Determination of crystal growth rates during rapid solidification of polycrystalline aluminum by nano-scale spatio-temporal resolution *in situ* transmission electron microscopy

K. Zweijacker,^{1,a)} J. T. McKeown,² C. Liu,¹ T. LaGrange,^{2,b)} B. W. Reed,^{2,c)} G. H. Campbell,² and J. M. K. Wiezorek¹

¹Department of Mechanical Engineering and Materials Science, University of Pittsburgh, 648 Benedum Hall, 3700 OHara Street, Pittsburgh, Pennsylvania 15261, USA

²Materials Science Division, Physical and Life Science Directorate, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, California 94551, USA

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In situ investigations of rapid solidification in polycrystalline Al thin films were conducted using nano-scale spatio-temporal resolution dynamic transmission electron microscopy. Differences in crystal growth rates and asymmetries in melt pool development were observed as the heat extraction geometry was varied by controlling the proximity of the laser-pulse irradiation and the associated induced melt pools to the edge of the transmission electron microscopy support grid, which acts as a large heat sink. Experimental parameters have been established to maximize the reproducibility of the material response to the laser-pulse-related heating and to ensure that observations of the dynamical behavior of the metal are free from artifacts, leading to accurate interpretations and quantifiable measurements with improved precision. Interface migration rate measurements revealed solidification velocities that increased consistently from $\sim 1.3 \text{ m s}^{-1}$ to $\sim 2.5 \text{ m s}^{-1}$ during the rapid solidification process of the Al thin films. Under the influence of an additional large heat sink, increased crystal growth rates as high as 3.3 m s^{-1} have been measured. The *in situ* experiments also provided evidence for development of a partially melted, two-phase region prior to the onset of rapid solidification facilitated crystal growth. Using the experimental observations and associated measurements as benchmarks, finite-element modeling based calculations of the melt pool evolution after pulsed laser irradiation have been performed to obtain estimates of the temperature evolution in the thin films. *Published by AIP Publishing.*

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I. INTRODUCTION

Laser processing of metals and alloys involves extreme thermo-mechanical conditions which are exploited in technologies for thin film device modification, material joining, and additive manufacturing. During selective laser melting (SLM), the bulk material, powders, or thin-films undergo driven first-order phase transformations and the resulting micro-structures will strongly deviate from equilibrium. The photon irradiation will result in large thermal gradients of $\sim 10^5\text{--}10^7 \text{ K m}^{-1}$ over small timescales which will ultimately lead to rapid cooling rates of $10^5\text{--}10^7 \text{ K s}^{-1}$ and transformation interface velocities of $\sim 10^{-2} \text{ m s}^{-1}$ to $\sim 10^2 \text{ m s}^{-1}$.^{1–3} Under these extreme conditions, growth at solid–liquid interfaces can be essentially barrier-less, limited only by the kinetic attachment of atoms to the growing solid phase or phases. This inherent non-equilibrium process enables extraordinary micro-structural changes such as scale refinements, solid solubility limit extensions, non-equilibrium

phase formation, and even partition-less crystal growth in alloys. Hence, the growth dynamics, and the micro-structures present, are scientifically interesting and technologically important. *In situ* transmission electron microscopy (TEM) studies of irreversible reactions in condensed matter often provide critical mechanistic understanding and measurements that can be uniquely effective to support computer model development.^{4–6} However, conventional TEM-based *in situ* studies typically offer temporal resolution in the millisecond range, which is insufficient for investigations of RS process dynamics.^{5,7,8} The dynamic transmission electron microscope (DTEM), a TEM modified by two complex laser systems, offers nano-scale spatiotemporal resolution, rendering it uniquely suited for studies of irreversible transitions in materials, including those associated with RS transformations.^{8–16} The DTEM uses intense electron pulses of durations as short as 15 ns for the acquisition of images or diffraction patterns. In its original operational mode, the DTEM was limited to acquisition of a single image or diffraction pattern at a preselected delay time after initiation of the irreversible transition event, i.e., a single-pump/single-probe mode.^{8,9,12,14} Hence, past DTEM studies of RS in Al and Al-Cu alloys required the performance of a series of multiple, separate experiments with varied delay times in order to obtain information on the transformation

^{a)}Present address: Empa - Swiss Federal Laboratories for Materials Science and Technology Ueberlandstrasse 129, 8600 Dübendorf, Switzerland. Electronic mail: Kai@zweijacker.org.

^{b)}École Polytechnique Fédérale de Lausanne, Interdisciplinary Centre for Electron Microscopy, MXC 134 (Batiment MXC), Station 12, CH-1015 Lausanne.

^{c)}Integrated Dynamic Electron Solutions, Pleasanton, CA 94588, USA.

rates.^{8,9,12,14} While a single-probe pulse acquisition intrinsically offers temporal resolution on the ns-scale for each single image or diffraction pattern, the uncertainty in the transformation rates determined from a series of separate DTEM experiments can be significantly larger, involving contributions from systematic and non-systematic errors. For RS in Al-Cu alloy thin films, a range of absolute error for the instantaneous solidification front velocity was reported as $\pm 0.6 \text{ m s}^{-1}$, representing a relative error of about 30% for a 2 m s^{-1} transformation rate measurement.¹⁴ Sources of error include the $\sim 5\%$ pulse-to-pulse fluence fluctuations of the specimen-drive-laser system that delivers the heating pulse to the specimen, and reflectivity variations from microstructure differences, e.g., grain size and surface roughness, between the multiple specimens used in single-pump/single-probe mode DTEM *in situ* studies, which may affect small variations in the initial melt pool dimensions. Furthermore, prior DTEM RS studies used a small field of view for locally resolved observations of small sections or segments of the evolving melt pool boundary.^{8,9,12,14} Thus, determination of the transformation interface velocity required reliance on assumptions regarding the melt pool size and shape with relatively large inherent uncertainty, further challenging the reliability of the reported transformation rates.^{8,14}

Recent upgrades of the DTEM instrumentation have successfully enabled single-pump/multiple-probe operation for acquisition of multiple images or diffraction patterns per each transformation event triggered by the pulsed-laser irradiation.^{15,17,18} In this operational mode, termed Movie Mode DTEM (MM-DTEM), the laser-pulse-driven photoelectron cathode of the modified instrument can provide electron pulse trains, permitting acquisition of up to nine (9) frames of images or diffraction patterns per single-shot stimulated dynamic event within as little as $\sim 1 \mu\text{s}$.¹⁷ This is equivalent to a frame rate $\sim 10^6$ times higher than those of conventional tv-rate *in situ* TEM experiments. Compared with prior *in situ* DTEM studies using the single-pump/single-probe operational mode,^{8,11,13,14,16,18} the MM-DTEM experiments offer potential to greatly reduce uncertainties in quantitative measurements of transformation front velocity evolution during RS and increase significantly the data density obtained from direct observations of the dynamics of the irreversible transformation event induced by a single laser pulse.^{15,17} The current paper reports and discusses first results of MM-DTEM *in situ* investigations of the dynamics of pulsed-laser-induced melting and RS in 160 nm thick Al thin films with a focus on establishing experimental methodology for reproducible quantitative measurements of the transformation rates. Specifically, we assessed the effects from the Si frame support of the window-type TEM grids used in the DTEM *in situ* experiments on the solidification velocity measurements. Compared to the regions of the thin film specimen in the electron transparent window, the Si frame support represents a massive heat sink and can alter the thermal transport geometry significantly. Monitoring of entire melt pools during the *in situ* experiments permitted measurement of location-specific differences in the interface migration rates during RS, which involved directional growth of columnar crystals and was facilitated by thermally driven migration of

morphologically planar solidification interface segments at rates as high as $\sim 3.3 \text{ m s}^{-1}$. Evidence for development of a partially melted, two-phase region during the initial stages after laser irradiation has been detected. Multi-physics-based computer numerical modeling of the melt pool size and shape changes, and associated transformation rate calculations enabled calculation of the thermal field evolution and confirmed the dominance of essentially two-dimensional, planar thermal transport during the RS of the Al thin films.

II. EXPERIMENTAL PROCEDURES AND MATERIALS

Polycrystalline Al thin films, 160 nm thick, were deposited on 50 nm thick amorphous Si_3N_4 membranes of commercially available windowed TEM grids (Ted Pella) by electron beam evaporation. During depositions using 99.999% purity Al as source material, the chamber pressure and substrate temperature were kept below 5×10^{-8} Torr and at 298 K, respectively. Thus, specimens suitable for *in situ* DTEM experimentation with electron transparent, square-shaped areas of $0.5 \text{ mm} \times 0.5 \text{ mm}$ dimensions have been obtained, as shown schematically in Figs. 1(a) and 1(b). Further details of the specimen preparation have been reported previously.^{13,14,16,19} Notably here, unlike in prior reports, no capping layers have been deposited on the Al layer.^{8,11,20,21} Regions of the TEM grid sample adjacent to the electron transparent region are supported by a substrate of Si. Relative to solid Al, the thermal conductivity of amorphous Si_3N_4 is about twenty times smaller, while that of solid Si is comparable.^{22,23} Also, within about $1 \mu\text{m}$ from the edge of the electron transparent window, the Si substrate frame thickness reaches about $1.4 \mu\text{m}$ (Fig. 1(a)). Therefore, it is necessary to evaluate the possible effects of the Si frame acting as an effective heat sink on the transformation dynamics in order to ensure that reliable solidification interface velocity measurements are obtained from *in situ* DTEM experiments using the TEM grid-based specimens. Hence, nominally identical MM-DTEM experiments have been performed for five different locations with systematically varied distances, Δx , in the range of $50 \mu\text{m} \leq \Delta x \leq 250 \mu\text{m}$, from the edge of the electron transparent window, as indicated schematically in Fig. 1(b). *In situ* TEM experiments were performed with the DTEM at Lawrence Livermore National Laboratory^{15,17} where an Nd-YAG laser produces a single, 12 ns duration pulse with a primary wavelength of 1064 nm and a Gaussian beam profile in order to stimulate transformations in the specimen. Laser pulses delivering a total of $\sim 72 \mu\text{J}$ to the specimen in the DTEM column provided photon stimuli to initiate the melting of the Al film (Figs. 1(a) and 1(b)). Pulse-to-pulse energy fluctuations of 5% have been determined for the Nd-YAG laser. The heating laser pulse is incident at an angle of $\sim 45^\circ$, producing elliptically shaped irradiation cross-sections with the thin film sample, as shown schematically by the superimposed intensity profiles with ISO-intensity lines ranging from 100 (red) to 13.5% or $\sim 1/e^2$ (gray) of peak fluence for location (1) in Fig. 1(b). Nominally identical laser pulses were placed on the electron transparent region of the Al thin film specimens at different locations with systematically varied distances Δx

FIG. 1. (a) Schematic of a cross-sectional view of the Al thin film on the amorphous Si_3N_4 membrane of the electron transparent window, inclusive of the thick Si substrate support frame of the windowed TEM grid. (b) Schematic plan-view depiction of the $500\text{ }\mu\text{m} \times 500\text{ }\mu\text{m}$ electron transparent window. At locations (1)–(5), nominally identical laser pulses were placed where the gray ellipses indicate the 13.5% ISO-Intensity line of the peak laser pulse fluence. The dashed line ovals are associated melt pools where $\Delta x, y$ describes the distances from Si substrate frame. (c) Schematic of the MM-DTEM electron pulse train with temporal resolution of 50 ns in individual image frames (gray shade blocks) and $2.50\text{ }\mu\text{s}$ inter-frame spacing.

from the edge of the Si substrate support frame as marked by the labels (1) to (5) in Fig. 1(b), in order to determine the effect of Δx on the phase transformation dynamics. The distances Δx have been measured from the center of the incident pulsed laser irradiation as the shortest distances to the edge of the electron transparent window (e.g., location marked by label 3 at $\Delta x = 100\text{ }\mu\text{m}$, Fig. 1(b)). The MM-DTEM electron pulse train selected for the *in situ* experiments performed here, illustrated schematically in Fig. 1(c), enabled observation of the entire melting and subsequent solidification sequence and minimized effects from motion blur while maximizing image contrast in each frame. Each experiment delivered nine 50 ns exposure-time image frames, collected with an inter-frame delay of $2.5\text{ }\mu\text{s}$ during the $20.4\text{ }\mu\text{s}$ total time interval of observation (Fig. 1(c)). The peak of the Gaussian sample-modifying laser pulse is referenced as time t_0 , with the first frame set to t_0 and each subsequent frame collected at time $t_{\text{img}} = t_0 + \Delta t$, i.e., at a time delay Δt after t_0 (Fig. 1(c)). The temporal resolution is therefore 50 ns for each individual frame, while temporal resolution for transformation dynamics observations is limited by the $2.55\text{ }\mu\text{s}$ inter-frame delay time of the electron pulse train (Fig. 1(c)). The image series have been recorded as laterally displaced individual images by using an electrostatic deflector system that translates each frame to a different segment of a $2\text{k} \times 2\text{k}$ charged-coupled device (CCD) camera with single-electron detection sensitivity.^{15,17} Post-acquisition image processing and analysis have been performed using the ImageJ(Fiji) software (NIH, <http://imagej.nih.gov/ij/>) environment in order to determine quantitatively the area of liquid Al in the DTEM BF images. For the regular elliptical shape melt pool area, measurements of the radii along the major and minor axes, r_{max} and r_{min} , as well as that of r , the geometric-mean radius, representing the radius of circular area equivalent in size to the actual melt pool area have been obtained for each DTEM BF image. The radii have been determined with an absolute error range no worse than six (6) pixels from the DTEM BF images, corresponding to $\approx \pm 500\text{ nm}$. Motion blur in a 50 ns exposure BF image of the

MM-DTEM series for a solid–liquid interface migrating at a rate of 1 m s^{-1} limits the spatial resolution to 50 nm and is not a limiting factor for the determination of the transformation interface velocities from the temporal evolution of the respective melt pool radii.

A JEOL JEM 2100F TEM instrument equipped with a device (ASTAR/DigiSTAR, NanoMEGAS) for precession electron diffraction (PED)-based automated crystal orientation mapping (ACOM) has been used for the microstructure analysis of the films.^{20,24} The PED-based ACOM has been performed with 200 kV electrons, 0.6° precession half-angle, 2 nm probe size, and 10 nm step size on typically $1.5\text{ }\mu\text{m} \times 1.5\text{ }\mu\text{m}$ to $2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$ area scans.^{20,24}

Multi-physics finite element modeling has been performed in the COMSOLTM (version 5.1, COMSOL, Inc.) software environment using a modified enthalpy model, which solves the Stefan problem by adopting the enthalpy density as the dependent variable, for calculations of temperature evolution in the thin film sample after delivery of a laser pulse.^{25,26} The Gaussian laser pulse profile characteristics used in the model calculations were constrained to the experimentally utilized parameters regarding the elliptical shape and size on the sample, e.g., diameters of $\sim 135\text{ }\mu\text{m}$ and $\sim 190\text{ }\mu\text{m}$ along the minor and major axes. The model calculations used temperature independent thermo-physical properties for the solid phases and the liquid Al phase consistent with literature and summarized in Table I.

The model assumed no contribution from convection in the liquid to the heat transfer. The model accounted for the heat of crystallization of Al, and considered the differences in densities and optical reflectivity for the incident laser radiation of the solid and liquid Al. A composite-model has been used for a phenomenological treatment of the relative contributions of the Al and amorphous Si_3N_4 layers to heat conduction for a simulated sample geometry comprising a $500\text{ }\mu\text{m}$ side length square area of initially solid Al equivalent to the 160 nm thick film with the 50 nm Si_3N_4 support layer and boundary conditions at the perimeter of an infinite heat sink representing the Si frame. The effective contribution of the nitride layer to

TABLE I. Thermo-physical Properties used in the COMSOL Simulations.^{22,23,27–29}

Property		Unit
Thermal conductivity Al_s	210–230	$W m^{-1} K^{-1}$
Thermal conductivity Al_l	90	$W m^{-1} K^{-1}$
Density Al_s	2640	$kg m^{-3}$
Density Al_l	2350	$kg m^{-3}$
Density Si_3N_4	3100	$kg m^{-3}$
Thermal conductivity Si_3N_4	8–20	$W m^{-1} K^{-1}$
Thermal conductivity Si	150	$W m^{-1} K^{-1}$
Heat capacity Al_s	1000	$J kg^{-1} K^{-1}$
Heat capacity Al_l	1095	$J kg^{-1} K^{-1}$
Heat capacity Si_3N_4	700	$J kg^{-1} K^{-1}$
Heat of fusion Al	398	$kJ kg^{-1}$
Melting point of Al	933	K
Reflectivity Al_s	0.95	
Reflectivity Al_l	0.9	

heat conduction after the laser irradiation pulse established an Al melt pool has been evaluated by varying the fraction of amorphous Si_3N_4 in the simulated composite sample. These calculations indicated that the small thermal conductivity of the amorphous Si_3N_4 resulted in thermal conduction being strongly dominated by the Al thin film during solidification. The experimentally determined metrics used to benchmark the model calculation results included the size of the melt pool of Al, the time delay between delivery of the laser pulse to the onset of directional rapid solidification, the total time to complete solidification, and the temporal evolution of the solid–liquid interface velocity during solidification.^{27–29}

III. RESULTS AND DISCUSSION

A. Al thin film structure

The PED TEM-based ACOM data sets displayed in Fig. 2 represent Al deposited thin films on the Si_3N_4 -membranes. The inverse pole figure (IPF) maps for the crystal directions parallel to the film normal (Fig. 2(a)) and the in-plane crystal directions parallel to the vertical y-direction (Fig. 2(b)), together with the associated pole figure plots (Fig. 2(d)), reveal a strong preference for alignment of the 111-poles parallel to the film normal direction, i.e., a fiber-type thin film 111-growth texture. No preferred orientations are discernible for the crystal directions contained in the

plane of the thin film (Figs. 2(b) and 2(d)). Using index quality maps superimposed on virtual BF images give accurate information on grain-size and grain-boundary character³⁰ (e.g., Fig. 2(c)), thus delineating clearly the grain boundaries and exhibiting orientation contrast. The Al film grain size has been determined as $160 nm \pm 10 nm$. Therefore, prior to the pulsed-laser-induced transformation during the DTEM experiments, the Al thin films exhibited polycrystalline nature with an average grain size about equal to the film thickness with a well-developed 111-type fiber texture along the film normal. These structural characteristics are consistent with standard models for face-centered cubic (fcc) metal thin film growth-related structural evolution for substrate temperatures of $T = 298 K \approx 0.32 T_m$, where $T_m = 933 K$ is the melting point of Al.²¹

B. In-situ DTEM movie mode observations

The low spatial resolution imaging in the DTEM enabled monitoring of the evolution of the entire melt pool in each of the $20.4 \mu s$ duration *in situ* experiments that capture the entire transformation sequence (Fig. 3). For melt pools produced by nominally identical laser irradiation pulses incident at the systematically varied distances, Δx , from the edge of the thick Silicon support frame, effects from the support frame should manifest in different interfacial dynamics during the transformation sequences observed in the experiments. In Fig. 3(a), $\Delta x = 50 \mu m$, the electron-opaque region is visible in the top part of frame ($0 \mu s$) at $t_{img} = 0 \mu s$, as marked by the yellow lines. The electron pulse train in the MM-DTEM series of Fig. 3 is timed such that the first 50 ns duration imaging electron pulse, frames (1) of Figs. 3(a)–3(e), annotated as (1), coincides with the peak of the 15 ns duration laser irradiation pulse on the sample (Fig. 1(c)). The characteristic diffuse oval shape with reduced contrast observed in the first 50 ns of the transformation sequence ($t_{img} = 50 ns$, frames (1) in Figs. 3(a)–3(e)) can be attributed to increased thermal diffuse scattering associated with the heating and melting of the Al. It is assumed that melting advances from the surface through the thickness of the film. Prior reports on DTEM experiments using BF imaging and selected area diffraction established that the heating and melting of crystalline metals and alloys induced by the incident laser irradiation result in increased scattering of the electrons in the image forming probe pulse, and thus reduced brightness in BF images (L in frame (4) of Fig. 3(c)) relative

FIG. 2. PED TEM ACOM of as deposited Al film, (a) IPF orientation map of film normal, (b) IPF orientation map for in-plane vertical y-direction, (c) virtual BF image and index quality map overlay, and (d) the respective 100, 110, 111 pole figures.

FIG. 3. *In-situ* DTEM Movie Mode bright field image series from locations (1) to (5) (Fig. 1). (a) $\Delta x = 50 \mu\text{m}$, (b) $\Delta x = 75 \mu\text{m}$, (c) $\Delta x = 100 \mu\text{m}$, (d) $\Delta x = 200 \mu\text{m}$, and (e) $\Delta x = 250 \mu\text{m}$. Each series contains nine individual frames marked (1) to (9). The labels L and S refer to all-liquid and all-solid regions. See text for further details.

to the brighter contrast levels of surrounding nanocrystalline solid Al (S in frame (4) of Fig. 3(c)).^{8–10} The image series is obtained for $\Delta x = 50 \mu\text{m}$ (location (1), Fig. 1(b)) document asymmetries in the melt-pool development from $t_0 = t_{\text{img}} = 0 \mu\text{s}$ to $t_{\text{img}} = 12.75 \mu\text{s}$ (Fig. 3(a)). The close proximity of the Si substrate affects the heat extraction geometry, resulting in notable deviation of the melt pool shape from the elliptical shape of the laser irradiation pulse profile (Fig. 3(a), frames (2)–(5)). Solidification rates are considerably higher for the liquid in closer proximity to the Si support frame than for locations on the opposite side of the melt pool at larger distances from the edge of the electron transparent window. As a result, the last remaining liquid resides at a significantly off-center location relative to the center of the incident elliptical laser irradiation pulse profile (marker x, Fig. 3(a), frames (1) and (5)). In Fig. 3(a), solidification completes after frame (5), $t_{\text{img}} = 10.2 \mu\text{s}$, and prior to frame (6), $t_{\text{img}} = 12.75 \mu\text{s}$. The transformation sequence shown in Fig. 3(b) has been obtained for $\Delta x = 75 \mu\text{m}$ (location (2) in Fig. 1(b)). Melt-pool shape distortions relative to the elliptical shape incident laser irradiation pulse profile are negligible, and the last remaining liquid Al is observed in frame (7) of Fig. 3(b) at $t_{\text{img}} = 15.3 \mu\text{s}$, approximately in the center of the laser irradiated area, and solidification completes prior to frame (8) in Fig. 3(b), $t_{\text{img}} = 17.85 \mu\text{s}$. The MM-DTEM series for pulsed laser irradiation at distances Δx of $100 \mu\text{m}$, $200 \mu\text{m}$, and $250 \mu\text{m}$ (locations (3) to (5), Fig. 1(b)) is shown in Figs. 3(c)–3(e), respectively. Elliptical melt pools of approximately the same size exhibit essentially identical temporal evolution for these latter locations at distances $\Delta x \geq 100 \mu\text{m}$ from the edge of the Si support frame. Solidification of the Al completes reproducibly in the symmetry center of the elliptical shape irradiated area after $t_{\text{img}} = 17.85 \mu\text{s}$ and prior to $t_{\text{img}} = 20.4 \mu\text{s}$ (Figs. 3(c) and 3(e), frames (8) and (9)). Minor qualitative differences can be inferred from the small variations in the fraction of liquid retained in the images obtained at $t_{\text{img}} = 17.85 \mu\text{s}$ (frame (8), Figs. 3(c) and 3(e)). However, these latter variations are not systematic with the magnitude of the distance, Δx , e.g., at $\Delta x = 200 \mu\text{m}$ less liquid Al remains than at $\Delta x = 250 \mu\text{m}$

(frame (8), Figs. 3(d) and 3(e)), but correlate with the small but significant differences in the initial melt pool dimensions measured at $t_{\text{img}} = 5.1 \mu\text{s}$ (Figs. 3(c)–3(e), frames (3)) and are attributed mainly to the effects of up to $\pm 5\%$ fluctuations in pulse-to-pulse energy specified for the sample drive laser system used to induce melting at t_0 . Thus, at distances $\Delta x \geq 100 \mu\text{m}$ from the edge of the electron transparent window, the pulsed laser irradiation induced melting and solidification dynamics for the Al thin films are reproducible within the spatio-temporal resolution margins of the *in situ* MM-DTEM experiments.

For the location with $\Delta x = 50 \mu\text{m}$, a very large portion of the Gaussian laser pulse photon distribution covers the thick Si frame support (Fig. 1(b), location (1)). For the location with $\Delta x = 75 \mu\text{m}$, still a small portion of the laser pulse profile is incident on the Si supported region of the specimen (Fig. 1(b), location (2)). For the locations with $\Delta x \geq 100 \mu\text{m}$ (Fig. 1(b), labels (3)–(5)), the incident laser pulse profiles are entirely contained on the electron transparent window. For the latter locations, the thermal transport from the melt pool is essentially two-dimensional and limited to the Al layer, resulting in symmetric heat extraction rates at opposite side melt pool interfaces during the transformation sequence, and the expected elliptically shaped melt pools are obtained. For the portion of the laser irradiation profile incident on the Si substrate supported thin film, the thermal transport geometry is three-dimensional, including heat extraction into the Si substrate along the z-direction through the thickness as well as along the x- and y-directions within the plane of the thin film.² Therefore, asymmetric thermal transport geometry results in locations where the laser pulse profile significantly overlaps the electron transparent window and the adjacent Si substrate supported regions. This causes large deviations from the expected elliptical shape of the melt pool and results in an overall smaller melt pool and shorter time to complete solidification observed in MM-DTEM experiments presented in Figs. 3(a) and 3(b) relative to those of Figs. 3(c)–3(e).

Hence, a safe distance ($\Delta x, y \geq 100 \mu\text{m}$) from the Silicon support frame needs to be maintained in order to prevent

artifacts resulting from modifications of the heat extraction geometry and ensure reliable RS transformation rate measurements. For laser irradiation induced melt pools within this region, the heat conduction is approximately two-dimensional, i.e., radially outward from the melt pool perimeter into the surrounding solid, and dominated by the Al layer in the thin film specimens. Numerical modeling of the solidification process supports this conclusion (see Section III D).

For each of the MM-DTEM image series in Fig. 3, a sharp interface between the liquid and surrounding solid Al (e.g., label L and S in Fig. 3(c), frame c) can be discerned for the times $t_{\text{img}} \geq 5.15 \mu\text{s}$ until completion of solidification. However, this is not the case for image frames acquired at $t_{\text{img}} = 2.55 \mu\text{s}$ (Fig. 3). Fig. 4 displays the frames (2) from Figs. 3(a)–3(e) at larger magnification. Consistently, the presence of crescent shaped regions exhibiting gray-level contrast intermediate to that of the dark gray liquid (L in Fig. 4(c)) and light gray of the nanocrystalline solid Al thin film (S in Fig. 4(c)) can be detected. As a result, the liquid–solid interface appears more diffuse, rendering confident measurements of melt pool size difficult. In Fig. 4(a), $\Delta x = 50 \mu\text{m}$, and Fig. 4(b), $\Delta x = 75 \mu\text{m}$, these intermediate gray-level contrast areas at the melt pool edge near label 2 are larger than those near label 1. This is consistent with the asymmetries in the thermal fields resulting from the Si support acting as an effective heat sink. Conversely, for laser pulse incidences at locations with $\Delta x \geq 100 \mu\text{m}$, these regions at opposite sides of the melt pools exhibit the same size. This is consistent with MM-DTEM observations at these locations being essentially free from artifacts introduced by the proximity of the Si support frame (Figs. 4(c) and 4(e)).

These diffuse intermediate-contrast regions along the melt pool perimeter appeared within the first stages, $t_{\text{img}} \leq 2.55 \mu\text{s}$, of the pulsed-laser-induced solid-to-liquid-to-solid transformation sequence of the Al and vanished over the subsequent $2.55 \mu\text{s}$, prior to onset of RS, recorded at $t_{\text{img}} \geq 5.15 \mu\text{s}$ (Fig. 3). We propose that these regions, present in MM-DTEM images at $t_{\text{img}} \leq 2.6 \mu\text{s}$ (e.g., Fig. 4), are associated with two-phase regions where liquid and solid coexist during the melting stage of the transformation sequence that precedes the solidification stage. The presence of narrow, $\sim 2 \mu\text{m}$ width, partially melted regions at the perimeter of top-hat profile laser-pulse-induced melt pools in thin films has been inferred in prior reports.^{31,32} The Gaussian laser irradiation pulse would be expected to induce surface

melting within sub-nanosecond time scales, followed by melting through the full Al layer thickness in the central region where the highest laser pulse power was delivered, presumably within time frames no longer than several nanoseconds.^{33,34} Subsequently, lateral expansion of the melt pool would involve migration of the liquid–solid interface that initially is inclined through the Al layer thickness. Solidification has been recorded in the MM-DTEM experiments to commence only for $t_{\text{img}} \geq 5.15 \mu\text{s}$ (Fig. 3). During the lateral expansion of the melt pool at shorter times, e.g., $t_{\text{img}} = 2.6 \mu\text{s}$, the grains of the solid polycrystalline Al thin film in contact with the liquid would be consumed from their external surfaces towards their centers. Such a process, which would also likely involve melting along some grain boundaries in the nanocrystalline thin film,^{4,35–37} would naturally establish regions of coexisting solid and adjacent liquid Al, since some solid volumes of grains larger than the average grain size would remain at instances when adjacent, initially smaller grains have been fully converted to liquid. Prior reports attributed the presence of partially melted regions at the perimeter of single laser-pulse-induced melt pools in thin films of amorphous Si to the limited sharpness in laser profile.³¹ The projected incidence of the laser pulse on the specimen in the DTEM results in elliptically distorted thermal fields with reduced spatial gradient along the major diameter of the elliptical shape pulse profile. The proposed two-phase regions of coexisting solid and liquid develop to their maximal size in the MM-DTEM frames for $t_{\text{img}} \leq 2.6 \mu\text{s}$ within the laser profile segments where the associated thermal field gradients in the Al layer are shallow. These would be the locations where partially melted Al would be expected to persist longer, and association of these consistently observed crescent-shaped regions of intermediate contrast with partially melted regions,³² where for durations of several μs solid and liquid Al coexist, therefore appears reasonable. Additional higher spatio-temporal resolution, MM-DTEM studies are planned for the future to study this hypothesis.

C. Determination of crystal growth rates

RS of the Al thin film commences at $2.55 \mu\text{s} < t_{\text{img}} < 5.15 \mu\text{s}$ upon development of a sharp liquid–solid interface that is smooth, with low curvature and perpendicular to the plane of the film. The transformation interface remains stable against morphological changes, e.g., development of

FIG. 4. Collage of frames at $t_{\text{img}} = 2.55 \mu\text{s}$ from each image series of Fig. 3. (a) $\Delta x = 50 \mu\text{m}$, (b) $\Delta x = 75 \mu\text{m}$, (c) $\Delta x = 100 \mu\text{m}$, (d) $\Delta x = 200 \mu\text{m}$, and (e) $\Delta x = 250 \mu\text{m}$. The minimal distance from the melt pool center to the Si support frame is marked in (a). The crescent-shaped regions of diffuse contrast separating the all liquid (label L in (c)) and all solid (label S in (c)) regions are marked in (b) and (c). See text for further details.

perturbations, during its migration radially towards the center of the melt pools (Fig. 3, $t_{\text{img}} \geq 5.15 \mu\text{s}$). This is consistent with prior reports on metal thin film RS and thermally driven, directional crystal growth into a super-heated liquid.^{8,20,21,38} Fig. 5 summarizes results for the RS related transformation rate determination based on quantitative measurements obtained from direct observations of the transformation events recorded in the MM-DTEM experiments (Fig. 3). Figs. 5(a) and 5(b) illustrate the approach for quantitative determination of the solidification rate, using as a representative example the evolution of the melt pool created by the pulsed laser irradiation incidence at $\Delta x = 200 \mu\text{m}$. Fig. 5(a) shows the measurements of the radii along the minor, r_{max} , and major, r_{min} , axes obtained for the evolving elliptical melt pool. Prior to the onset of RS, $t_{\text{img}} = 2.55 \mu\text{s}$, the major and minor radii of the elliptical melt pool initially differ by about 33%, i.e., $r_{\text{max}}/r_{\text{min}} \approx 1.33 \pm 0.04$, which is consistent with the dimensions of the laser pulse profile within the error of the measurements. The error bars in Fig. 5 represent the variance σ , which includes the statistical error in the measurement as well as the systematic error introduced due to the fluctuation in laser energy. Both r_{max} and r_{min} monotonically decrease with time until the RS transformation completes. The rate of the melt pool radius reduction is faster for r_{max} than for r_{min} . Hence, depending on their specific location along the elliptically

shaped melt pool perimeter, liquid–solid interface segments exhibited a range of solidification velocities. The melt pool area has been determined from measurements of the radii along the major and minor axes of the elliptical pools of liquid Al, r_{max} , and r_{min} , respectively (e.g., Fig. 5(a)). The average solidification velocity along the entire interface of the elliptical shape melt pools can be obtained from the rate of change of the geometric-mean radius, r , which represents the radius of a circle of equivalent area to that measured for the corresponding elliptical melt pools observed experimentally. The geometric-mean radius data for the melt pool at $\Delta x = 200 \mu\text{m}$ are also shown in Fig. 5(a) and fall between the upper and lower bounds given, obtained for r_{max} and r_{min} .

In order to determine the rapid solidification interface velocity from the rate of change of the melt pool dimensions, both linear regression and second-order polynomial best-fit analyses have been performed for measurement points between $t_{\text{img}} = 5.1 \mu\text{s}$ and $t_{\text{img}} = 18.4 \mu\text{s}$ (e.g., solid and dashed lines in Fig. 5(a)). The measurement points for $t_{\text{img}} = 2.55 \mu\text{s}$ have been disregarded mainly due to uncertainty in the present interface behavior. The linear regression analyses deliver constant interface migration rates for the RS process. For the example illustrated in Figs. 5(a) and 5(b), $\Delta x = 200 \mu\text{m}$, the linear regression based constant solidification interface velocities were determined as $V_{\text{min}} \approx 1.6 \text{ m s}^{-1}$ and $V_{\text{max}} \approx 2.2 \text{ m s}^{-1}$

FIG. 5. (a) Evolution of the melt pool radii along the major axis, r_{max} , and minor axis, r_{min} , and for the geometric mean, the converted radius, during rapid solidification in the Al thin film for $\Delta x = 200 \mu\text{m}$, inclusive of linear regression and second-order polynomial best-fit, respectively; (b) RS interface velocity along major and minor radii directions for constant interface accelerations, inclusive of polynomial best fit curves for the respective major, minor, and geometric mean radii; (c) temporal evolution of the respective geometric radius for the experimental data sets for different Δx (Fig. 3) obtained by numerical modeling calculation (label Simulated); (d) associated solidification velocities. See text for further details.

along the minor and major axes, respectively, together with an extrapolated time to complete RS of $20.2 \mu\text{s}$ (Fig. 5(a)). At first glance, the constant migration rates would appear to be consistent with the experimental observation of RS completion in the interval $17.9 \mu\text{s} < t_{\text{img}} < 20.4 \mu\text{s}$ (Fig. 3(d)). However, the melt pool retained at $t_{\text{img}} = 17.9 \mu\text{s}$ for $\Delta x = 200 \mu\text{m}$ is considerably smaller than those observed for $\Delta x = 100 \mu\text{m}$ and $\Delta x = 250 \mu\text{m}$ (Figs. 3(c)–3(e), frames (h)) and would be expected to solidify before the latter two within the $2.55 \mu\text{s}$ interval prior to $t_{\text{img}} = 20.4 \mu\text{s}$. Hence, the extrapolated solidification time for $\Delta x = 200 \mu\text{m}$ of $20.2 \mu\text{s}$ predicted for the case of a constant interface migration rate during RS is too close to the upper bound of the experimentally determined interval $17.9 \mu\text{s} < t_{\text{img}} < 20.4 \mu\text{s}$ for completion of the RS process. Furthermore, it consistently initiates in the early stage and in the late stage of solidification overestimated and at intermediate stages underestimated the experimentally measured melt pool radii. These characteristic deviations from a linear rate of change for the radii of the melt pools during the RS stage indicate that the crystallization front interface migration rates may in fact not be constant but rather accelerate during RS. Using weighted $(1/\sigma^2)$ second-order polynomial best-fit functions, equivalent to the simple case of constant acceleration of the solidification interface, delivered improved match with the experimentally measured radii for the evolving melt pools for $t_{\text{img}} \geq 5.15 \mu\text{s}$ (e.g., Fig. 5(a)). The insert in Fig. 5(a) shows the residuals between measurements, the linear regression fit (circles), and the polynomial fit (squares). For early times, $t \sim 5 \mu\text{s}$, the polynomial fit reduces the residual by one order of magnitude for the major axis, and by a factor of two for the geometric-mean and the minor radius. For times between $t \sim 7 \mu\text{s}$ and $t \sim 10 \mu\text{s}$, the linear regression fit and the polynomial fit deliver comparable residuals. Near the end of the solidification processes between $t \sim 13 \mu\text{s}$ and $t \sim 18 \mu\text{s}$, the second-order polynomial fit shows the most significant reductions in the residual relative to the linear regression. Furthermore, the polynomial fit provided a reduced extrapolated time required for completion of solidification, for example, with $\Delta x = 200 \mu\text{m}$ from $20.2 \mu\text{s}$ to $19.3 \mu\text{s}$, now well within the experimentally determined interval $17.9 \mu\text{s} < t_{\text{img}} < 20.4 \mu\text{s}$ (Figs. 5(a) and 5(b)). Fig. 5(b) displays the polynomial best-fit functions obtained for the major and minor axes radii and the associated accelerating solidification interface velocities during RS for the minor and major radii of the melt pool example with $\Delta x = 200 \mu\text{m}$. The minor and major radii provide a lower and upper bound to the experimentally observed RS velocities V_{rmin} and V_{rmax} , and increase from $V_{\text{rmin}} \approx 1.4 \text{ m s}^{-1}$ and $V_{\text{rmax}} \approx 1.4 \text{ m s}^{-1}$ to reach $V_{\text{rmin}} \approx 2.0 \text{ m s}^{-1}$ and $V_{\text{rmax}} \approx 3.1 \text{ m s}^{-1}$, respectively, for the melt pool at $\Delta x = 200 \mu\text{m}$ during the RS process. The arrows in Fig. 5(b) mark the equivalent constant velocities of interface segments for migration along the minor (1.6 m s^{-1}) and major (2.2 m s^{-1}) radii. The ratio of the upper-bound to lower-bound RS facilitating interface velocities, e.g., $V_{\text{rmax}}/V_{\text{rmin}} \approx 2.7/2.0 = 1.35$ for the case of interface migration with constant acceleration and also for the constant interface velocity (e.g., $2.22/1.64 = 1.35$), simply scale with the initial dimensions of the elliptical melt pools, $r_{\text{max}}/r_{\text{min}} \approx 1.33 \pm 0.04$. The area

changes of the elliptical melt pools obtained for the laser irradiation incidence at locations with different values of Δx are represented by the changes of the respective geometric-mean radius, r , with time in Fig. 5(c). All melt pools monotonically reduce size for $t_{\text{img}} > 2.6 \mu\text{s}$, consistent with solidification by directional crystal growth (Fig. 5). The melt pool at $\Delta x = 50 \mu\text{m}$ is located closer to the substrate support frame (location 1, Fig. 1), which changes the heat extraction geometry and leads to the smallest and asymmetric starting melt pool dimensions. This ultimately results in a RS process with the highest interface migration rate and the shortest time to completion (Fig. 5(c)). For the laser incidence located at $\Delta x = 75 \mu\text{m}$, a melt pool with initial radius $r = 32 \mu\text{m}$, only slightly smaller than those for $\Delta x \geq 100 \mu\text{m}$ with $33 \mu\text{m} \leq r \leq 34.4 \mu\text{m}$, resulted at $t_{\text{img}} = 2.6 \mu\text{s}$ (Fig. 5(c)). Using the second-order polynomial best-fit functions for the geometric-mean radii, the solidification velocity evolutions shown in Fig. 5(d) have been obtained. Within the uncertainty associated with the MM-DTEM experiments, the melt pool size evolution rates are identical for locations with $\Delta x > 75 \mu\text{m}$ (Fig. 5(d)). During the RS stage, $t_{\text{img}} \geq 5.15 \mu\text{s}$, the average solidification interface section along the perimeter of the melt pools migrated at a constantly accelerating velocity, which increased from about 1.35 m s^{-1} to 2.5 m s^{-1} , with an average of 1.9 m s^{-1} , for locations with $\Delta x \geq 100 \mu\text{m}$ on the electron transparent window (Fig. 5(d)). The effects of the proximity to the Si substrate produce not just smaller size and asymmetric shape melt pools (Figs. 3 and 5(c)), but also faster RS interface migration rates. For the location with $\Delta x = 50 \mu\text{m}$ crystallization, we measured an interface velocity in the range of 2.9 m s^{-1} to 3.3 m s^{-1} and with an average of 3.1 m s^{-1} (Fig. 5(d)). The MM-DTEM based *in situ* observations enabled measurements of changes in the liquid–solid interface migration rate, e.g., accelerations and not just average velocity, as well as detection of the initial melting stage prior to the onset of crystal growth during the rapid solidification. The latter was associated with durations longer than $2.55 \mu\text{s}$ and shorter than $5.1 \mu\text{s}$, based on the MM-DTEM measurements, and lasted $4.2 \mu\text{s}$ according to the model calculations (see Section III D.). Experiments that utilize the total time elapsed after the delivery of the ns-laser pulse to detection of completion of solidification would inherently neglect to account for the substantial duration of melting processes in the Al prior to onset of the actual RS crystal growth. Given a total time of $18 \mu\text{s}$ – $20 \mu\text{s}$ required for the melting-solidification sequence, neglecting to take into account the ~ 3 – $5 \mu\text{s}$ delays prior to RS onset would result in systematically underestimating the average solidification velocity by about 20%–25%. The MM-DTEM experiments performed here for Al within the central region of approximate dimensions $300 \mu\text{m} \times 300 \mu\text{m}$ of the electron transparent window exhibit identical initial melt pool size and shape, duration of the melting stage, and crystal growth rates during the RS stage of the laser induced transformation sequences. The accelerating RS interface sections migrate at considerably different rates for different locations along the perimeter of the melt pools, i.e., $V_{\text{rmax}} \approx 1.35 V_{\text{rmin}}$ have been measured.

D. Numerical modeling of Al thin-film rapid solidification

Numerical modeling of the melt pool evolution has been performed for pulsed laser incidence located centrally, i.e., for $\Delta x = 250 \mu\text{m}$, in a $500 \mu\text{m} \times 500 \mu\text{m}$ wide area of Al thin film equivalent to those used in the MM-DTEM experiments. Considering only the heat conduction laterally within the thin film, we calculated the thermal field evolution in the specimen after delivery of a laser pulse. The model calculations were constrained to adjustments of the total energy delivered by the laser pulse for a profile matching the experimentally determined size of the irradiated elliptical area on the specimen, and the effective thermal conductivity of the amorphous Si_3N_4 supported Al thin film. Calculations that delivered excellent matches to the experimentally determined metrics of initial melt pool dimension in terms of $r_{\text{max}} = 37 \mu\text{m}$, $r_{\text{min}} = 27 \mu\text{m}$, and other experimental benchmark metrics, i.e., the total area and temporal evolution of melt pool size, resultant solidification velocity, and total time to complete solidification, have been obtained using laser energy of $85 \mu\text{J}$ for films with 160 nm thick Al layers and $45 \mu\text{J}$ for films with 80 nm Al layers with effective thermal conductivities of $210 \text{ W K}^{-1} \text{ m}^{-1}$ for the solid and $90 \text{ W K}^{-1} \text{ m}^{-1}$ for the liquid, respectively. Using values of the effective thermal conductivity of the solid, which represents the combined contributions to heat conduction from the Si_3N_4 and Al layers, that lie within the range of thermal conductivity values reported for solid Al, $205\text{--}230 \text{ W K}^{-1} \text{ m}^{-1}$ implies that the Al heat conduction dominated during the laser pulse induced transformation sequence. The calculations that matched the experimental benchmark metrics within the constraints imposed on the laser pulse showed maximum temperatures at the center of the superheated liquid Al of 1365 K and dwell times associated with melting prior to onset of solidification of $4.2 \mu\text{s}$ (e.g., Fig. 6). Fig. 6 shows two example thermal field evolution calculations equivalent to observations at $t_{\text{img}} = 2.6 \mu\text{s}$ prior to the onset

of the RS stage and $t_{\text{img}} = 18 \mu\text{s}$ just prior to completion of RS. The Al melt cooled at rates on the order of 10^7 K s^{-1} and regions of the Al thin film located outside of the Gaussian elliptical shape laser pulse profile with $r_{\text{max}} = 94 \mu\text{m}$ and $r_{\text{min}} = 68 \mu\text{m}$ experienced minimal heating for the $17.9 \mu\text{s}$ duration of the transformation sequence (Fig. 6). Akin to the experimental measurements, the calculation results of the melt pool size evolution exhibited consistent deviations from linear behavior, e.g., regarding overestimating the total time to complete solidification, which could be mediated by applying second-order polynomial best-fit procedures. Hence, the case of interface migration with a constant acceleration also provides better agreement with the numerical modeling based calculations. The numerical modeling results for the evolution of the melt pool size and velocity during RS of the 160 nm thick Al thin film are included in Figs. 5(c) and 5(d). The geometric-mean radius related metrics, which represent the behavior of average interface segment, are used here for illustrating a comparison of the model calculation results with the five different experimental data sets. While, of course inherently not predictive, the qualitative and quantitative agreements of the numerical modeling results with the experimental measurements support the conclusion that for a good approximation, the solid–liquid interface velocity accelerates during RS and the associated melt pool evolution is dominated by the thermal transport from the superheated Al radially outward into the surrounding solid. Since the thermal conductivity of the solid Al exceeds that of liquid Al significantly, it appears reasonable to propose that the migration rate of the solid–liquid interface is limited by the two-dimensional heat-flow of the excess heat of fusion evolved at the interface and the thermal conductivity of the solid surrounding the melt.

IV. SUMMARY AND CONCLUSIONS

In summary, *in situ* dynamic transmission electron microscopy studies of rapid solidification in polycrystalline

FIG. 6. Numerical simulation based calculations of thermal field evolutions for laser pulse induced melt pools (solid line ellipse) in Al thin film for central location, $\Delta x = 250 \mu\text{m}$, for the central $300 \mu\text{m} \times 300 \mu\text{m}$ section on the $500 \mu\text{m} \times 500 \mu\text{m}$ electron transparent window; example visualizations of the thermal fields at (a) $t_{\text{img}} = 2.6 \mu\text{s}$ and (b) $t_{\text{img}} = 17.9 \mu\text{s}$.

Al have been performed in Movie-Mode operation using windowed membrane TEM grids and revealed changes in crystal growth rates due to effects from differences in the heat extraction geometry. Quantification of the dynamic behavior of rapid solidification that is free from artifacts and reproducible can be achieved by controlling the position of the solidification experiment on the TEM grid, thus ensuring that the heat extraction remains the same during multiple experiments. The high temporal resolution *in situ* TEM experiments permitted discovery of regions of coexisting solid and liquid Al at the perimeter of the melt pool that persisted for several microseconds prior to the onset of directional crystal growth during rapid solidification. This is attributed to distorted thermal fields with reduced spatial gradient along the major diameter of the elliptical melt pool. The *in situ* TEM experiments confirmed a range of solidification front velocities for different interface segments along the perimeter of the elliptical melt pool, with a maximum and minimum velocity along the major and minor axes of the melt pool, respectively. This is a consequence of heat extraction due to variations in the local curvature of the solid-liquid interface. Using several metrics obtained directly from the *in situ* MM-DTEM experiments for constraining inputs and for benchmarking results of finite-element modeling calculations enabled determination of the temperature evolutions during the pulsed laser induced RS transformation of Al thin films. Experiments and matching calculations showed that the solid-liquid interface accelerated during the rapid solidification facilitated crystal growth. Melt pool evolution was dominated by thermal transport from the superheated Al and the heat of crystallization evolving at the solid-liquid interface radially outward into the surrounding solid, indicating that the migration rate of the solid-liquid interface was limited by the thermal transport properties of the surrounding solid.

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