

Tellurium Single-Crystal Arrays by Low-Temperature Evaporation and Crystallization

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Thermally evaporated tellurium possesses an intriguing crystallization behavior, where an amorphous to crystalline phase transition happens at near-ambient temperature. However, a comprehensive understanding and delicate control of the crystallization process for the evaporated Te films is lacking. Here, the kinetics and dynamics of the crystallization of thermally evaporated Te films is visualized and modeled. Low-temperature processing of highly crystalline tellurium films with large grain size and preferred outof-plane orientation ((100) plane parallel to the surface) is demonstrated by controlling the crystallization process. Tellurium single crystals with a lateral dimension of up to 6 μ m are realized on various substrates including glass and plastic. Field-effect transistors based on 5 °C crystallized Te single grains (6-nm-thick) exhibit an average effective hole mobility of ≈100 cm² V⁻¹ s⁻¹, and on/off current ratio of ≈3 × 10⁴.

1. Introduction

Large-scale growth of high-quality semiconductors, the active component of devices, is the foundation of modern electronics.^[1] Recently, evaporated tellurium (Te) was identified as a promising *p*-type material for flexible electronics due to its appealing electrical properties and potential low-temperature wafer-scale production.^[2–6] Beyond that, tellurium also shows great potential for applications in optoelectronics,^[4,7] sensors

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Te is composed of 1D helical atom chains packed in a hexagonal array believed to be bonded via van der Waals force (Figure 1a). It has a thickness-dependent bandgap, tunable from 0.31 to 1.04 eV with the thickness decreasing from bulk to monolayer.^[2,3] Material vapor condensed on an unheated substrate typically forms amorphous-phased films, therefore hightemperature post-deposition annealing is required for film crystallization.[11] Interestingly, an amorphous-crystalline phase transition takes place in the evaporated Te films at near-ambient temperature during or immediately after the deposition,^[12,13] yielding crystalline Te thin films with respectable electrical properties after

and energy harvesting devices,^[6,8] etc.^[9,10]

optimizing the deposition conditions such as substrate temperature,^[14] deposition rate, or applying nucleation layer.^[15,16] Post-annealing treatments were previously performed on the evaporated Te films in order to further improve crystallinity, decrease the density of grain boundaries, and control crystal orientation, but the relatively high vapor pressure of tellurium leads to re-evaporating of films during post-annealing, creating a rough surface and pinholes in films, thus poor electrical properties.^[17–20]

Although deposition and post-treatment optimization were previously investigated to enhance the quality of evaporated Te film.^[14,15,18,21,22] control of the amorphous to crystalline phase transformation kinetics has not yet been fully explored. In this work, we characterize and model the kinetics and dynamics of the crystallization of thermally evaporated amorphous Te films. The understanding so obtained is then used to fabricate large grain Te films (average grain area of 150 µm²) with preferred out-of-plane orientation ((100) plane parallel to the surface) at low temperatures. Te single crystal arrays (lateral dimension as large as 6 µm) were also realized on various substrates by patterned thermal evaporation and low-temperature crystallization. P-type field-effect transistors (FETs) based on the low-temperature crystallized ultrathin Te films (6 nm) are demonstrated, with an average effective mobility of $\approx 100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and on/off current ratio of $\approx 3 \times 10^4$.

Te thin films were deposited on a cold SiO_2/p^+ -Si substrate (-80 °C). X-ray diffraction (XRD) was performed on the as-deposited Te film (see Section 2). The absence of peaks in XRD measurement demonstrates the as-deposited Te film is amorphous (Figure 1b). The amorphous to crystalline phase







Figure 1. Phase transition process of evaporated Te films. a) Crystal structure of Te. b) XRD patterns of a Te thin film (50 nm) evaporated on cold SiO_2/p^+ -Si substrate (-80 °C) after deposition (red line) and crystallization (blue line). c) The crystallization process for an as-deposited 10-nm-thick Te film at room temperature. Images were taken by an optical microscopy.

transformation including nucleation and growth process was observed with optical microscopy as shown in Figure 1c (at room temperature) and Videos S1 and S2, Supporting Information. Crystalline nuclei initially appear with variable shapes ranging from faceted to elliptical (Figure S1, Supporting Information). The nuclei grow over time, retaining their shape. New crystalline nuclei appear within the non-transformed portions of the sample throughout the transformation process. Eventually, the entire film is transformed into a polycrystalline sample. The phase transformation is confirmed by the occurrence of the intense (100) peak after the crystallization from XRD measurement (Figure 1b).

At low temperatures, the crystalline phase is preferred, as it is expected to have a lower Gibbs free energy. The reduction in free energy, then, drives the transformation. In many similar circumstances, however, the thermodynamically favorable phase transformation is impeded by kinetic constraints (**Figure 2a**).^[23] Amorphous Te films are able to crystallize at low temperature (ambient temperature or even lower) due to the low activation energy for diffusion of Te atoms or re-arrangement of short chains.^[13,24–26] To explore the kinetics of recrystallization, we conduct experiment to characterize both the nucleation and growth rates as a function of crystallization temperature. Our experiments follow the pathway described using the time temperature transformation (TTT) diagram as a guide (Figure 2b). First, Te is thermally deposited on a cold substrate (-80 °C) and forms an amorphous film due to the suppressed diffusion of Te adatoms at such low temperature. After deposition, the substrate temperature is increased to a desired temperature (see Section 3), at which the crystallization of the amorphous Te films starts. This substrate temperature is held constant during the whole process until the phase transition is completed (Figure 2b,c). Last, the substrate temperature is recovered back to room temperature after the completion of crystallization.

The dynamic crystallization processes at different temperatures were captured under an optical microscopy as shown in Video S2, Supporting Information. The videos enable measurement of the fraction of the film transformed as a function of time. **Figure 3**a shows the experimentally observed transformation curves (the curves have been shifted in time for clarity). Note that as the temperature is increased, the incubation time



Figure 2. Schematic of the crystallization process. a) Gibbs free energy change during amorphous-crystalline phase transition. b) TTT diagram showing the heat treatment pathway of evaporated Te films. c) Schematic of the controlled phase transition process (CT: crystallization temperature).







Figure 3. Kinetic model for Te crystallization. a) The kinetic growth data obtained from analysis of experimental data for (i)...(vii) = 35, 30, 25, 20, 15 and 10 °C, respectively. The solid red curves are the experimental data obtained from the digitized movies, and the black dashed curves represent the fits of the data to Equation (1). b) The growth and nucleation rates determined by the fitting of Equation (1), along with their respective fits to the Arrhenius form. (All lengths are measured in microns, and times in seconds. c) TTT for Te films crystallized at different temperatures. 5% and 95% means the coverage of the crystallized Te extracted from videos. d) Plot of growth rate as function of temperature. The line represents the fit to the experimental data resulting in Arrhenius equation of $\nu \propto e^{-0.81/k_sT}$ for grain growth.

decreases quickly, starting from over 10 min at 10 $^{\circ}\mathrm{C}$ to around 30 s at 35 $^{\circ}\mathrm{C}.$

To gain a more detailed understanding of the transformation, the data in Figure 3a can be fitted to a kinetic model. The model chosen here assumes that both the nucleation and growth rates of the crystalline phase in the amorphous phase are constant throughout the transformation process (an isolated growing 2D grain thus appears circular). The nucleation and growth process are modeled as 2D, to reflect the aspect ratio of the thin films. Defining the nucleation rate per unit area and linear dimension growth rates to be N and ν , respectively, and applying the arguments of Johnson and Mehl,^[27] Avrami,^[28] and Komolgorov,^[29] (JMAK) one arrives at the following expression for the transformed fraction, $f \equiv A_c/A$, with A_c the area of the film that has transformed to the crystalline state, and A the total area of the film:

$$f = 1 - \exp\left(-\frac{\pi}{3}\dot{N}\nu^2 t^3\right) \tag{1}$$

where *t* is the time, measured from the time at which the first nucleus appears. Fitting the experimental data to the form of Equation (1) yields an experimental measurement of the product Nv^2 . The same model also predicts that the final

number density of grains at the completion of the transformation *N*, is given by:

$$N = \Gamma\left(\frac{4}{3}\right) \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \left(\frac{\dot{N}}{\nu}\right)^{\frac{2}{3}}$$
(2)

with $\Gamma(x)$ the Euler gamma function. Equations (1) and (2), therefore, provide the means to assess independently the nucleation and growth rates for the crystalline phase.

Figure 3a shows the fitted curves obtained by using Mathematica's NonlinearModelFit function as compared with the experimental data (as described in Figures S2–S4, Supporting Information). Equation (1) represents the experimental data quite well. This data is combined with the measured grain number densities in the films to obtain the growth velocities and grain nucleation rates. The computed radial growth rates range from around 0.014 μ m s⁻¹ to around 0.1 μ m s⁻¹. Assuming that the growth facet is (111), this corresponds to completion of an additional atomic layer approximately every 10⁻⁴ s. Figure 3b displays Arrhenius plots for the growth and nucleation rates. The growth rate corresponds to an energy barrier of $\Delta E_{\nu} = 0.91 \pm 0.11$ eV. This, presumably, is the average

energy barrier for attachment of an atom to the growing cluster from the amorphous surroundings.

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The nucleation rate also obeys an Arrhenius form, but with an energy barrier of $\Delta E_{\text{nucleation}} = 1.98 \pm 0.21$ eV. This form can be rationalized using classical nucleation theory. To wit, the nucleation rate is the product of the attachment rate, governed by the same processes as the growth rate, and an exponential term that depends on the free energy of the nucleus:

$$\dot{N} \approx \nu \exp\left(-\frac{\Delta E_{\dot{N}}}{k_{\rm B}T}\right) \sim \exp\left(-\frac{\Delta E_{\nu} + \Delta E_{\dot{N}}}{k_{\rm B}T}\right)$$
(3)

with $k_{\rm B}$ Boltzmann's constant and $\Delta E_{\rm N}$ the energy barrier for nucleation. Approximating the nuclei as spherical, we arrive at an expression for $\Delta E_{\rm N}$:

$$\Delta E_{\rm N} = \frac{16 \, \pi \gamma^3}{3 \Delta G_{c \to a}^2} \tag{4}$$

where γ is the interfacial free energy for the amorphous crystalline interface, and $\Delta G_{c\rightarrow a}$ is the free energy increase per unit volume for converting the crystalline to the amorphous phase. Applying Equations (3) and (4) along with the experimentally determined values for the activation energies, we conclude that $\Delta E_{\rm N} = 1.08 \pm 0.24$ eV. The Materials Project tabulates the air/ crystal surface energies for Te and these range from 0.005 to 0.023 eV Å⁻².^[30] Assuming that the interfacial energy for the crystalline/amorphous interface is $\approx 1/2$ the smallest of these energies minimum energy, or 2.5 ± 0.6 meV Å⁻², one concludes that $\Delta G_{c\rightarrow a} = 17 \pm 7$ meV per atom, and the critical nucleus size over the temperature range studied includes roughly 127 atoms.

The growth velocity can also be measured directly from the videos (as described in Figure S5, Supporting Information). As temperature is decreased from 35 to 10 °C, the incubation time, that is the time to 5% transformation, increases from \approx 30 s to



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even lower). Based on the observations above, larger grain size can be obtained by reducing the ratio N/ν , which according to Equation (3) has an Arrhenius form with an activation energy barrier equal to ΔE_{N} (directly fitting the grain density data to an Arrhenius form yields the value $\Delta E_{N} = 0.72 \pm 0.21$ eV, which is in reasonable agreement with the value derived above). Consequently, over the range of temperatures modeled here, a lower temperature corresponds to a lower number of grains. Therefore, we crystallize 10-nm thick amorphous Te films in the temperature range from 100 to -10 °C (see Section 3). We analyzed the microstructure of the crystalized Te films by polarized optical microscopy, where the grains with different orientations can be identified via contrast due to the anisotropic optical properties of Te. When crystallization temperature decreases from 100 to 5 °C, the average area of the domains increases from sub- μ m² to \approx 150 μ m² (Figure 4 and Figure S6, Supporting Information). The average domain size has no change when we further decrease the crystallization temperature to -10 °C (Figure 4e). For higher temperatures (higher than 100 °C), amorphous Te films start rapidly crystallizing during the ramp-up process toward the targeted high temperature (it just takes seconds to

of the amorphous Te films at the low temperature (-10 °C or



Figure 4. Characterization of Te thin films crystallized at different temperatures. a–d) Polarized light microscopy image of the Te films (10 nm) crystallized at 100 °C (a), 50 °C (b), 20 °C (c), and 0 °C (d). e) The calculated average domain areas of Te films (10 nm) crystallized at different temperatures. f) XRD pattern of a Te thin film (50 nm) crystallized at 0 °C.

finish the crystallization at 100 °C), yielding small grains; reevaporation of Te in high-temperature range (vapor pressure is 10⁻⁶ mTorr at temperature of \approx 220 °C) would cause a rough surface with pinholes, and films became discontinuous after a 5 min annealing at 300 °C. (Figure S7, Supporting Information).

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XRD measurements were performed on the crystallized Te to investigate the crystallinity of the films (Figure 4f and Figure S8, Supporting Information). Comparing with the 25 °C crystallized 50-nm-thick film, where two dominated peaks (100), (101) and two weak peaks (110), (200) were observed (Figure S8a, Supporting Information), only two peaks corresponding to (100) and (200) facets were observed for the 0 °C crystallized 50-nm-thick Te film (Figure 4f). A layer-by-layer restacked 0 °C crystallized 8-nm-thick Te sample also exhibits a strong out-ofplane texture (Figure S8b, Supporting Information), indicating that highly crystallized Te films with a preferred out-of-plane orientation ((100) plane parallel to the surface) can be achieved by crystallizing the evaporated amorphous films at low temperature. This preferred orientation is because (100) planes of Te have the lowest surface energy, and the growth rate is low at low temperature, so that the atoms have enough time to find their positions with the minimized energy. Angle-resolved Raman was performed on four patterned Te single grains to determine their in-plane orientations (Figure S9, Supporting Information). These grains showed four different in-plane orientations, which implies that the in-plane orientation for the Te films was random. The mosaicity of the film was characterized by electron back scattering diffraction (EBSD). Based on the EBSD map, (10-10) and (01-10) planes (Miller-Bravais notation) were parallel to the surface, which is consistent with the XRD result (Figure S10, Supporting Information). The color in the map showed a minimal variation, indicating a small misorientation.

The channel for an ideal device should only have one single grain, since the grain boundaries can decrease the carrier mobility, increase leakage current, and cause the threshold voltage shift.^[32] Therefore, realization of single-crystalline Te patterns at desired locations is important for electronic and optoelectronic applications. To study the effect of crystallization temperature and feature size on the number of grains, 10 nm Te films were deposited on defined patterns (SiO₂/ p^+ -Si

substrate, see Section 3) with lateral size varying from 1 to 19 μ m at -80 °C and crystallized at different temperatures (**Figure 5** and Figure S11, Supporting Information).

The introduction of edges and small areas has the potential to alter the nucleation problem. Presumably, there are two competing mechanisms for grain nucleation-that for nucleation in the area of the film and that for edge nucleation. Under these circumstances, it can be difficult to construct an algebraic theory for the number of grains.^[33] To explore the effects of the finite size of the lithographic samples, we developed a simulation capable of predicting the number of grains appearing within a sample (for details, see the Supporting Information). For these simulations, the nucleation rate for the area-based nucleation was taken to be the fitted Arrhenius form obtained from the blank thin film samples. The edge nucleation rate was used as a parameter, and was tuned to get general agreement with experimental observations. At T = 0 °C, simulations based on the fitted Arrhenius forms without an enhanced nucleation rate at the edge of the samples are not able to reproduce the experimental data. Increasing the areal nucleation rate by a factor of 2.9 over the extrapolated rate, and decreasing the growth velocity by a factor of 0.54 from its predicted value produces simulation results that are in reasonable agreement with the experimental data (see Supporting Information). However, the data is better fit by retaining the parameters based on the Arrhenius forms and including an edge nucleation process. The comparison of the simulation predictions to experimental results for T = 0 °C is shown in Figure 5. The simulations are based on an area nucleation rate of $N_{area} = 3.32 \times 10^{-7} \, \text{s}^{-1} \, \mu \text{m}^{-2}$, a growth velocity of $\nu = 1.05 \times 10^{-3} \,\mu\text{m s}^{-1}$, and an edge nucleation rate of $\dot{N}_{edge} = 6.8 \times 10^{-6} \text{ s}^{-1} \mu \text{ m}^{-1}$. The experimental data is described quite well by the simulations.

Growth of highly crystalline Te arrays, which has near-unity average number of grains per pattern with lateral size as large as $6 \,\mu m$, was realized on an amorphous SiO₂/ p^+ -Si substrate by controlling the crystallization process (Figure 5a and Figure S11d,e, Supporting Information). Transmission electron microscopy (TEM) was performed on a transferred pattern Te film (Figure S15, Supporting Information). Selected-area electron diffraction showed a single-crystalline diffraction pattern and



Figure 5. 0 °C crystallized Te array with different pattern area. a) Polarized light microscopy image of the patterned 0 °C crystallized Te (10 nm) array with lateral dimension ranging from 6 to 19 μ m. b) Log–log plot of number of nuclei as a function of pattern area. Blue triangles are the experimental measurements and black circles are the simulation results. Both areal and edge nucleation were considered in the simulation. More simulation details can be found in Supporting Information.





Figure 6. Field-effect transistors based on Te films crystallized at different temperatures. a) Schematic diagram of the device structure. b) Optical image of a typical FET based on the single grain Te film crystallized at 5 °C. c–e) I_d-V_g transfer curves (c), I_d-V_d output characteristics (d), and derived effective mobility (e) for the Te transistor (6 nm) shown in (b). f,g) The statistical distribution of effective mobility (f) and log (I_{on}/I_{off}) for Te FETs (7 nm) crystallized at different temperatures. h) Thickness-dependent effective mobility (blue) and on/off current ratio (red) for Te FETs crystallized at different temperatures.

high-resolution TEM image exhibited interplanar spacing of 5.9 Å corresponding to (001) planes (Figure S15b,c, Supporting Information), confirming the quality of the patterned Te film. Single crystalline Te arrays (lateral size of $\approx 6 \ \mu m$) could also be grown on various substrates including glass and polymer (polyethylene terephthalate (PET) and Kapton) by using the same method (Figure S16, Supporting Information), demonstrating the potential of this method for a broad range of application in flexible and transparent electronics.

FETs were fabricated using Te films as the channel, and SiO₂ (50 nm thick)/p+-Si as dielectric layer and back-gate to examine the electronic properties of low-temperature crystallized Te as shown in Figure 6a,b. Ni was used as the contact metal, as it can form near ohmic contact for holes due to the Fermi level pining near valence band for Te.^[34,35] Te FETs exhibit a typical *p*-type characteristic due to the native defects (Figure 6c) with a common hysteresis behavior (Figure S17, Supporting Information). The transistor based on a single-grain Te (≈6 nm) crystallized at 5 °C shows an effective hole mobility of 93 cm² V⁻¹ s⁻¹ subthreshold swing of 2.7 V dec⁻¹ and on/off current ratio of $\approx 10^5$ (Figure 6c–e) at room temperature in vacuum environment ($\approx 10^{-5}$ mTorr). Statistic distribution of the device performance measured from 30 FETs based on the Te films (7 nm) crystallized at two different temperatures is shown in Figure 6f,g. When the crystallization temperature decreases from 35 to 5 °C, the average effective hole mobility with standard deviation increases from 67 \pm 4 to 100 \pm 14 cm² V⁻¹ s⁻¹ and average

on/off current ratio gets improved by >20 times increasing from 1×10^3 to 3×10^4 , which is due to the higher crystallinity and less grain boundaries for 5 °C crystallized Te films. For 5 °C crystallized Te films, as the grain size was comparable to the channel dimensions, a relatively wider distribution in effective hole mobility was observed, which is caused by the random in-plane crystal orientations along the channel and the anisotropic in-plane electrical transport properties of Te. The 35 °C crystallized films had smaller grain size comparing to the 5 °C crystallized ones (Figure S6a,f, Supporting Information), the device channel based on which contained tens of small grains with random in-plane orientations and grain boundaries. The effective mobility extracted from the 35 °C crystallized films is an averaged value from these grains and grain boundaries, which had a smaller fluctuation comparing to the 5 °C crystallized one's. We then investigated the thickness-dependent effective mobility and on/off current ratio for the films crystallized at two different temperatures with the thickness ranging from 4 to 19 nm. 5 °C crystallized Te FETs shows a higher effective mobility and on/off current ratio compared to the 35 °C crystallized Te FETs in the measured thickness range, demonstrating electronic properties of the films get improved by optimizing the crystallization process. For 5 °C crystallized Te FETs, a maximum effective mobility of 264 cm² V⁻¹ s⁻¹ is achieved on a 19 nm thick film (Figure S18, Supporting Information) and the average effective mobility with standard deviation decreases monotonically from $182 \pm 42 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (19 nm) to $30 \pm 4 \text{ cm}^2$



V⁻¹ s⁻¹ (4 nm) due to the enhanced effect of surface roughness scattering for thicker films (Figure 6h).^[36] On/off current ratio increase from 4.5×10^2 (19 nm) to 6×10^5 (4 nm), which is caused by the larger bandgap and stronger electrostatic control of Te channel for thinner films. We performed Hall measurements on the Te films (lateral dimensions: 5 mm × 5 mm) crystallized at 5 °C and room temperature (≈20 °C) with a thickness of \approx 30 nm to estimate the hole concentration and Hall mobility. They showed a similar hole density of $\approx 2.7 \times 10^{18}$ cm⁻³. The 5 °C crystallized Te film exhibited a Hall mobility of 162 cm² V⁻¹ s⁻¹, which is higher than the room temperature crystallized one (102 cm² V⁻¹ s⁻¹). To understand the carrier scattering mechanisms, we measured the temperature-dependent $I_d - V_g$ transfer curves ranging from 77 to 300 K on an 8-nm-thick 5 °C crystallized tellurium FET (Figure S19a, Supporting Information). The effective mobility increases as temperature is reduced with maximum value of 197 cm² V⁻¹ s⁻¹ at 77 K. The temperature-dependent effective mobility in high-temperature regime (T > 175 K) can be fitted with a power law $\mu_{\rm eff} \propto T^{-\gamma}$, where $\gamma = -0.56$, which is consistent with the reported result for a single crystal Te (Figure S19b, Supporting Information).^[37]

In summary, we realize the growth of highly crystalline Te films with a preferred out-of-plane orientation and large grain size (average grain area of ~150 μ m²) and single-crystalline tellurium arrays (lateral size as large as 6 μ m). We analyzed the growth kinetics, and using the understanding so obtained to control the crystallization process of thermally evaporated amorphous Te. A typical Te FET based on the low-temperature crystallized Te exhibit high performance in effective hole mobility. This method is compatible with various substrates due to its near-ambient processing temperature. In the future, it is possible to realize the growth of wafer-scale single-crystalline Te films by further inducing the in-plane orientation of the Te atom chains, since a preferred out-of-plane orientation is achieved.

2. Characterizations

XRD measurement was performed on a Rigaku SmartLab X-ray diffractometer system with a Cu X-ray source ($\lambda = 1.5406$ Å). For Figure 1b, as-deposited 50-nm-thick Te samples were kept at ≈ 0 °C to prevent the crystallization during the XRD measurement. Then we recovered the sample temperature to room temperature for crystallization and performed XRD measurement on the crystallized Te film again. For Figure S8b, Supporting Information, we transferred and restacked 0 °C crystallized 8-nm-thick Te films layer by layer for seven times using a PDMS stamp to enhance the XRD signal. Raman spectrums were measured on a LabRAM HR Evolution Raman microscope with an excitation line of 532 nm. EBSD measurements were performed using an FEI Quanta field emission gun SEM and an Oxford EBSD detector with a fluorescent screen. TEM characterization was performed on 50-nm thick pattern Te transferred on a SiO₂ support TEM membrane (TED PELLA, INC). TEM characterization was carried on a FEI Titan 60-300 microscope with an acceleration voltage 200 kV at the National Center for Electron Microscopy at Lawrence Berkeley National Laboratory. The optical microscopy images of Te thin films were taken by a homemade polarized optical microscopy.

2.1. Video Analysis

Images were extracted from the videos and then processed and analyzed using Mathematica.^[38] The processing and analysis for each video was done as follows: first, it was observed that the transformation from the amorphous phase to the crystalline phase resulted in an increase in intensity of the image. The fraction transformed was then determined simply as being equal the fraction of the overall intensity change observed over the course of the experiment. (The results so obtained were compared with a more complicated image processing steps involving binarization of the images, as well as computing the intensity change on a per pixel basis. All three methods yielded very similar results, and the differences between the three methods were used to assign uncertainties. See the Supporting Information for details.) All the fitting was done using Mathematica's NonlinearModelFit. Similarly, the growth rates were obtained by fitting an ellipse to crystals before coalescence using the Component Measurements package and tracking its major and minor axis growth.

2.2. Simulation of Nucleation and Growth within a Finite Size Region

The nucleation problem within the defined lithographic regions is based on a kinetic Monte Carlo algorithm. Using the initially available areas and edge lengths, the total rate for nucleation is computed. Assuming that nucleation is a Poisson process, we generate a list of nucleation positions and times for a fixed number of grains using standard kinetic Monte Carlo methods.^[39] Following JMAK,^[27–29] it is assumed that the growth of the grains is 2D and circular.

The kinetic data for our model was derived from movies of the crystallization process, analyzing one movie for each temperature. The movies captured information from an area of 6912 μ m², and, for the lowest temperatures, included \approx 60 nuclei. The growth area is then meshed with a regular array of points. The time of arrival for each grain is computed for every grid point (every nuclei is presumed to start a grain at this stage). Each grid point is then labeled by the grain number that arrives at that point first and the time of that first arrival. The time at which the last grid point is transformed is checked to make certain that it is before the last grain nucleation event in the event list. If so, the number of grains and the finish time of the simulation are recorded. If not, the simulation is thrown out, the number of nucleated grains is increased, and the simulation is run again. Results of 64 accepted simulations with meshes of 128×128 points are averaged to produce the data in the plot (see Supporting Information for details).

3. Experimental Section

Growth Method of Te Thin Films: Te pellets (99.999%, Sigma-Aldrich) were used as the thermal evaporation source. The Te source pellets were loaded in a tungsten boat, which was beneath the substrate. Substrates such as $SiO_2/p+-Si$, quartz or polymers were sticked on a steel sample chuck, which can be cooled by cold nitrogen gas flow, using Kapton tape. Bilayer positive photoresist (LOR 5A and S1818 with a thickness





of \approx 0.5 μ m and 2 μ m) was used to define the pattern on the substrate. When the pressure reached 2×10^{-6} mbar, a cold nitrogen gas flow was used to cool down the sample chuck to -80 °C before deposition. Thermally evaporated Te was deposited on the bare/patterned cold substrates (-80 °C) to form the amorphous-phased Te films/arrays. The deposition rate (around 10 Å s^{-1}) and thickness of Te thin film was controlled during deposition by use of a quartz crystal microbalance. A room-temperature nitrogen gas flow was used to recover the temperature of the chuck after deposition. Samples were taken out from the chamber until the substrate temperature recovered to ≈ 5 °C, preventing the condensation of water from ambient air. It took ≈10 min for the temperature of the chuck increasing from -80 to 5 °C. As the crystallization process was very slow at low temperature (incubation time is tens of minutes at 5 °C), it was assumed the crystallization had not started, while the samples were unloaded from the evaporator. The amorphous samples were placed onto a thermoelectric module with a controlled constant temperature immediately after unloading for crystallization (thermoelectric module temperature was set to the desired crystallization temperature in advance). Considering silicon substrate is a good heat conductor, the size of the chip is small for the heat source/sink, contact between substrate and thermoelectric module is good, and the temperature difference is small, the Si substrate temperature would stabilize at the desired temperature in seconds. The sample was removed from the thermoelectric module when the crystallization process completed. The atmosphere was not controlled during the crystallization. Note that, the process required protection from light, especially when the crystallization temperature is below 5 °C, since the light had an influence on the crystallization. The crystallization processes were monitored under an optical microscopy, when the crystallization temperature was above 5 °C. For the patterned Te samples, photoresist was removed after the crystallization by lift-off process.

Device Fabrication and Measurements: FETs were fabricated on 50 nm SiO_2/p^+ -Si substrates. Heavily doped p-Si substrate was used a global back gate and 50 nm SiO₂ is the dielectric layer. Te channel regions were patterned by electron-beam lithography. Te films were deposited on the -80 °C patterned SiO_2/p^+ -Si substrates and crystallized at different temperatures as mentioned in growth method of Te thin films. After lift-off process, source and drain regions were patterned by electron-beam lithography. Ni (30 nm) was deposited using e-beam evaporation as metal contact. Room-temperature and temperaturedependent electrical measurements were performed under vacuum in a cryogenic probe station (LakeShore) with a B1500a Semiconductor Device Analyzer (Keysight). Effective mobility is calculated using: d*I*_d $\mu_{\text{eff}} = \frac{dI_d}{dV_d} \frac{L}{WC_{\text{ox}}(V_g - V_t)}, \text{ where } C_{\text{ox}} \text{ is the gate oxide capacitance, } L$ is the channel length, W is the device width, and V_t is the threshold voltage. I_d was measured at low bias ($V_d = -0.1$ V).

Hall measurement devices were fabricated in a square configuration with an edge length of 5 mm. 30 nm Ni was used as the contact metal. An Ecopia HMS 300 Hall measurement tool with $a \approx 0.55$ T permanent magnet was used to measure the carrier concentration and Hall mobility by van der Pauw method.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

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- Y. Taur, T. H. Ning, Fundamentals of Modern VLSI Devices, Cambridge University Press, Cambridge 2013.
- [2] C. Zhao, C. Tan, D.-H. Lien, X. Song, M. Amani, M. Hettick, H. Y. Y. Nyein, Z. Yuan, L. Li, M. C. Scott, *Nat. Nanotechnol.* **2020**, *15*, 53.
- [3] Y. Wang, G. Qiu, R. Wang, S. Huang, Q. Wang, Y. Liu, Y. Du, W. A. Goddard, M. J. Kim, X. Xu, *Nat. Electron.* 2018, 1, 228.
- [4] M. Amani, C. Tan, G. Zhang, C. Zhao, J. Bullock, X. Song, H. Kim, V. R. Shrestha, Y. Gao, K. B. Crozier, ACS Nano 2018, 12, 7253.
- [5] W. Wu, G. Qiu, Y. Wang, R. Wang, P. Ye, Chem. Soc. Rev. 2018, 47, 7203.
- [6] S. Lin, W. Li, Z. Chen, J. Shen, B. Ge, Y. Pei, Nat. Commun. 2016, 7, 10287.
- [7] Z. Xie, C. Xing, W. Huang, T. Fan, Z. Li, J. Zhao, Y. Xiang, Z. Guo, J. Li, Z. Yang, Adv. Funct. Mater. 2018, 28, 1705833.
- [8] D. Tsiulyanu, S. Marian, V. Miron, H.-D. Liess, Sens. Actuators, B 2001, 73, 35.
- [9] L. Wu, W. Huang, Y. Wang, J. Zhao, D. Ma, Y. Xiang, J. Li, J. S. Ponraj, S. C. Dhanabalan, H. Zhang, *Adv. Funct. Mater.* **2019**, 29, 1806346.
- [10] Z. Shi, R. Cao, K. Khan, A. K. Tareen, X. Liu, W. Liang, Y. Zhang, C. Ma, Z. Guo, X. Luo, *Nano-Micro Lett.* **2020**, *12*, 99.
- [11] S. Park, B. L. Clark, D. A. Keszler, J. P. Bender, J. F. Wager, T. A. Reynolds, G. S. Herman, *Science* **2002**, *297*, 65.
- [12] K. Okuyama, M. Chiba, Y. Kumagai, Japanese J. Appl. Phys. 1979, 18, 507.
- [13] K. Okuyama, Y. Kumagai, Thin Solid Films 1988, 156, 345.
- [14] K. Okuyama, Y. Kumagai, J. Appl. Phys. **1975**, 46, 1473.
- [15] A. De Vos, J. Aerts, Thin Solid Films 1977, 46, 223.
- [16] R. W. Dutton, R. S. Muller, Proc. IEEE 1971, 59, 1511.
- [17] R. Dutton, R. Muller, Thin Solid Films 1972, 11, 229.
- [18] K. Okuyama, T. Yamashita, M. Chiba, Y. Kumagai, *Jpn. J. Appl. Phys.* 1977, 16, 1571.
- [19] M. A. Dinno, M. Schwartz, B. Giammara, J. Appl. Phys. 1974, 45, 3328.
- [20] C. Zhao, L. Hurtado, A. Javey, Appl. Phys. Lett. 2020, 117, 192104.
- [21] E. Weidmann, J. Anderson, Thin Solid Films 1971, 7, 265.
- [22] E. Bianco, R. Rao, M. Snure, T. Back, N. R. Glavin, M. E. McConney, P. Ajayan, E. Ringe, *Nanoscale* **2020**, *12*, 12613.

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www.advancedsciencenews.com



- [23] J. L. Ericksen, Introduction to the Thermodynamics of Solids, Springer, New York, 1998.
- [24] Y.-H. Cheng, S. W. Teitelbaum, F. Y. Gao, K. A. Nelson, Phys. Rev. B 2018, 98, 134112.
- [25] T. Ichikawa, Phys. Status Solidi 1973, 56, 707.
- [26] A. Koma, O. Mizuno, S. Tanaka, Phys. Status Solidi 1971, 46, 225.
- [27] W. A. Johnson, Trans. Am. Inst. Min., Metall. Pet. Eng. 1939, 135, 416.
- [28] M. Avrami, J. Chem. Phys. 1939, 7, 1103.
- [29] A. N. Kolmogorov, Bull. Acad. Sci. USSR, Math. Ser. 1937, 1, 355.
- [30] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, APL Mater. 2013, 1, 011002.
- [31] N. A. Blum, C. Feldman, J. Non-Cryst. Solids 1976, 22, 29.
- [32] G. Blatter, F. Greuter, Phys. Rev. B 1986, 33, 3952.

- [33] J. W. Cahn, Acta Metall. 1956, 4, 449.
- [34] P. Dasika, D. Samantaray, K. Murali, N. Abraham, K. Watanbe, T. Taniguchi, N. Ravishankar, K. Majumdar, *Adv. Funct. Mater.* 2021, 31, 2006278.
- [35] K. Okuyama, J. Tsuhako, Y. Kumagai, Thin Solid Films 1975, 30, 119.
- [36] H. Ko, K. Takei, R. Kapadia, S. Chuang, H. Fang, P. W. Leu, K. Ganapathi, E. Plis, H. S. Kim, S.-Y. Chen, *Nature* **2010**, *468*, 286.
- [37] G. Zhou, R. Addou, Q. Wang, S. Honari, C. R. Cormier, L. Cheng, R. Yue, C. M. Smyth, A. Laturia, J. Kim, *Adv. Mater.* **2018**, *30*, 1803109.
- [38] S. Wolfram, *The Mathematica Book*, 4th ed., Cambridge University Press, Cambridge 1999.
- [39] P. Maksym, Semicond. Sci. Technol. 1988, 3, 594.