GST crystallite-density TEM-analysis finds no crystalline structure

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TEM analysis techniques: high resolution, bright-field and dark-field imaging; electron diffraction, and STEM showed crystallite area density in a sputtered GST ($Ge_xSb_yTe_z$) thin film to be less than one crystallite per 0.0527 μm^2, which restated is less than 19 crystalites/μm^2 . Beyond the quantified data, a qualitative search of the sample failed to find any crystallites.

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Introduction:

Nanostructures in a GST ($Ge_xSb_yTe_z$) thin film (x= 2, y= 2, z= 7 is referred to as 227) were investigated using the Tecnai F30 and F20 Transmission Electron Microscopes (TEM). Bright field and dark field imaging were used to search for the postulated crystallite seed particles that may nucleate the rapid phase change. The imaging modes, bright field (BF) and dark field (DF) exploit the drastically different diffraction scattering from amorphous and crystallite regions to create image contrast. Features of these seed particles that were searched for are size, composition, crystal structure, and particle density.

Background:

The sample of GST, a chalcogenide glass, originated from Craig Taylor's group at the Colorado School of Mines. The sample (a 227 compound) is a thin film formed through argon bombardment-sputtering on a silicon substrate. It has received no additional processing other than what we might do through normal handling. A second sample (225) had conduction-AFM work done on it, which found low-resistance spots, which may indicate seeds, but no analysis was done on this sample.

GST is a chalcogenide glass, a class of glass which exhibits thermally-driven amorphous-crystalline phase changes with correspondingly large differences in optical and electrical properties.

Optical Memory

The contrast enables storage of binary information, and this glass is already applied in Compact Disk (CD-RW) and Digital Versatile Disk (DVD-RW) technologies, which harness the optical properties of the glass. It is thermally induced to change phase through laser stimulation; sufficient laser intensities can heat up the material, and thus change the material phase. GST will change to a crystalline if heated up to a crystallization temperature, which is less than the melting point. When melting temperatures are reached with shorter, higher intensity laser blasts, then the material melts and solidifies with amorphous structure.[i] Thus, the material can be switched between its crystalline or amorphous phases by controlling the laser intensity and exposure time duration. See Figure 1 for an illustration of the concept.

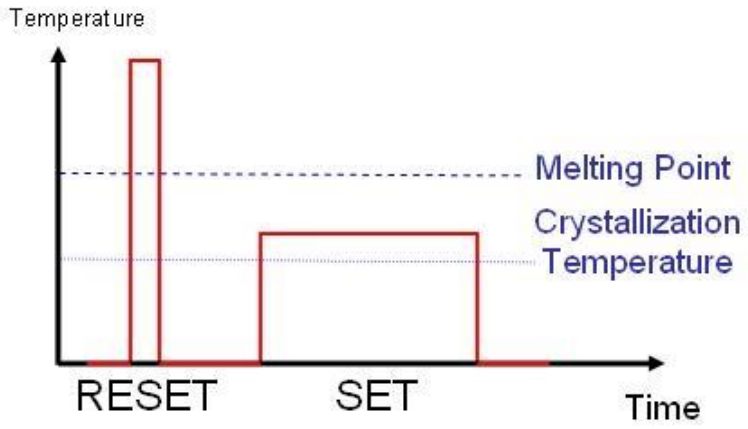


Figure 1: Phase-Changing Laser—Taken from
http://en.wikipedia.org/wiki/GeSbTe

Crystalline GST has much higher reflectivity than the amorphous phase. A less intense laser and photodiode receiver can detect the differences in reflection due to phase state: crystalline or amorphous. The phase states are manipulated easily with fast pulse lasers[ii], the states are set in nanoseconds for thin films, and so the system can quickly function as binary phase-state memory. This is the basic system used in re-write optical memory systems (i.e., DVD-RW, CD-RW).[iii] In the case of optical disks, the large laser widths allows for a relatively low level of precision.[iv]

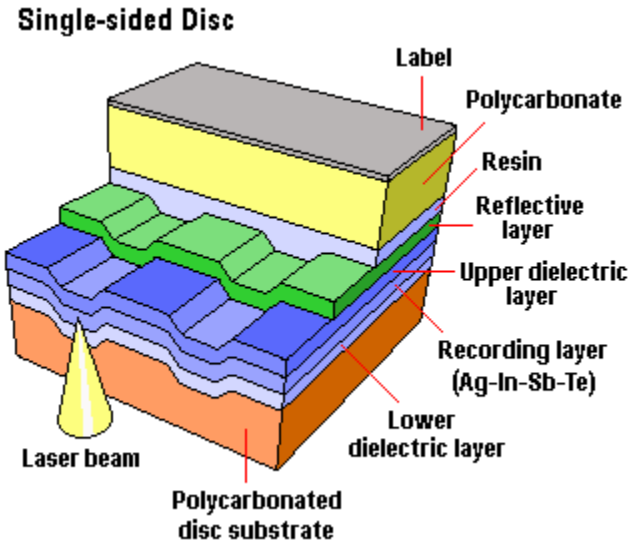


Figure 2: Optical Disk Memory—Taken from
http://www.pctechguide.com/34DVD_DVD+RW.htm

In Figure 2 we see a structural diagram of an optical disk system using Ag-In-Sb-Te, which is another chalcogenide glass and functions similarly. One might wonder why the system has dielectric layers:

"The first dielectric layer, i.e. the layer between the substrate and the phase-change recording layer, protects the recording layer from humidity and the substrate from thermal damage, and optimizes the optical contrast…. When this [second dielectric] layer is too thin, the thermal insulation between the recording layer and the metal mirror layer is adversely affected. As a result, the cooling rate of the recording layer is increased, which leads to a slow crystallization process and a poor cyclability." [v]

Electrical Memory

Besides the optical properties of GST, engineers would like to further harness the electrical properties of the material. The amorphous state is high resistance, which could represent a binary 0, and the crystalline, low resistance state could represent a 1.[vi] See Figure 3 for a basic diagram of a transistor that could use GST.

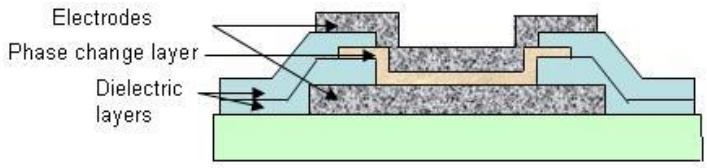


Figure 3: Phase-Change Transistor—Taken from http://en.wikipedia.org/wiki/GeSbTe

Engineers want to make microelectronic devices[vii] with GST and if there are inconsistencies in electrical resistance of the material due to crystallite seeds, then the density of these seeds would have to be understood. Transistors, for instance, require precise conductivity changes in the analogous "channel region" to function.

Similar to how large crystals form in geological formations after energy is introduced over hundreds of years, micro-crystals could form in GST after small amounts of energy and time are added. The formation of crystals is accelerated if crystallite-seeds are already present, as seen in such processes as the Czochralski process. If the crystallite seeds were in high enough densities, then amorphous regions would start to behave more like crystal regions. The electrical systems assume that the regions don't change without system intervention, so the output would be confusing and unpredictable: a broken system. Looking at seed densities helps us understand the electrical and optical engineering possibilities.

GST devices have already been fabricated at the nano-scale: IBM has made a small prototype device with a cross-section 3 by 20 nanometers in size,

which is approximately the industry goal for traditional silicon transistors in the future year of 2015. Another advantage over traditional flash memory cells is that those can degrade and become unreliable after as few as 10,000 writes, but GST memory will last through 100 million write cycles.[viii] Another engineering experiment, Intel and STMicroelectronics have partnered to create a wafer of transistors that have 2 extra states between the normal two binary values. That creates twice the amount of memory potential for each transistor.[ix] So GST is being utilized by engineers, and adding to the body of knowledge for this material makes sense when prioritizing research projects. The manufacture possibilities of scaled-down devices of this material need more illumination, which is what this project hoped to shed some light on.[x]

Methods:

TEMs need very thin materials (100 nm or less)[xi] through which to pass the electron beam. One way of doing this is by grinding a material very gradually to a wedge; a wedge with a smooth, micro-thin tip. We used diamond lapping film and an adjustable tripod to gain this smooth wedge. The wedge is formed precisely by mounting it on a tripod polisher, as show in Figures 4 and 5.



Figure 4: Polishing Tripod 1—Taken from http://www.emsdiasum.com/microscopy/products/materials/tripod_polisher.aspx

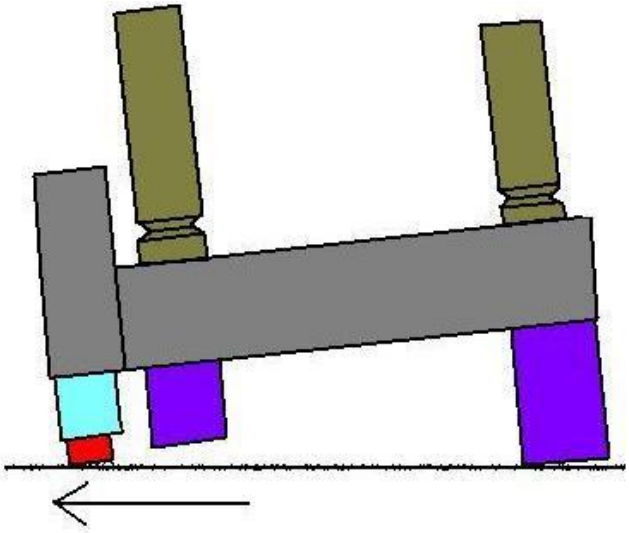


Figure 5: Polishing Tripod 2

The red piece represents the sample attached to the tripod polisher apparatus, and the arrow represents the motion of the diamond lapping film. If looked at from above, you could see that the film is circular, and the motion is rotary. The steps below were followed to prepare the samples for investigation. [xii]. (** Steps used only for making a cross-section sample)

- Using a diamond scribe to notch the wafer pieces and to make 2mm wide strips, similar to Figure 6.

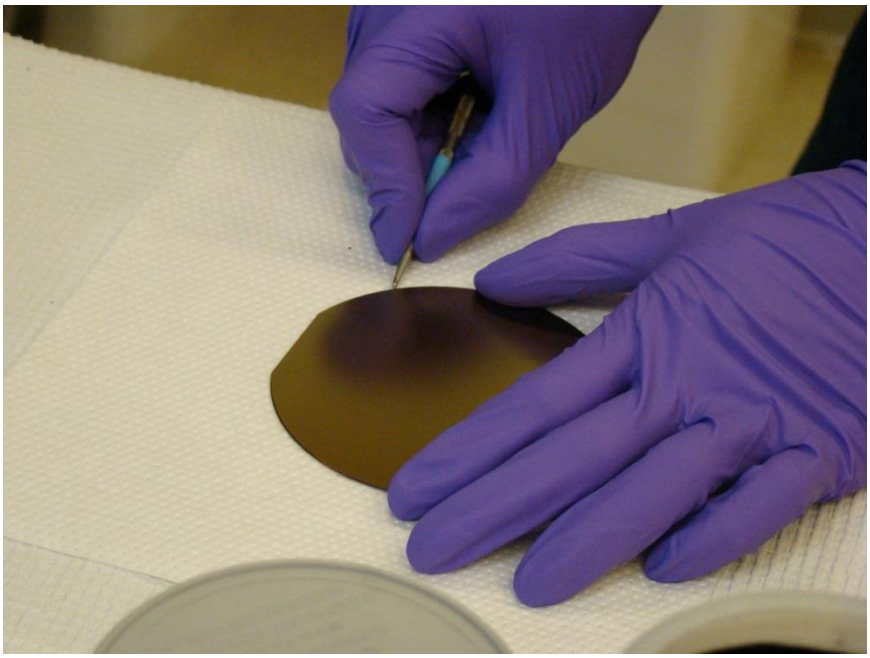


Figure 6: Wafer Notching—Taken from http://lh5.ggpht.com/_opHB9nf8bPg/Rqi9dUNTsSI/AAAAAAAAAcQ/ftMdMQvAEmo/DSC00308.JPG

- Cleaning sample-source wafer with acetone and isopropyl
- Waxing cleft sample pieces to a glass slide for cutting **
- Sawing the samples into 2 mm pieces **
- Gluing 2 mm pieces together, like a sandwich, with thin GST film on the inside, not unlike peanut butter inside slices of bread** (see Figure 7)
    - Curing glue with hot plate until the glue becomes a dark amber color; the pieces are spring clamped together during heating
        - This heating of the sample is actually a part of the procedure that didn't work. The glue was replaced functionally by generic super glue. The super glue provided adhesion without the need to heat the sample.

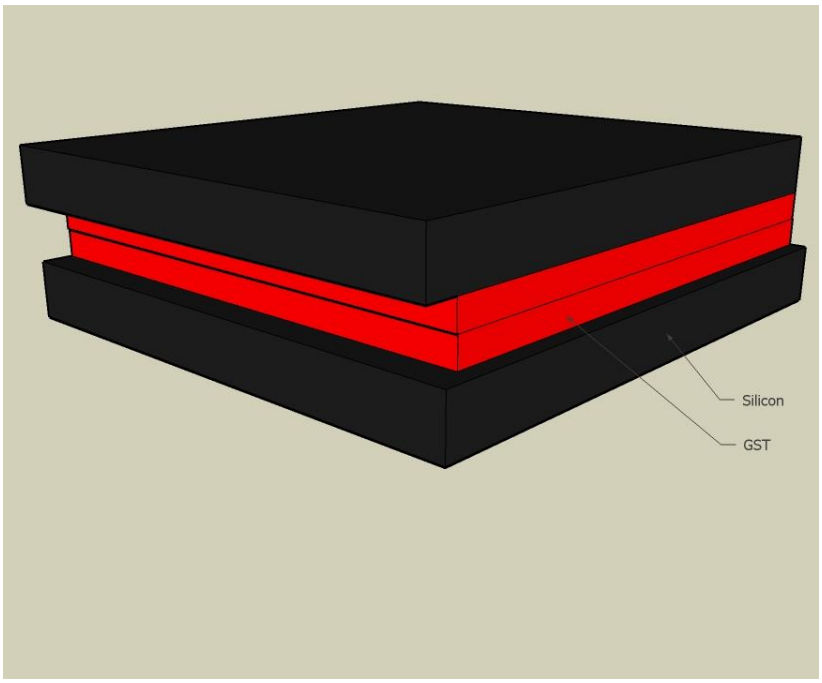


Figure 7-Cross-section "Sandwich"

- Glass foot polishing on the tripod
- Adhere sample to glass foot with wax (place cross-section sandwich onto glass foot with the glue plane parallel to the polishing direction). See Figure 8.

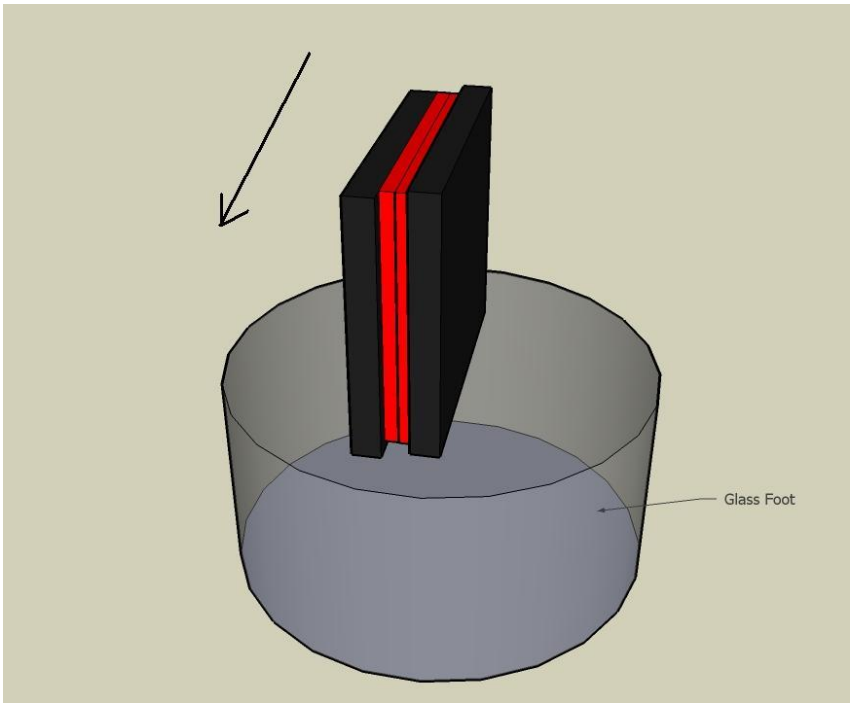


Figure 8: Glass Mounting for Cross-section

- Polish the rough top of the sandwich till edges are even and then continue until sufficiently smooth (a finish polish of colloidal silica), which will become the side in contact with the glass foot **
- Flip cross section and wax with Crystal Bond, a specialized wax. This it where you would start the polishing procedure for plan view samples. See Figure 9. **

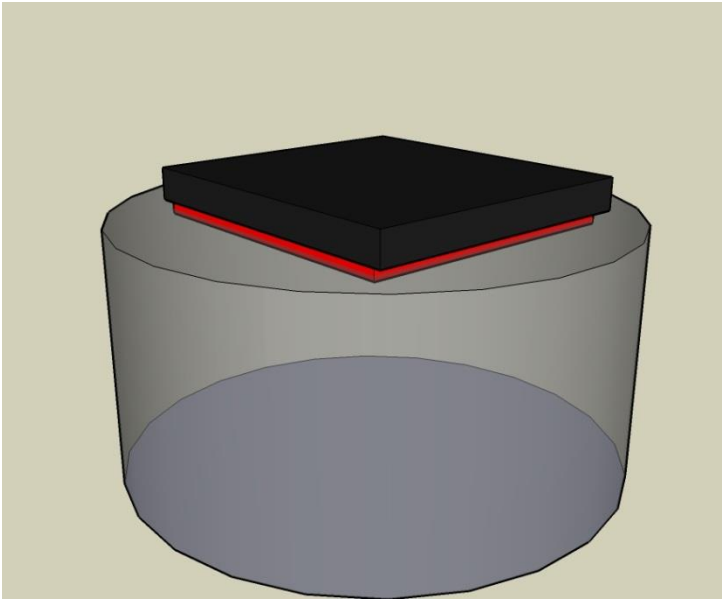


Figure 9: Glass Mounting for Plan View

- Wedge polishing
    - Tripod feet heights determine wedge angles
        - We used a 1 mm difference from the sample to the two rear tripod feet. This would create an angle of approximately 1.25 E -2 radians
- Use the optical microscope check for scratches and cracks throughout polishing process
    - Cracks are the bigger problem
    - Each size of diamond lapping film is similar to a different grade of sandpaper; as the polish gets finer, then so should the film particles. See Figures 10 and 11.



Figure 10: Diamond Lapping Films—Taken from
http://www.alliedhightech.com/polishing/dialapingflm/

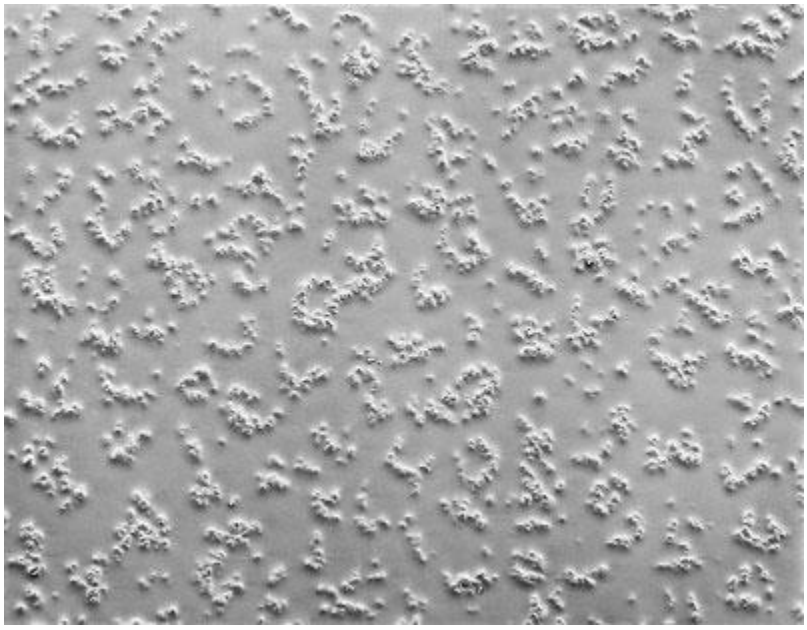


Figure 11: Magnification of Lapping Film—Taken from
http://www.alliedhightech.com/polishing/dialapingflm/

- Use colloidal silica (CS), a suspended liquid polish, to finish the preparation
    - One dropper full of CS on fresh final A cloth (brown)
    - Dropper should be acquired from middle of solution to avoid heavy chunks and floating chunks
    - Have one dropper sitting in water beaker to protect from air dry

    - Run for 3 minutes at a 90° to the radial line of the polishing wheel and add extra CS
    - If all the scratches and fractures are gone, then add a few more drops of CS and polish for 30-60 seconds
    - Rinse and spin dry the cloth
    - Polish on the white cloth ("vel" cloth) for 10 passes without motorized spin
- Mounting procedure:
    - Make filter paper wings with 7 cm diameter filter paper and put that atop a 9 cm filter in the tray
    - Acetone-bathe the wax until the sample falls off the glass foot; replenish acetone to get dissolved wax away
    - Repeat bath with methanol
    - Put M-Bond 610 on left side of the mounting ring; in this case we used Titanium (see Figure 12)



Figure 12: Mounting Ring

    - Look at it the sample and mounting ring under the microscope with sample's thin-wedge edge on the right
    - Touch M-Bond 610 bit on the ring to the sample's thick-wedge edge, lift, and turn over. The thinnest part of the wedge should hang into the open region of the ring. Be careful not to break the tip.
    - M-Bond 610 glue is not to be shaken
    - Give it 2 hours minimum to evaporate before heat curing
    - Heat glue 20-30 minutes on standard mark (between 3 and 4); if not heating, then allow 24 hours to cure at room temperature

TEM analysis was done in FEI Tecnai F30 and F20 microscopes. We followed standard procedures for viewing the sample: bright field, dark field, diffraction patterns, and scanning modes.

We analyzed the images we got from the TEM, enabling us to calculate seed densities since we know the cross-sectional areas and the quantity of particles.

Seeds are crystallite regions in the material, which scatter electrons differently than the amorphous regions. Dark field images typically give better signal to noise ratios, so that was the preferred method of analysis. The Tecnai F20 TEM was used for its STEM and EDX modes, which aren't available on the F30. STEM mode focuses the beam on a very tiny area of the material, and the information from that tiny area is recorded in the computer and correlated to the position of the beam as it is scanned over a region of the sample. This information helps us to detect the contrast made by smaller seeds better than with bright/dark field images. The EDX mode will allow measurement of possible compositional variations between the seed and amorphous material.

The first time I went through this procedure, I found that the sample was completely polycrystalline. We could see the crystallinity in both BF and DF. The diffraction patterns were a clear fingerprint of the polycrystalline state. We will cover the results more in the next section, but the solution we used was to use super glue instead of the using wax to adhere the sample to the glass foot. This avoids heating of the sample. Otherwise we followed the procedure in a similar manner. The superglue processing of the specimen was done only with plan view samples.

Results and Discussion:

Once we investigated our first attempted samples into the TEM, we discovered a major problem. The samples were entirely polycrystalline. Figure 13 shows a diffraction patter from that sample, the distinct rings show that the sample is crystalline and not amorphous.[xiii] We hypothesize this is a result of too much heating as we cured glues and melted waxes.

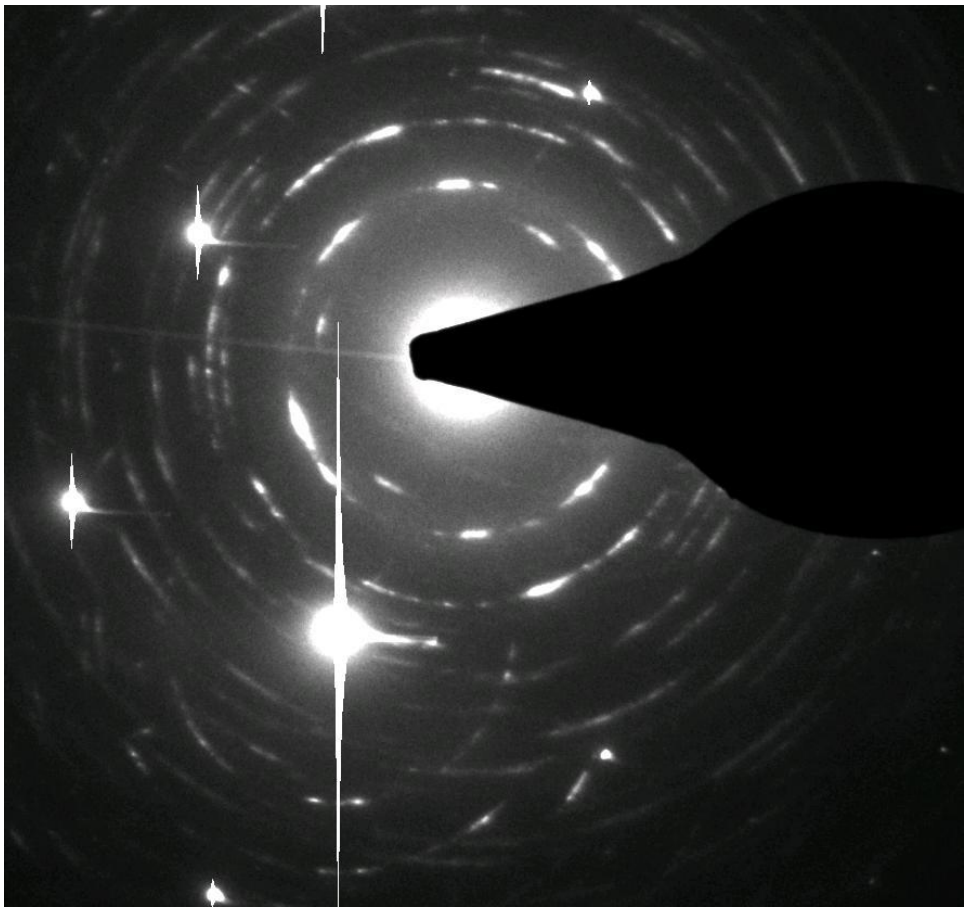


Figure 13: Polycrystalline DP

The bulk of our discussion will be on the super glued plan view sample.



Figure 14: Amorphous GST with Silicon DP

Figure 14 is the diffraction pattern of Si and GST together on the superglued sample. The sharper points represent the consistent, periodic spacing of Si atoms. The GST is amorphous, and we see the characteristic fuzzy rings that we would expect. Amorphous material makes fuzzy rings, instead of just a continual fuzzy field because there is still a nearest-neighbor spacing which has a Gaussian distribution about an average distance.

From this diffraction pattern image (Figure 14), and using the known silicon nearest-neighbor distance to be 1.92 Å, we can approximate the nearest-neighbor distances for GST to be 3.03 Å. This is a close match to what we would expect.[xiv]

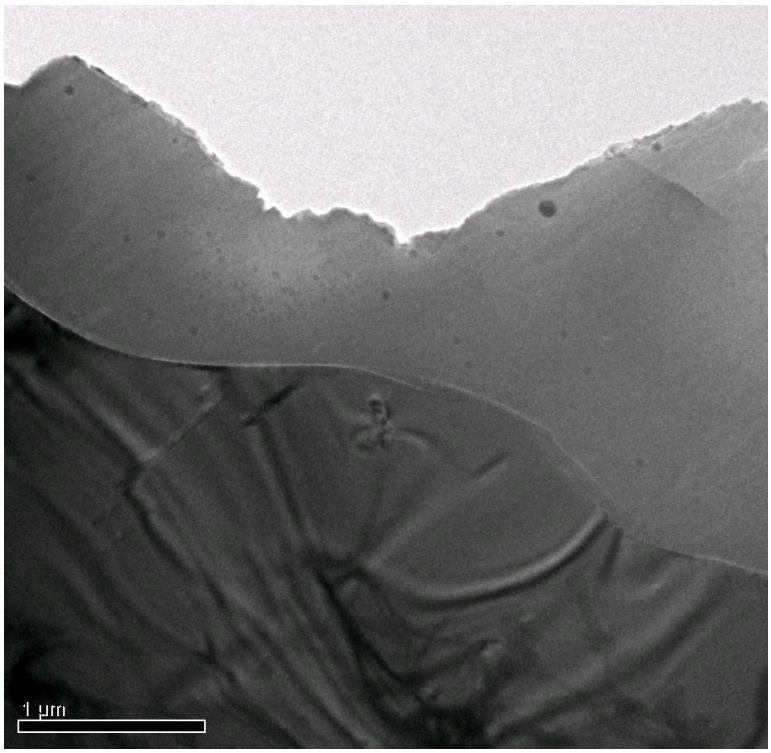
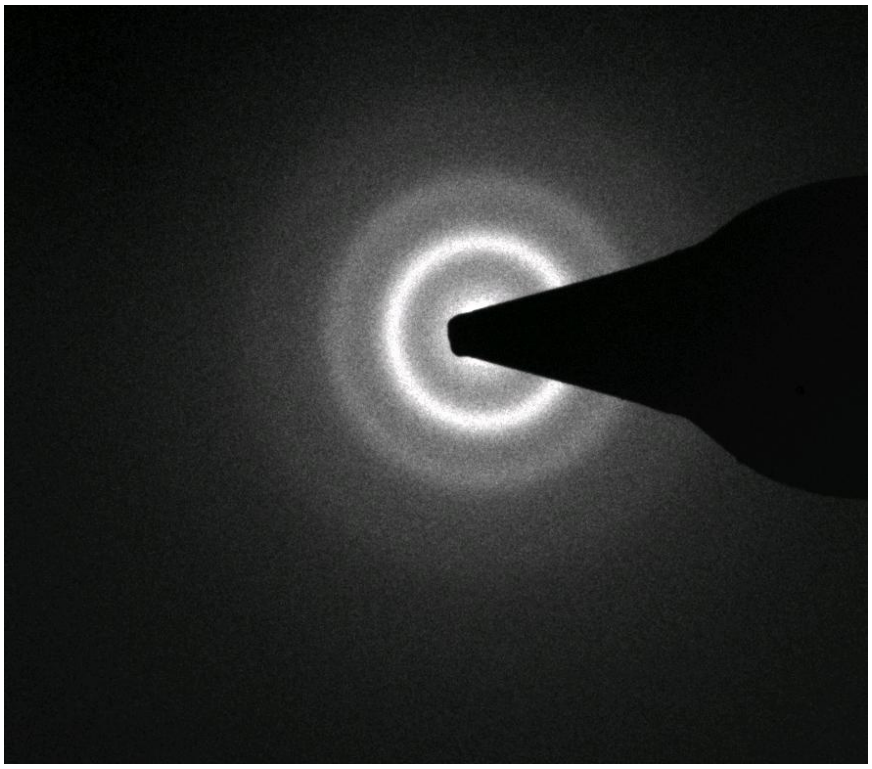


Figure 15: Si and GST BF

Figure 15 is a bright-field image of the area where the diffraction pattern was collected shown in Figure 14 (plan view sample using superglue).


Figure 16: GST DP

Here, Figure 16, is a diffraction pattern of pure, amorphous GST. We can see that the rings are not sharp like in the first generation samples. They are very fuzzy which is indicative of amorphous materials. Notice that the Si points are absent.

In the bright field and dark field images, Figures 17, 18, and 19, we would expect to see sharp features if there were crystallites. We did not see any. We can see some intensity fluctuations in the images, but these are both consistent with the phase contrast imaging mode and the fluctuations changes as the sample is moved. We concluded that this texture does not represent physical features but is fluctuations due to phase contrast imaging. Additionally, the speckles are ~3 angstroms, which is the size of an atom. The significant crystallites we're searching for would be 25–100 atoms, or approximately 5 nm in size.

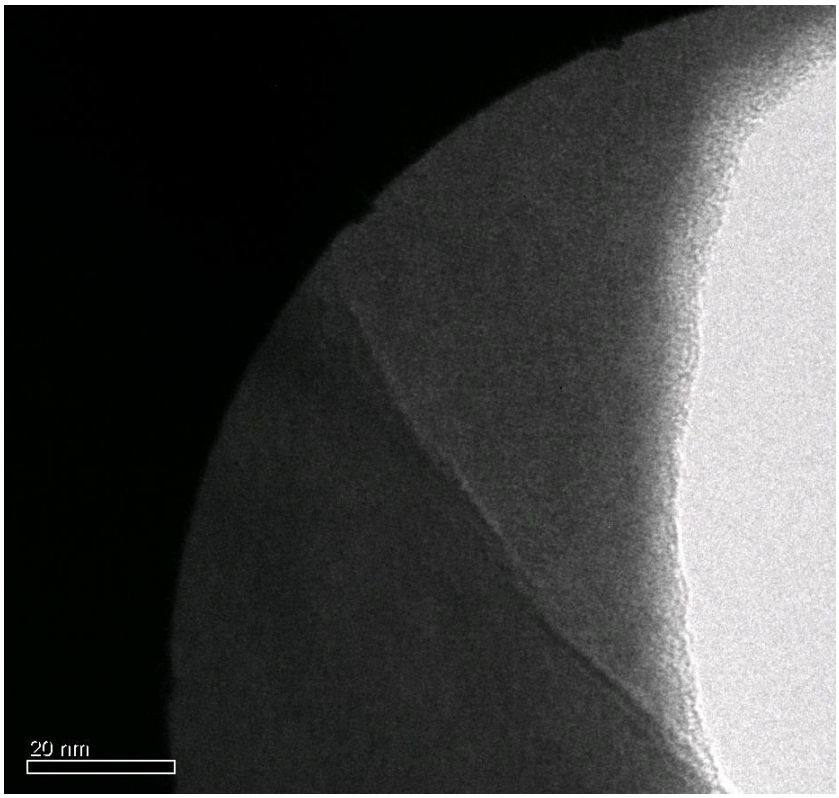


Figure 17: Si and GST BF

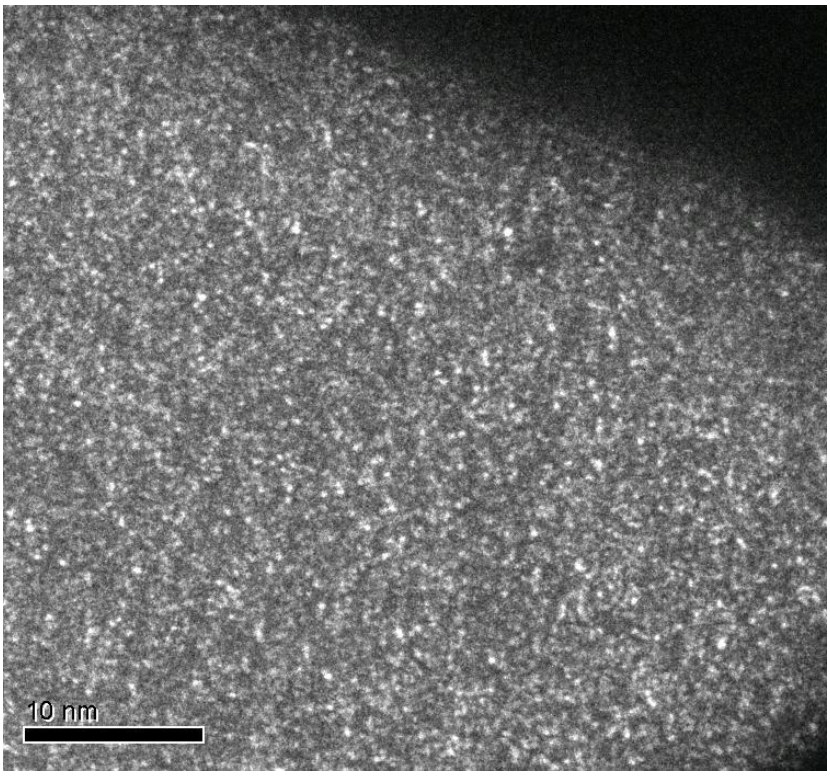


Figure 18: GST DF

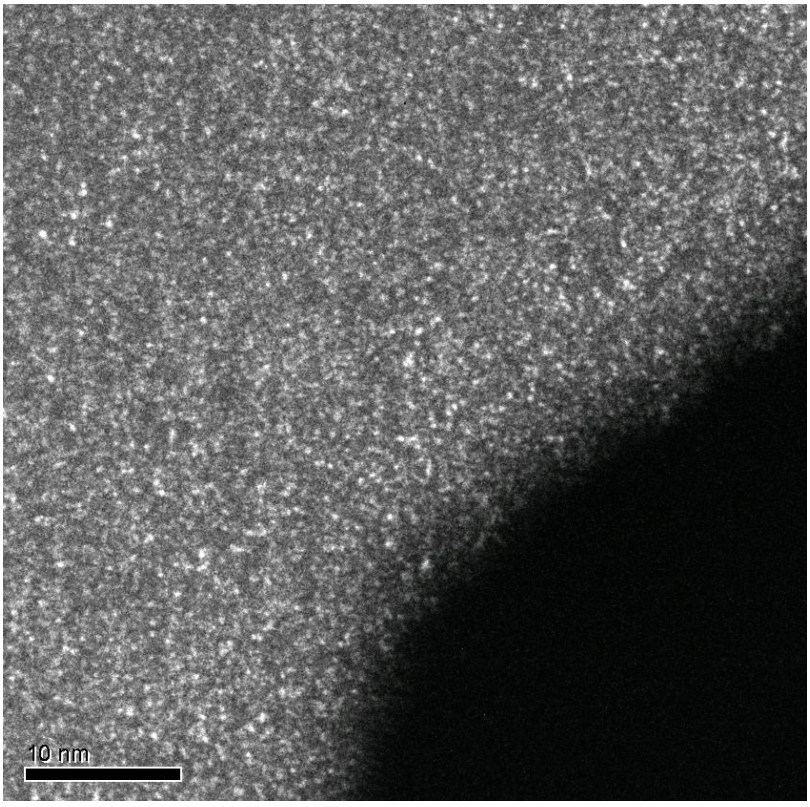


Figure 19: GST DF

With the Tecnai F20 we also did STEM mode, shown in Figures 20 and 21. In this mode, the beam of electrons is narrowed and scanned over the surface. This image mode is sensitive to both changes in crystal structure and in the distribution of the elements. This additional image mode also yields no evidence of crystallites. It is notable that in STEM mode, the beam will pin free carbon to the sample, which will show up. You can see evidence of the scanned and idle beam regions. They show-up as a more intense white.

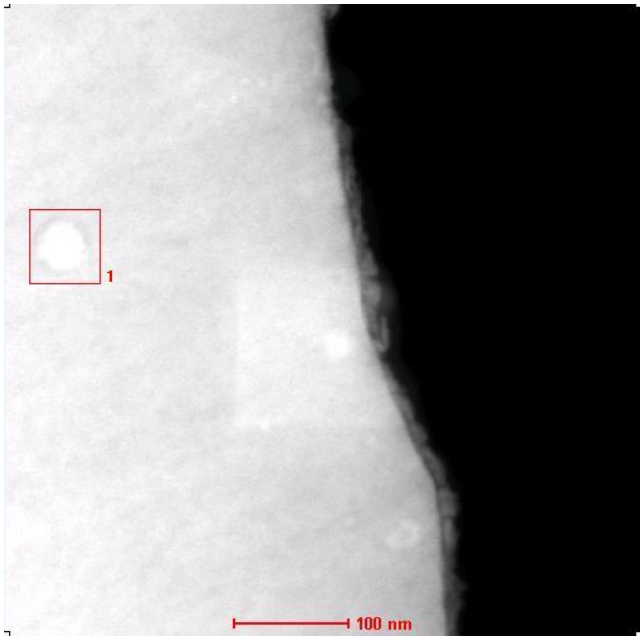


Figure 20: GST STEM

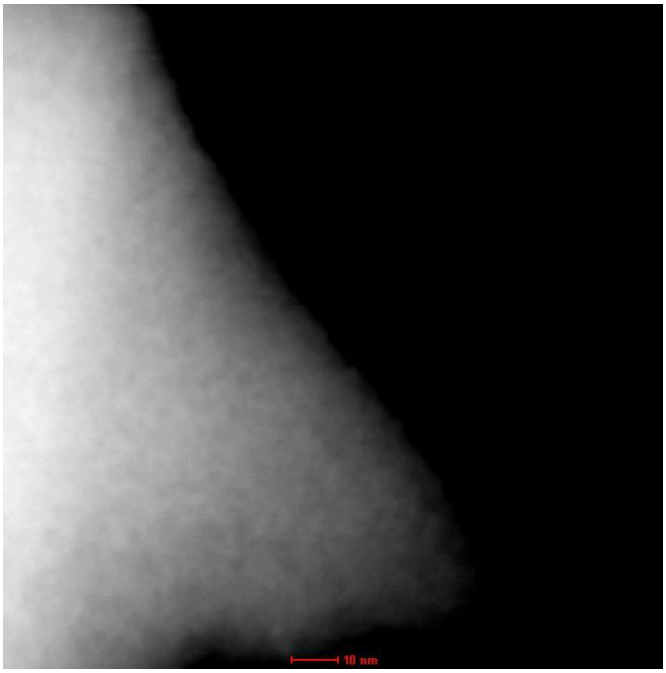


Figure 21: GST STEM

Also with the F20 TEM we can do a compositional analysis process called energy dispersive X-ray spectroscopy (EDS, EDX or EDXRF). This detects x-rays radiating from the atoms of the material when they have been excited by the incoming electron beam. See Figure 22 for an illustration of electron shells and how they are affected by external stimulation (an electron beam). X-rays are radiated from atoms when electrons at relatively high energy states jump to lower energy states, replacing electrons states that were cleared by the electrons from the incident beam.[xv] In the illustration, the amount of energy in the X-rays detected is proportional to the energy level drop (ex. Lα)

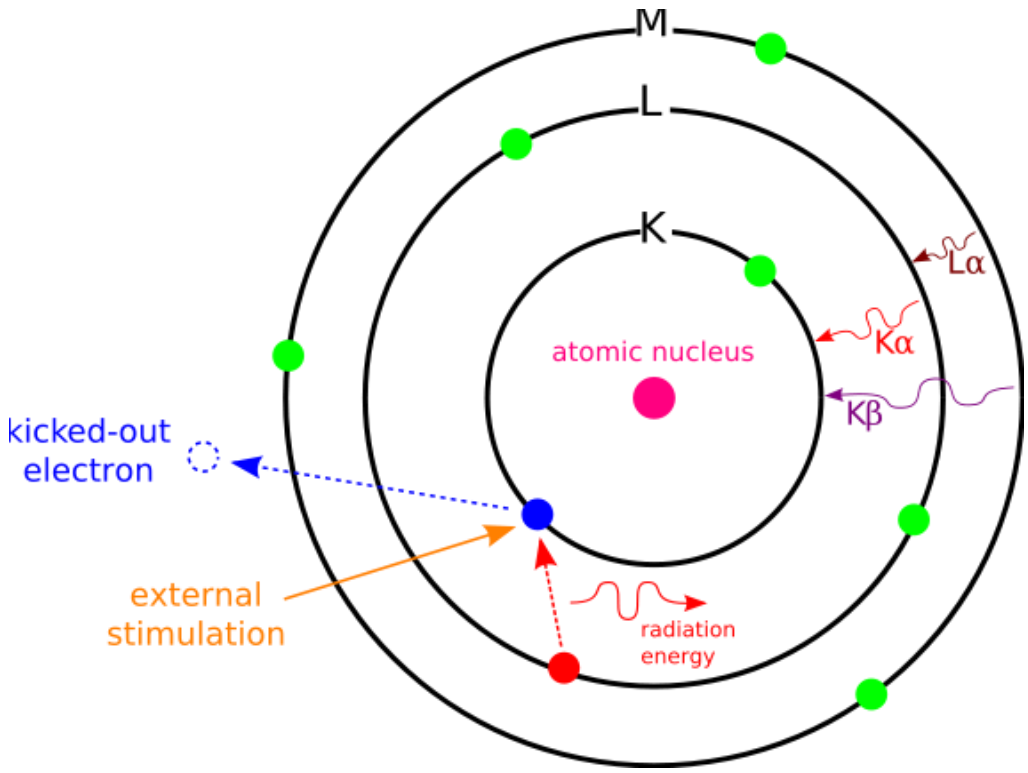


Figure 22: Discrete Electron Energy Levels—Taken from http://en.wikipedia.org/wiki/Energy-dispersive_X-ray_spectroscopy

The radiation spectrum can be quantified to deduce the elemental material ratios. Either this isn't the most precise technique or the sputtering doesn't give a very consistent film because we got varied results each time. We expected a ratio of GST to be 2:2:7, but instead we measured a ratio of 17:16:67. And another time we measured 23:14:62. So the material doesn't appear to be exactly 227. An interesting question would be "Why is that the case?"

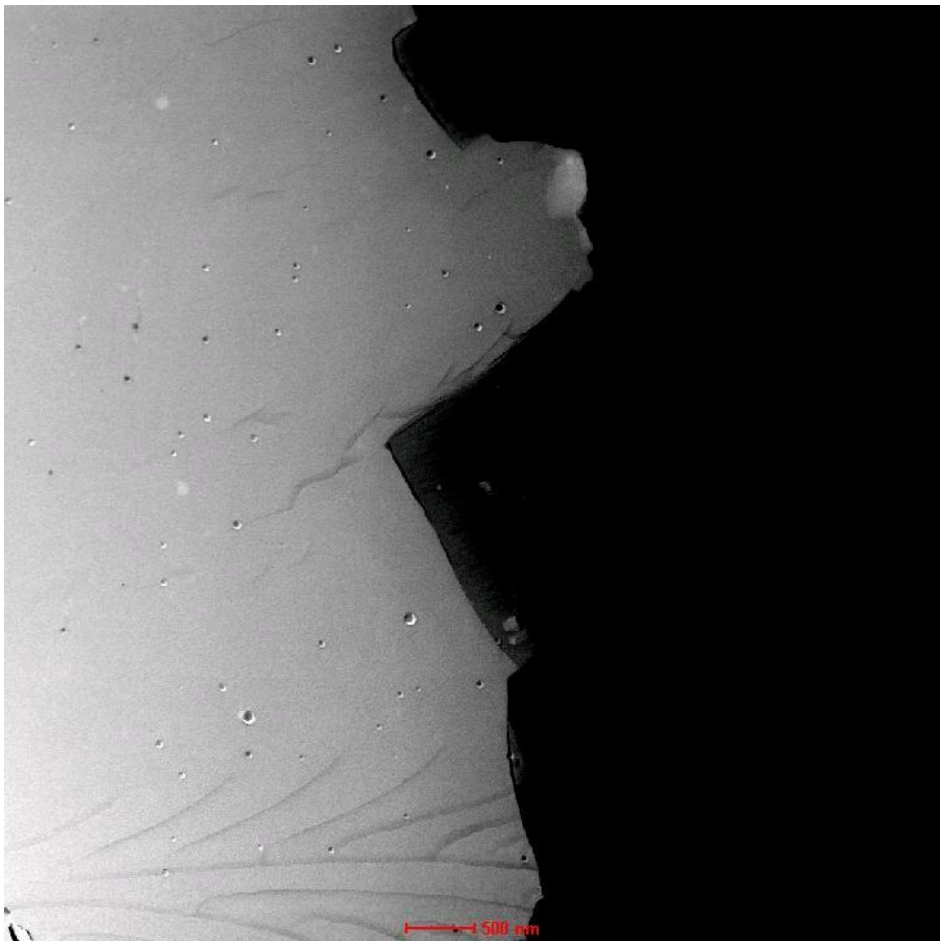


Figure 23: GST STEM

Image contrast is from compositional and thickness variations. The images look pretty smooth, so we aren't seeing any surprises besides some little craters: see Figures 23 and 24. We did EDX on the little craters and didn't find elemental contrast. One hypothesis is that the craters formed from imperfections in the deposition. Features on the predeposited surface that could dissolve in acetone left marks, or perhaps particles were formed during the deposition by gas phase nucleation

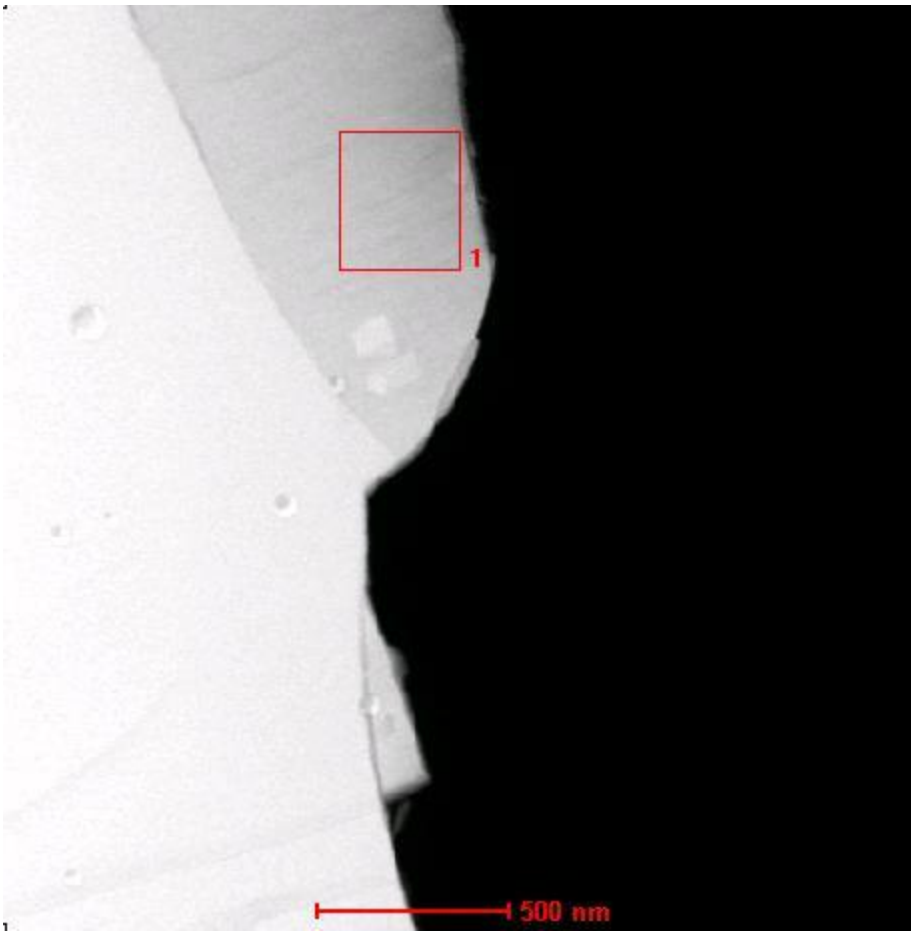


Figure 24: GST STEM

Beyond the quantification I've done here, we did more qualitative searching without saving photos of each view, and we found no evidence of crystallites. We looked using high resolution, bright-field and dark-field imaging, electron diffraction, and STEM; no significant crystal features were detected by our investigation. We quantified the density using photos, measuring areas with the program DigitalMicrograph by Gatan. Crystallite area density approximations in the GST were less than one crystallite per 0.0527 μm^2 which is fewer than 19 crystalites/μm^2 .

Conclusion:

A GST 227 film was analyzed in the Tecnai F20 Transmission Electron Microscope after using a polishing process outlined above. It was useful to search for crystallite seeds because high densities of seeds would decrease the usefulness of the material as a phase-change memory device in nano-circuital applications.

It is notable that the preparation techniques we used were not successful on early attempts. The process takes a while, so a technician needs to gain experience on what steps require the most attention. Otherwise the sample can be lost to the surface of the irrigated diamond lapping film. For me, only after several attempts could I hope that useful samples would be successfully prepared for TEM analysis by my hands.

It is also notable that the crystallization temperature of the film was lower than we were expecting, which manifested in the poly-crystallization of our samples during the heat-curing of our epoxy and perhaps during the melting of wax. Future experiments should carefully monitor any application of heat on amorphous GST films if the crystal structure is relevant to that investigation.

A significant finding is that sputtered 227 GST films don't have any detectable crystallite seeds. This experiment should be repeated with the 225 sample and with other samples treated in other ways to see what could affect the material; specifically what could hinder it from being a next-generation, electrical-component material.

Beyond the quantification, we did more quality searching without saving photos of each view, and we found no evidence of crystallites. Quantifying the density using photos we calculate a crystallite area density in the GST to be less than one crystallite per 0.0527 μm^2 which is fewer than 19 crystalites/μm^2 .

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[i] http://en.wikipedia.org/wiki/GeSbTe

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[iv] http://en.wikipedia.org/wiki/GeSbTe

[v] http://www.wipo.int/pctdb/en/wo.jsp?IA=EP2000009501&DISPLAY=DESC

[vi] http://en.wikipedia.org/wiki/Phase-change_memory

[vii] http://www.cise.ufl.edu/~mssz/CompOrg/CDAintro.html "1.4.3. Circuit Implementation of Digital Logic"

[viii] http://www.dailytech.com/article.aspx?newsid=6371

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