to

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that extends to a radius of $\sim 45 \mu m$, roughly the size of the \(1/e^2\) radius of the laser spot that initiates the crystallization; zone II–consisting of large radially elongated crystals, extending from the periphery of zone I to an outer radius of $\sim 52 \mu m$; and zone III–layered structure composed of nanocrystalline bands exhibiting some texture surrounding large tangentially oriented crystals. Our first study investigated the kinetics of laser-induced nanocrystallization in zone I using DTEM imaging.\(^{27}\) We also investigated the complex explosive crystallization processes involved in the formation of zones II and III, directly determining the modes of crystal growth, their associated timescales and the relationship between the abrupt change in morphology and the underlying temperature field.\(^{15}\) In contrast, the current work investigates the kinetics of explosive crystallization in a-Ge films through a quantitative study of time-resolved DTEM images. In particular, we use DTEM imaging to measure the time/position dependent speed of the crystallization front through zone II. This information, together with robust modeling of the temperature field, provides an experimental determination of the interface response function (IRF) for the explosive crystallization front over the full range of relevant temperatures. The IRF relates the front propagation speed to the local temperature and is essential for numerical modeling of the transformation process as well as determination of ranges of conditions that are and are not capable of supporting steady-state transformation fronts moving at constant speed. Previous experiments aimed at determining this information operated under steady-state conditions and have therefore only been able to access segments of the full, temperature dependent interface response function.\(^{22,23,31,32}\) The ability of DTEM to capture transient crystallization processes directly \textit{in situ} is the key enabling feature of the current study.

II. METHODS

The DTEM investigations were performed on 110 nm thick freestanding a-Ge films supported on 150-mesh copper TEM grids. The a-Ge films were first deposited using electron beam evaporation on optically polished rock salt and then floated off in deionized water onto the TEM grids. The crystallization process was observed using the DTEM at LLNL, an instrument and approach that are described in detail elsewhere.\(^{29,30,33}\) Briefly, crystallization of the a-Ge films was initiated using a nanosecond laser pulse focused to a Gaussian spot of $\sim 90 \mu m \ 1/e^2$ full width, a wavelength of 532 nm (where a-Ge has reasonable absorption\(^{34}\)), a pulse duration of 15 ns and a fluence of $\sim 110 \text{ mJ/cm}^2 \pm 5\%$. The time evolving microstructure of the film was observed in the DTEM by using a nanosecond electron pulse produced by UV laser driven photoemission that is synchronized with the specimen drive laser used to heat the sample. By performing multiple experiments on fresh specimen areas, with different time delays set between the electron probe pulse and drive laser pulse, we directly observed the reproducible details of the crystallization dynamics. Time resolved images with delays ranging between 20 ns and 10 \(\mu s\) were acquired. The time range was chosen to capture the evolution of all three morphologies as follows: zone I–nanocrystalline region that propagates together, separated by some tens of nanometers.\(^{21-23}\) The nature of the amorphous-liquid phase transition that underpins the ELPC mechanism has not been well characterized due to the metastability of the short-lived liquid phase (persisting for only a few ns), however, it has been argued that a first order phase transformation of the amorphous phase equivalent to “melting” occurs at $T_{\text{m}} = 0.8 T_{\text{mc}} = 969 \text{ K}$.\(^{26}\) A transition with these characteristics has been observed in molecular dynamics (MD) simulations of a-Ge using classical Stillinger-Weber type interatomic potentials.\(^{24}\) Additionally, indirect evidence has been obtained using transient conductance and time-resolved reflectivity measurements in Si,\(^{23}\) as well as the redistribution of dopant impurities in Ge (i.e., by assuming the material at the interface has diffusion characteristics of l-Ge).\(^{25}\) Gibbs free energy calculations suggest that this liquid is metastable in the temperature range $T_{\text{m}} < T < T_{\text{mc}}$, since the crystalline phase has the lowest free energy over this range. The appearance of a transient liquid-like phase in this temperature range is due to the rapid rate of the a-l transition compared to the direct a-c transformation. The final microstructure of the material is highly sensitive to these transition rates.

This is the third in a series of articles\(^{15,27}\) in which we demonstrate the application of dynamic transmission electron microscopy (DTEM) to the \textit{in situ} observation of rapid laser-induced crystallization phenomena in a-Ge films. The dynamic transmission electron microscope, developed at Lawrence Livermore National Laboratory (LLNL), offers the appropriate combination of high spatial (10 nm) and high temporal (15 ns) resolutions for investigation of irreversible fast-evolving laser-induced crystallization processes.\(^{28-30}\) DTEM is unique in its ability to make direct observations of rapid microstructural evolution under a spatially and temporally evolving temperature field \textit{in situ}. Our earlier work used these capabilities to investigate how laser excitation of a-Ge films with a single nanosecond pulse results in the development of a complex microstructure with three distinct morphological zones.\(^{15}\) An example of the final laser crystallized microstructure is shown in Fig. 1, where we differentiate three morphologies as follows: zone I–nanocrystalline region
zones according to earlier studies on laser-induced crystallization in germanium.15,27,35–37

The temporal uncertainty between measurements is defined by a combination of the timing jitter between the two laser systems (± 1 ns) and reproducibility of the experiments that depends on the relative positioning of the electron probe and drive laser and the shot-shot energy variation of the drive laser. To minimize timing errors associated to the electron probe and laser positioning, observations were made in the center of the TEM grid and crystallization was initiated by a laser pulse irradiating the film in the corner of the TEM grid. Using this experimental configuration, the uncertainty in quantifying the relative position of the crystallization front as a function of delay time is due to the shot-shot variation in the laser fluence and its influence on crystallization dynamics. Using the observed variation in time delays in which the transition zone between zones I and II forms (shown in Figs. 1 and 2), we estimated the overall temporal uncertainties to be ± 50 ns. The shot-shot variation in the laser fluence was also taken into account for the error analysis in the interface temperature modeling.

The interface temperatures are not available directly through experiment; so, a numerical modeling approach was adapted using known thermal parameters for amorphous and crystalline Ge together with DTEM observations to estimate the temperature evolution in the film. This modeling employed the 2D time dependent heat equation with a source term

\[
\frac{\partial T(x,y,t)}{\partial t} = \alpha \nabla^2 T(x,y,t) + f(x,y,t),
\]

where \(T(x,y,t)\) is the temperature of the film at position \(x,y\) and time \(t\), \(f(x,y,t)\) is a time and position dependent heat source term, and \(\alpha = k/\rho C_p\) is the thermal diffusivity of the material, where \(k\) is the thermal conductivity, \(\rho\) is the mass density and \(C_p\) is the specific heat at constant pressure. To solve Eq. (1) for \(T(x,y,t)\), we used a finite element algorithm implemented in MATLAB using matrix methods. A Dirichlet boundary condition of \(T = 300\) K was set at the radial position \(r = 150\) µm. The temperature dependence on the \(z\) coordinate (in the direction of the film normal) may be neglected, since the 110 nm film thickness is small compared to the heat diffusion length, \(l_D = 2\sqrt{\alpha t}\), which is approximately 3.6 µm for the \(t = 800\) ns time scale associated with zone II growth. Conversely, the characteristic heat diffusion time for the 110 nm thickness is less than 1 ns.

The initial temperature profile of the film before crystallization commences is determined by the deposited laser energy. The initial conditions for the calculation were set to reproduce the temperature profile of the film immediately after illumination by a single DTEM pump laser pulse. Taking into account uncertainties in the laser fluence and amorphous density, and assuming the 2D spatial laser profile is Gaussian, the temperature of the film immediately after excitation at the zone I boundary is 1150 ± 30 K, which was calculated with the temperature dependent specific heat capacity, \(C_p\), density, \(\rho = 5.0 \pm 0.3\) g cm\(^{-3}\), reflectivity, \(R = 0.47\), and absorption, \(1/\alpha = 50\) nm, of a-Ge. The process of crystallization, however, also evolves heat at the crystallization front which moves radially outward from the incident laser spot. This is included in the model through a source term that describes the latent heat generated in the interfacial region as a whole (the combined c-l and l-c interfaces).

\[
f(x,y,t) = \frac{v_{\text{front}} L}{C_p} \delta(r - r_{\text{front}}),
\]

where \(L = 1.59 \times 10^5\) J kg\(^{-1}\) is the latent heat of the a-c phase transition, \(C_p = 376\) J kg\(^{-1}\) K\(^{-1}\), is the specific heat capacity of c-Ge at \(T_m\), \(r_{\text{front}}\) is the radial coordinate, \(v_{\text{front}}\) is the time-dependent position of the transformation front as determined from the DTEM measurements (discussed in detail below), and \(v_{\text{front}}\) is the time derivative of \(r_{\text{front}}\), i.e., the front velocity. This model was developed to explore the

FIG. 2. Time resolved images of the LREC growth. The scale bars are 1 µm given in each block image.
coarse behavior, on the scale of tens to hundreds of nanoseconds, of the average temperature with time and radius through zone II. The model is pertinent to the discussion on the mechanisms of explosive crystallization, yet does not address detailed fine variations on the length scale of individual nanocrystals within the front. The value of $L$ used in Eq. (2) includes the sum of both endothermic and exothermic latent heats, for the $a$-$l$ and $l$-$c$ transformations respectively. The expected separation between these fronts is only a few tens of nanometers (much less than the spatial resolution of the finite-element model), thus the delta function term accounts for the entire interfacial region.

III. RESULTS

The laser crystallized microstructure of zone II consists of large radially oriented crystals with lengths between 5 and 9 $\mu$m that are highly faceted and terminate in a wedge-shaped geometry characteristic of a dendritic morphology.37,40 The growth of these radially oriented dendrites initiates between 100 and 250 ns after the initial laser heating pulse, and the growth of the crystalline region transitions to the zone III morphology at delays of $\sim$1000 ns (See Fig. 2). Dendritic growth initiates at preferred sites at the periphery of zone I, producing rosette shaped undulations that fan-out from the crystallization front (Fig. 2). These undulations may result from anisotropic growth along different crystallographic planes and perturb local temperature profiles that stimulate the formation of Mullins-Sekerka type growth instabilities which produce the large dendrites observed in the outer regions of zone II. The average growth rate of these dendrites in the free-standing films is estimated to be $\sim$8 $\pm$ 2 m/s, similar to the mean growth speed reported for membrane supported $a$-Ge films.38 The dendrites become more faceted with time suggesting that growth is more anisotropic at the later stages crystallization.

A deeper understanding of the explosive crystallization kinetics requires that we determine the time-dependent velocity profile (the IRF) of the crystallization front through zone II. The growth front velocity can be directly measured by tracking the change in the mean radial length of zone II with time that was measured from a series of DTEM experiments and images taken at different time delays. The corresponding crystallization front velocity with delay time (triangles) was calculated by taking a discrete derivative of the radial length data.

IV. DISCUSSION

As stated in the introduction, ELPC of amorphous semiconductors is understood to occur by co-propagation of two fronts: a liquid-amorphous interface ($l$-$a$), where the latent heat associated with the endothermic amorphous melting transition is absorbed, followed by a crystal-liquid ($c$-$l$) interface where the latent heat of crystallization is released (Fig. 4).21 The existence of a liquid-like layer mediating the crystallization of the amorphous material is ascribed to the $\sim$245 K difference between the melting temperatures of the amorphous and the crystalline phases.26 When the amorphous material is heated to temperatures above the amorphous melting temperature ($T_{ma}$) but below the melting temperature of crystalline Ge ($T_{mc}$), there is a fast first order phase transition to a metastable liquid-like phase; i.e., this metastable liquid is supercooled relative to $T_{mc}$. Gilmer and Leamy43 were among the first to

FIG. 3. A plot of the change in the mean radial length of zone II (squares) with time that was measured from a series of DTEM experiments and images taken at different time delays. The corresponding crystallization front velocity with delay time (triangles) was calculated by taking a discrete derivative of the radial length data.

FIG. 4. Schematic of an explosive crystallization front and the corresponding temperature profile.
suggest the presence of a mediating liquid layer to describe the extremely high crystallization velocities (~20 m/s) reported for laser induced crystallization of amorphous semiconductors. They estimated that the width of the layer ranges between 2% and 10% of the thickness of the a-Ge film. Atomistic simulations of the crystallization process in a-Ge, performed by Albenze and co-workers, estimated the width of this layer to be ~15 nm, indicating that the liquid persists locally for only ~200 ps between the passage of the two fronts. In addition, they showed that once the liquid layer has been created its existence is determined exclusively by the heat supplied from the exothermic reaction of the liquid to crystalline phase transition.

Of particular interest are the details of the interface response function that describe the dependence of the solidification/melting front speed on the front temperature which can be defined for both the c-l and l-a interfaces. The velocities of the c-l and l-a interfaces are expected to depend on the interfacial temperatures, $T_{ci}$ and $T_{ai}$, according to the Frenkel-Wilson kinetic law:

$$v_{a,c} = b_{a,c} A_{a,c} \exp \left[ - \frac{E_{al,cl}}{k_B T_{ai,ci}} \right] \times \left\{ \exp \left[ \frac{L_{a,c}}{k_B N_{a,c}} \left( \frac{1}{T_{ma,mc}} - \frac{1}{T_{ai,ci}} \right) - 1 \right] \right\}, \quad (3)$$

where $E_{al,cl}$ are the activation enthalpies associated with the phase transitions, $A_{a,c}$ are Arrhenius pre-exponential factors, $T_{ai,ci}$ is the interface temperature, $T_{ma,mc}$ is the melting temperature, $L_{a,c}$ are the latent heats of fusion, $N_{a,c}$ are the number densities, and $b_{a,c} = \pm 1$ for the amorphous and crystalline phases, respectively. By convention, speed is positive for solidification and negative for melting (Fig. 5).

Schematic IRFs for the c-l and l-a interfaces, reflected through the temperature axis for the l-a interface, are shown in Fig. 6. Depending on the value of the parameters in Eq. (3) the curves can present two qualitatively different relationships which are distinguished in Figs. 6(a) and 6(b). On these graphs, the IRF curve for the c-l interface is shown on the same set of axes as the reflected IRF curve for the l-a interface to illustrate the location of the IRF intersection position. The $T_{ci}$ curve in Fig. 6(a) shows a situation (i.e., set of parameters) in which the reflected amorphous melting branch of the l-a IRF intersects the c-l IRF on the high temperature side of the curve’s maximum. This has previously been called the “front-side” intercept scenario by Chojnacka and Thompson. The curve $T_{ci}$ in Fig. 6(b) shows a distinct situation in which the reflected amorphous melting branch of the l-a IRF intersects the c-l IRF on the low temperature side of the maximum (called the “backside” intercept scenario). The nature of the intercept mode (frontside/backside) is determined primarily by the position and width of the positive going peak in the c-l IRF, the maximum crystallization velocity observed and—in experiments described above—the nature of the time/temperature dependence of the crystallization front velocity.

Under steady-state explosive crystallization, the velocities of the c-l and l-a interfaces must be equal in magnitude to ensure constant motion of the macroscopic interface. Under the non-steady-state conditions of the current experiments the instantaneous velocities $v_a$ and $v_c$ (as determined through Eq. (3)) need not be precisely identical at all times. However, explosive crystallization in general requires that $T_{ai} < T_{ci}$, to ensure that the heat transfers from the crystallizing front to the melting front (Fig. 4), and even under non-steady state conditions, explosive crystallization cannot persist under front temperature conditions (i.e., $T_{ai}$ and $T_{ci}$) in which $v_a$ is below $v_c$ for more than a few nanoseconds (given a liquid layer thickness of ~10 nm); i.e., the c-l interface cannot overtake the a-l interface at an ELPC front.
Experimentally accessing the section of the IRF below $T_{mc}$ has been challenging since previous investigations have been limited to steady-state situations. The results presented in Fig. 3 can be used to address these details of the c-l IRF and the intercept scenario provided a connection can be made between the position of the time dependent front and the front temperature. Since the crystallization front temperature is not available directly through experiment, we use numerical modelling to obtain an estimate of the temperature evolution through zone II as described in the Methods section. The essential feature of these results, as described previously, is that the front temperature through zone II is bounded at the inner radius by $T_{mc}$ and at the outer radius by $T_{ma}$, and that between these bounds the front temperature decreases monotonically with a trend following the Gaussian tail of the temperature distribution initially imprinted on the material through laser heating. The functional form of this temperature decrease is well approximated as linear with a small quadratic residual over the range $T_{mc}$ to $T_{ma}$. These features of the time-evolving temperature profile are a robust outcome of the modelling and not sensitive to the specific value of the material parameters used.

Using the results of this modelling to map delay time (or crystallization front position) onto front temperature (with uncertainties estimated from the quadratic residual), we plot the data in Fig. 3 as a function of temperature in Fig. 7.\textsuperscript{47} Previous experimental investigations of explosive crystallization have been limited to estimates of the peak crystallization velocity or the investigation of steady-state modes of crystallization, neither of which have allowed an experimental determination of the crystallization front IRF over a broad range of temperatures.\textsuperscript{22} By using the unique capabilities of DTEM to follow the evolution of an explosive crystallization front under rapidly evolving, non-steady-state conditions that cover the range of temperatures between $T_{mc}$ and $T_{ma}$ we were able to determine the IRF of the c-l interface over this entire range (Fig. 5). Such information has previously only been accessible through molecular dynamics simulations.\textsuperscript{44}

Qualitatively, the results presented in Fig. 7 suggest the following explanation for the time-dependence of the crystallization front velocity that is observed through zone II. Initially the average temperature at the crystallization front is high (close to $T_{ma}$) and the metastable liquid layer is only weakly undercooled. Under such conditions the front velocity is limited by the bracketed term in Eq. (3), which approaches zero as $T_{ma}$ approaches $T_{mc}$. The thermal modelling demonstrates that the interfacial undercooling increases as zone II grows, and this trend increases the front velocity up to the temperature associated with the maximum of the IRF in the back-side intercept scenario or the temperature associated with the intercept of the l-a and c-l IRFs in the front-side intercept scenario (Fig. 5). Following this peak crystallization speed of $\sim 16$ m/s, on par with the fastest reported for explosive crystallization phenomena, there is a gradual slowdown in the crystallization speed along with a significant increase in faceting. These combined observations suggest that the back-side intercept scenario best describes the relationship between the c-l and l-a IRFs for explosive crystallization in a-Ge. In the frontside intercept scenario we would initially expect a gradual increase in the speed of crystallization (as observed), but only to the intercept point with the melting branch of the l-a IRF. This lower peak velocity would be followed by an abrupt slowdown of the crystallization without a significant transition to faceted growth as the temperature dropped further since the crystallization front cannot persist in the region of the IRF where $v_c > v_p$. This is not in agreement with our observations. In the backside intercept scenario we expect a gradual slowdown in crystallization as the front temperature drops towards $T_{ma}$ due to the Arrhenius prefactor in Eq. (1). This should be accompanied by increased faceting of the dendrites towards the outer edge of zone II where growth is limited to low energy crystal directions as the front temperature approaches $T_{ma}$ (see Fig. 6). Both qualitative predictions of the backside intercept scenario are in agreement with observations.

At a microscopic level the crystallization front velocity is determined by the difference in the rates of atomic attachment and detachment at this interface. Two qualitatively distinct theories have been developed to describe the effective temperature dependence of this difference in rates on the IRF: transition state theory (TST) and diffusion limited theory (DLT).\textsuperscript{22,46,48} Both lead to an expression for the IRF that is identical to Eq. (3), yet differ in terms of the physical meaning of the parameters that appear in that equation. In conventional TST the Arrhenius prefactor, $A_c$, is taken to be fundamentally limited by the speed of sound, $v_s$, in the material,\textsuperscript{46} i.e., $A_c \leq v_s \sim 4$ km/s in Ge. In the DLT, on the other hand, the Arrhenius prefactor is given by

$$A_c = A_{0c} v_s f,$$

where $f$ is the fraction of active sites at the interface (i.e., $f \leq 1$), $d$ is the average distance the interface moves through

\[E_C(x) = \begin{cases} 3 \times 10^{-19} & 0 < x < 0.05 \\ 0.05 \chi^2 & \text{contour shown in the inset.} \end{cases}\]
atomic attachment, and \( \omega_0 \) is an attempt frequency. The attempt frequency depends on the prefactor for the diffusion constant \( D(T) = D_0 \exp\left[-Q/k_BT\right] \) in the interfacial region and the characteristic diffusion distance for attachment, \( \lambda_c \), according to
\[
\lambda_c = \sqrt{D_0 df/A_c}.
\]
This expression contains several variables \((D_0, d, f)\) that are not known with precision under the metastable conditions that are thought to prevail in the local region of the crystallization front. However, estimates of \( \lambda_c \) can be made under the limiting cases of diffusion in equilibrium crystalline and liquid Ge, and the reasonable assumptions that \( d \) is approximately equal to half the lattice constant for crystalline Ge, 5.66 Å, and that \( f = 1 \). The prefactor for diffusion, \( D_0 \), has been previously reported as \( 2.54 \times 10^{-3} \text{m}^2/\text{s} \) for crystalline Ge and \( 4 \times 10^{-8} \text{m}^2/\text{s} \) for liquid Ge. Thus, for \( A_c \), in the range of \( 5 \times 10^{-3} - 1 \times 10^{11} \text{m/s} \) (providing agreement with the data at the \( p \approx 0.05 \) level) we obtain characteristic diffusion distances for the crystal-like case, \( \lambda_{cl} \sim 10^{-10} - 10^{-12} \text{m} \) and for the liquid-like case, \( \lambda_{li} \sim 10^{-13} - 10^{-16} \text{m} \). The range determined for crystal-like diffusion overlaps with length scales that are characteristic for the mean-square vibrational amplitude of atoms about their lattice sites, while the range determined for liquid-like diffusion appears to be unphysically small. Taken together, the observations of solid-like activation energies and a characteristic diffusion length in the range of vibrational motion suggest that the phase of Ge in the local region of the explosive crystallization front is kinetically distinct from an equilibrium liquid.

The model of ELPC outlined in the introduction was put forward to account for the observation of explosive crystallization front velocities in a-Si that were considerably higher than expected for an all solid-state crystallization process.

The presence of a thin “liquid-like” layer between the crystalline and amorphous phases was introduced as a possible explanation for these high velocities, since the presence of such a layer would enhance atomic diffusivity in the local region of the crystallization front relative to a direct crystal-amorphous interface. Several earlier indirect measurements have provided important support for this picture. In particular, transient conductance and time-resolved reflectivity measurements demonstrated that the electronic and optical properties of the material near the explosive crystallization front (or under the conditions thought to prevail at the front) are consistent with those expected for a phase change from amorphous to liquid germanium. These measurements, however, are not directly sensitive to the details of atomic diffusivity that are central to the crystallization kinetics.

The measurement presented here for the complete IRF of the explosive crystallization front, and subsequent fitting to the Frenkel-Wilson law, reveals atomic diffusivity in the local region of the explosive crystallization front that is not at all liquid-like and calls into question such a characterization of the mediating material. An alternate view that preserves many of the same features of this model and is in better agreement with the current data is to identify this leading interface with a change in bonding rather than a change in phase. In liquid Ge, a transition between covalent and metallic bonding character has been reported on heating the liquid from the melting point. A similar transition in bonding character from covalent to metallic (with an associated density change) could also occur in the amorphous phase of Ge under rapid heating. The activation energy for self-diffusion near the interface reported here is significantly lower than expected for the crystalline phase and may be a result of this change in bonding character.

Future work will employ ultrafast electron diffraction to specifically interrogate the nature of structural relaxation in laser excited a-Ge with the aim of addressing this issue. High-resolution imaging of the interfacial region at the explosive crystallization front is beyond the capabilities of current generation DTEM instruments given the spatio-temporal resolution required. The crystallization front moves at speeds up to 16 m/s (or 16 nm/ns) and the effective exposure time of a single image is currently 15 ns due to the electron pulse duration (see Methods section). Thus, the front moves by as much as 240 nm during exposure and motion blur obscures the details of the c-l and l-a interfacial region in the current experiments. Exposure times on the order of 100 ps (or below) would be required to preserve interfacial details in the images, since this region is expected to be only a few tens of nm thick. Unfortunately, space
charge dynamics in the electron beam may make single shot imaging with spatio-temporal resolution approaching 1 nm/100 ps an impossibility. In addition, the differential imaging contrast between the two disordered phases at the crystallization front (the hot amorphous phase and the undercooled “liquid-like” phase) will be extremely small even if the DTEM has the required resolution to see the interface in principle. Since the challenges associated with obtaining high-resolution DTEM images of the interfacial region are immense, follow-up studies will focus on time-resolved electron diffraction of the laser-induced structural relaxation in a-Ge. Ultrafast electron diffraction is extremely sensitive to changes in the atomic-pair correlation function (radial distribution function) of the material and can be expected to yield important new information on this transition.

V. CONCLUSIONS

Recent enhancements in DTEM allow the following of complex microstructural evolution with nanosecond temporal and nanometer spatial resolutions. Here, we applied this technique to quantitatively study nanosecond laser initiated explosive crystallization in amorphous germanium films. Specifically, DTEM observation of transient explosive crystallization fronts evolving through material that is subject to a laser-imprinted temperature gradient has enabled a direct determination of the interface response function for this process over the entire range of relevant temperatures. This has not previously been possible using steady-state experimental approaches. Fitting this data to the Wilson-Frenkel kinetic law demonstrates that the conventional TST model that sets the speed of sound as an upper limit for the Arhenius prefactor is in very poor agreement with measurements. DLT is in better agreement with the data, yet indicates that the self-diffusion characteristics of the material in the local region of the explosive crystallization front are solid-like rather than liquid-like. These observations suggest that the nature of the co-propagating c-l and l-a interfaces that form the ELPC mechanism commonly used to describe this process should be revisited. A modification of this model that is in better agreement with measured interface response function replaces the phase change at the leading l-a interface with a more subtle change in bonding character from covalent to metallic in the hot amorphous material.

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47 The temperature plotted in Fig. 7 is the crystallization front temperature that we extract from the lumped interface modeling one gridpoint in advance of the delta-function source. The horizontal/temperature error bars on the points in Fig. 7 represent our best estimate of the way that the uncertainty in the time-dependent position of the delta-function source (the uncertainties associated with the data in Fig. 3) propagates through the modeling into c-l front temperature. This was determined by computing the time-dependent temperature field (with the model described above) with the range of source trajectories that is consistent with the data in Fig. 3 in a monte-carlo like manner.