Nucleation and Growth During the Crystalization of Amorphous Te Thin Films

MSE 130: Experimental Materials Science and Design

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Contents

1 Abstract

2 Introduction

novel electronic devices such as flexible displays will require the fabrication of semiconductors on noncrystalline substrates...the low melting points of such substrates (such as polymers etc) means that such processes must function on a low thermal budget...the semiconductor tellurium (Te) is an attractive candidate due to its relatively low melting point (449.5 degrees C)...this allows it to be deposited amorphously at low temperature, after which it may be crystallized near room temperature...additionally, the narrow band gap of bulk Te (0.32 eV) allows for straightforward bandgap engineering through electron confinement...depositing and crystallizing Te in a thin film allows its bandgap to be tuned to optimum values for a given application, such as FETs

the amorphous-deposition-crystallization manufacturing process may be understood in the context of classical Becker-Doering nucleation theory, which models the physical system as a distribution of atomic clusters. The free energy change (ΔG) of such a cluster is:

$$\Delta G(i) \approx -g_{c\to a} i + \gamma i^{2/3} \tag{1}$$

where i is the number of atoms in the cluster, -$g_{c\to a}$ is the atomic free energy of the amorphous-to-crystalline transition, and γ is a factor convolving the cluster surface energy and the surface-area-to-volume ratio. Becker-Doering theory then uses steady-state and detailled-balance assumptions in order to derive the area nucleation rate $\dot{N}$:

$$\dot{N} \approx \dot{N}_0 \exp\left[-\frac{\Delta E_{attach} + \Delta G(i_c)}{k_T T}\right] \tag{2}$$

where i_c is the critical cluster size and ΔE_{attach} is the activation energy for an atom to jump across the amorphous-crystalline interface. The assumption of a spherical nucleus (Equation

1) motivates a critical nucleation energy of $\Delta G(i_c) = \frac{4\gamma^3}{27 g_{c\to a}^2}$. The units of $\dot{N}$ are $m^{-2}s^{-1}$.

The crystallization process may be additionally described through Johnson-Mehl-Avrami-Kolmogorov theory in the 2D limit, wherein a nucleus grows to span the thickness of the film faster than the next nuclus can appear. In such a limit, the area fraction transformed (α) is described by:

$$\alpha = 1 - \exp\left[-\frac{\pi}{3}\dot{N}v^2(t-t_0)^3\right] \tag{3}$$

where t_0 is a fitting factor and the growth velocity (in units of $\frac{m}{s}$) follows an Arrhenius dependence:

$$v \approx v_0 \exp\left[-\frac{\Delta E_{attach}}{k_B T}\right] \tag{4}$$

Finally, JMAK theory produces an expression for the average number of grains nucleated per unit area:

$$\rho = \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \Gamma\left[\frac{4}{3}\right] \left(\frac{\dot{N}}{v}\right)^{\frac{2}{3}} \tag{5}$$

where $\Gamma\left[\frac{4}{3}\right] \approx 0.8929795...$ is the Euler Gamma function.

Taken collectively, B-D theory and JMAK theory yield a straightforward method for calculating $\dot{N}$, v, and their associated activation energies and prefactors. An amorphous Te thin film may be monitored during its anneal in order to measure the crystalline area fraction as a function of time, which may be fitted to Equation 3 to calculate $\dot{N}v^2$. Afterwards, the grain density may be assessed and Equation 5 may be employed to calculate $\dot{N}/v$. These values may be trivially solved for $\dot{N}$ and v.

Repeating the procedure at different annealing temperatures allows the Arrhenius forms (Equations 4 and 2) to be fit, thus providing estimates of the activation energies governing nucleation and growth in the low-temperature Te manufacturing process.

The equations presented in this section represent the core results of B-D and JMAK theory. For a detailled discussion of their derivations and assumptions, as well as a demonstration of the validity of the 2D limit, see Reference [1].

3 Experimental Procedure

An Edwards 306 Thermal Evaporator was loaded with Te source pellets of 99.999% purity from Sigma-Aldrich. Te was deposited on a substrate at a deposition rate of approximately 10 Å/sec. Film thicknesses, as controlled by a quartz crystal microbalance, ranged from 4 to 20 nm. Since the substrate was maintained at -80°C, the deposited film was amorphous; this was verified by x-ray diffraction.

Six deposited films were selected for experimental analysis. Immediately after deposition, each film was heated to its target annealing temperature (10°C, 15°C, 20°C, 25°C, 30°C, or 35°C). Optical microscopy was used to observe the crystallization at an imaging rate of 2.87 frames/sec, with the intent that these data be used to assess the area fraction transformed (Equation 3).

After annealing, the samples were allowed to return to room temperature, then examined via transmission electron microscope. Bright field and dark field images of a 140 µm x 105 µm region were obtained, with the intent that they be used to determine the films' grain density (Equation 5). Due to their finer microstructure, additional images of a zoomed-in 140 µm x 105 µm region were collected for the 20°C, 25°C, 30°C, and 35°C samples.

4 Results

obtaining and fitting fraction transformed curves

assessing grain density from microstructural images

calculating parameters and estimating free energies/critical nuclei

there is a book living inside your chest with dilated instructions on how to make a safe landing.

5 Discussion

discussion of validity of free energy and critical nuclei result

discussion of validity of grain counting algorithm

discussion of improvements to the estimation procedure and attempt to derive gamma

6 Conclusions

7 Acknowledgments

8 References

[1]D. C. Chrzan, *MSE 130 Laboratory: Nucleation and Growth During the Crystallization of Amorphous Te Thin Films*, tech. rep. (Department of Materials Science and Engineering, University of California, Berkeley, 2020).