

# Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, Prof. Bassam Z. Shakhashiri, the director of the Wisconsin Initiative for Science Literacy (WISL), encouraged all UW-Madison chemistry Ph.D. candidates to include a chapter in their Ph.D. thesis communicating their research to non-specialists. The goal is to explain the candidate's scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, program officers at appropriate funding agencies, state legislators, and members of the U.S. Congress.

Over 50 Ph.D. degree recipients have successfully completed their theses and included such a chapter.

WISL encourages the inclusion of such chapters in all Ph.D. theses everywhere through the cooperation of Ph.D. candidates and their mentors. WISL is now offering additional awards of \$250 for UW-Madison chemistry Ph.D. candidates.



The dual mission of the Wisconsin Initiative for Science Literacy is to promote literacy in science, mathematics and technology among the general public and to attract future generations to careers in research, teaching and public service.

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# **Structure-property correlations in metallic glass and amorphous carbon films**

By

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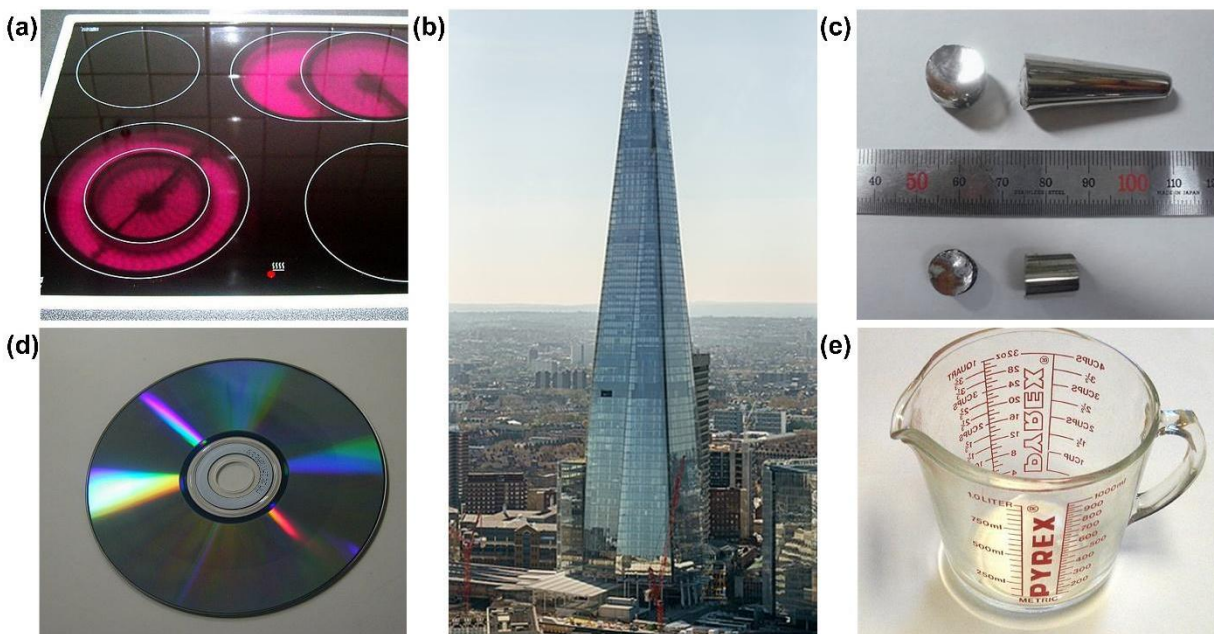
## **Chapter 1** Wisconsin Initiative for Science Literacy thesis chapter

This chapter of my PhD thesis aims to provide context for the general public to understand the new knowledge I created during my graduate school studies. Here, I discuss one (albeit major) out of three themes in my PhD thesis. Through this chapter, a more important personal goal for me is to share the deep sense of wonder and curiosity that I have experienced in trying to understand the physical world around me. I take this opportunity to thank all the members of the Wisconsin Initiative for Science Literacy at UW-Madison, especially Prof. Bassam Shkhashiri, Elizabeth Reynolds and Cayce Osborne for providing this platform, and for enabling the creation of this chapter. I have drawn inspiration from WISL Thesis Chapters written by my fellow students, namely Drs. Camille Bishop and Madeleine Beasley. I also want to acknowledge the very useful feedback on this chapter by my advisor Prof. Paul Voyles, mentor Dr. Felix Lu, Dr. Anne Lynn Gillian-Daniel and Dr. Matt Stilwell from the Wisconsin MRSEC, and my friends Ashley Tucewicz and Prarthana Prabhakar.

### **1.1** What is a metallic glass or any glass for that matter?

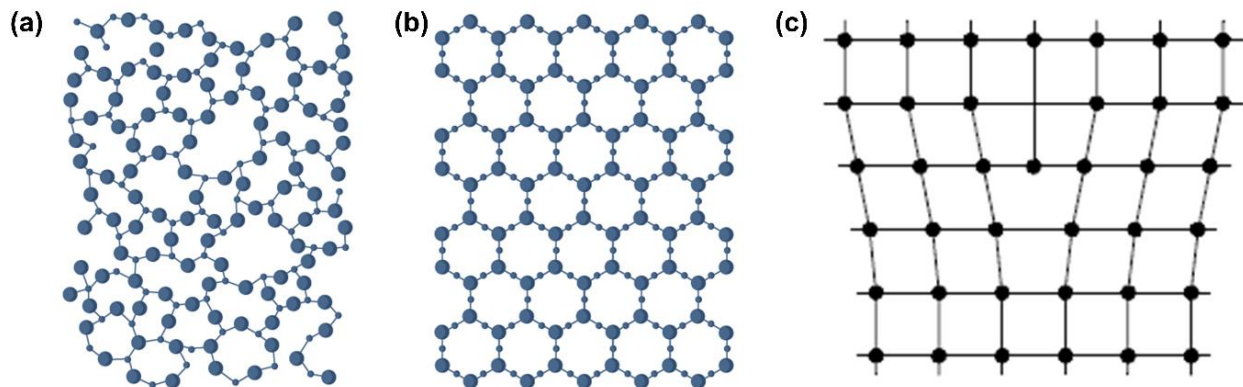
Glass, as a word, is most familiar to us through windows, cookware, and phone screens. Given that I am writing this document in the year 2020, most of us are now spending a lot of time staring at phone screens. Although a cracked cell phone screen is a pet peeve most people have experienced, modern cell phone screens are truly at the cutting edge of current glass technology. Over the past several years, phone manufacturers have improved the glass materials used to make phone screens to the point where we do not need screen protectors. The newly released Apple iPhone 12, developed with Corning Inc., boasts of a practically shatter-proof glass display. The carefully engineered glass structure provides a mechanism to deflect and arrest cracks.

Interestingly, glasses have been made for over 3000 years, yet glass making technology continues to evolve together with advances in our understanding of glass science.



**Figure 1:** Glasses used in common everyday applications such as (a) ceramic glass cooktop[1], (b) glass building[2], (c) metallic glass[3], (d) rewritable compact disc coated with chalcogenide glass[4], and (e) Pyrex measuring cup[5] are shown.

Solids come in two main types: crystals and glasses. In crystals, like table salt, atoms pack together in a repeating pattern. In glasses, the atoms pack together without a repeating pattern. A wide range of materials, like metals (e.g. copper, iron), polymers (e.g. nylon), and pharmaceuticals (e.g. aspirin), form glasses, so long as their microscopic structure is disorganized as shown in Figure 2(a). When melting and cooling something, like water/ice, the atoms typically have enough time while cooling down to rearrange into repeating patterns. The most common way to make a glass is to melt something and then cool it down so quickly that the atoms do not have enough time to find their places in the repeating pattern before they freeze into place. In theory, glasses could be made from any kind of liquid. In practice, only some materials form a glass.



**Figure 2:** Example atomic structures of a (a) glass and (b) crystal are shown. (c) shows a type of dislocation or imperfection in solid. Reproduced from [6,7]

Crystalline metals such as copper and iron are commonly used in many everyday applications. Metal atoms in a solid crystal are like marbles in a jar that pack together in repeating patterns, just touching, and with little spaces in between. Upon filling the jar with sand, the much smaller sand grains fill gaps and make displacing the marbles more difficult than before. Similarly, metallic alloys are mixtures of metal atoms and commonly form regularly arranged crystals. For example, iron is a metal composed of one type of atoms, but steel made by adding small amounts of carbon to iron is an alloy. People use alloys since metals composed of only one type of atoms may not have exactly the right properties for a particular application. Iron can be a versatile material for many uses, but steel is stronger, harder, and rust proof. However, crystalline metals show a common crystal defect called a dislocation, as seen in Figure 2(c). Dislocations can occur when an atom is missing from a crystal or when an atom sneaks in where it does not belong, disrupting the repeating pattern. Dislocations govern many of the mechanical property limitations, like strength, of common alloys.



**Figure 3:** *Picture of frictionless gearboxes being developed by NASA. Source[8]*

Alternatively, promoting a non-repeating arrangement of atoms can result in potentially useful properties. While fast cooling is essential to form a non-repeating structure, such a structure can be further promoted by mixing metallic atoms. Such materials formed by fast cooling and mixing different sized atoms to form non-repeating patterns are also called metallic glasses. Shaking the previously mentioned jar of marbles and sand particles vigorously will move its contents around, like continually moving atoms in molten metals. When the shaking is stopped abruptly, the contents will freeze in their place in a disordered way, just like atoms in a fast-cooled glass would. This analogy explains the common way to make glasses by fast cooling. Their non-repeating atomic structure results in a lack of dislocations resulting in metallic glasses being much stronger (3-4 times or more) than their crystalline counterparts. Metallic glasses, when heated and processed, provide great flexibility in the shapes they can be made into. These unique properties mean potential uses in novel applications. For example, exploring remote, extreme space environments presents an opportunity to develop materials so the hardware can survive harsh, cold conditions like Jupiter's icy moon, Europa. Since metallic glass does not get brittle in extreme cold, NASA is developing frictionless gearboxes made from them, shown in Figure 3.

## 1.2 Thesis research summary

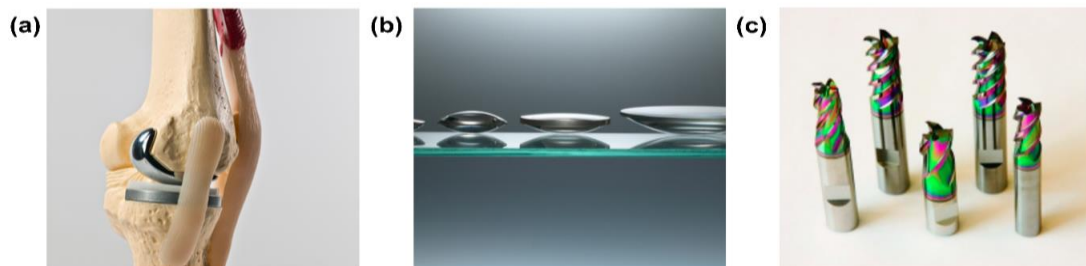
During my Ph.D., I made novel glasses using a new approach called thin film deposition to make glasses with a higher hardness than is possible when using the more common method of fast cooling. With this approach, I slowly built up very thin layers of atoms, kind of like stacking marbles in a box one layer at a time while gently shaking the box. To make these new glassy materials, I needed to add atoms slowly enough that the atoms could pack together tightly, but fast enough that the atoms did not find their spots in a repeating pattern (if they did this, it would be a crystal). This technique depends on many factors and is somewhat difficult to optimize. Nevertheless, it opens many doors for new applications, like coatings on complex geometries (e.g. gears), that are quite difficult to achieve without it. The result is thin layers of hard metallic glass – about 100 times thinner than a hair – with the atoms packed together very tightly. These hard, heat stable glasses are scientifically interesting because they may find uses as hard coatings in biomedical devices like scalpels, needles, and implants.

## 1.3 What is thin film versus bulk?

Thin films are defined as material layers being as thin as human hair or even thinner. Rather like how dust coats every surface on your desk, thin films are created as hot atoms are floating over a cool surface and stick, or condense, onto the cool surface. One way to create thin films is to deposit materials as layers on bulk objects to modify their surface properties. Depositing a thin film material is like applying paint to your house's exterior for protection against weather conditions. Thin films are technologically important and can be used because they alter surface properties resulting in a range of functionalities. In the house painting example, water resistant paint (thin film) on a wooden house would protect the wood (bulk) from being easily damaged by water. Likewise, thin films made from chromium metal on automobile parts can protect them

against ultraviolet rays and prolong their life while saving on materials and cost. Diamond coatings applied to drill bits can impart extreme hardness so they can be used to drill hard things like ceramics, porcelain, and gemstones. These materials can be made 10-10,000 times thinner than a human hair, depending on the application requirements. While the most popular application is in the materials making up computer chips, thin films have been engineered for a variety of applications, including:

- improved surface hardness and protection against wear
- resistance to oxidation and corrosion
- display screens and reflective or anti-reflective coatings
- heat sinks and barrier layers in thermal applications
- solar cells
- next generation memory devices for computers



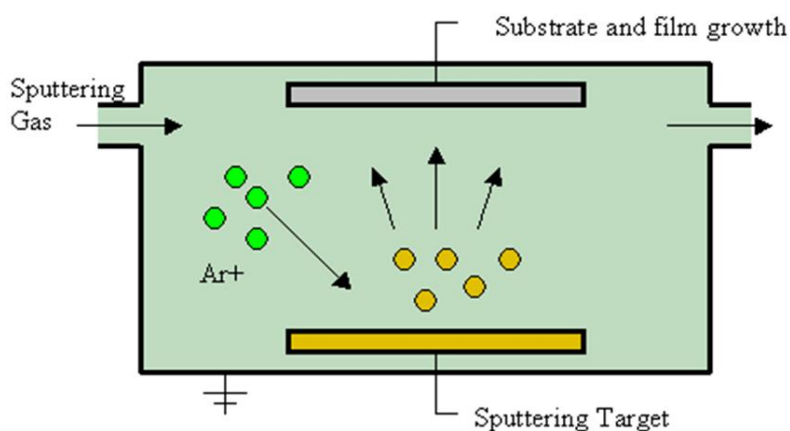
**Figure 4:** Examples of thin films used in (a) biomedical implants to protect against corrosion[9], (b) optical applications requiring anti-reflective properties[9], and (c) cutting tool[10] applications to prolong drill bit lifetimes.

#### 1.4 How do you make thin films?

One common technique to make thin films is called physical vapor deposition (PVD). Solid or liquid materials, including metals, are vaporized in low pressure environments (or vacuum) by



physical methods (such as heating). The vapors travel through vacuum and condense onto “substrates” or the bulk solids we want to coat. A useful analogy to thin film deposition would be water vapor from air fogging up a bathroom mirror or frosting on cold ice cream tubs taken out of the refrigerator. In my research, I used a PVD technique called sputtering.

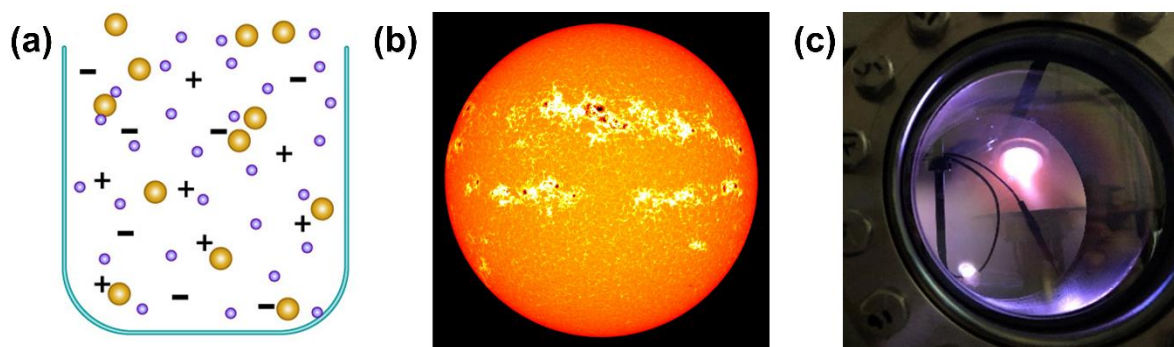


**Figure 5:** Simple schematic showing sputtering process. Ar is argon gas and substrate is where you want to grow your thin film. Argon hits the sputtering target, knocking off atoms that then slowly accumulate on the substrate and grow a thin film one atom-layer at a time. Reproduced from[11]

Sputtering uses plasma as the heat source to vaporize the material that is going to condense on the substrate. Plasma is one of the four fundamental states of matter (solid, liquid, and gas being the other three) and is composed of electrons and ions (atoms missing some of their electrons). The most familiar example of a plasma state is the sun, which is almost entirely a ball of plasma. In the lab, we create plasmas by subjecting a non-reactive inert gas (such as argon) to powerful electromagnetic fields that creates a mixture of neutral gas atoms, ions and electrons.

Early on in my graduate school career, I did not know much about glasses. As an undergraduate student, I had dabbled in some research and was motivated by working with graduate students who clearly knew a lot more about the inner workings of the experiments we did

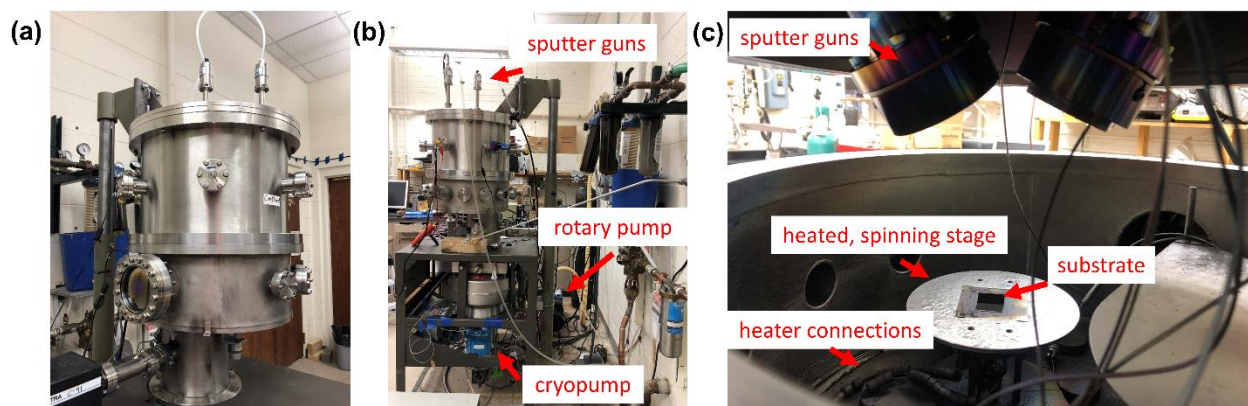
together. Therefore, at the beginning, I was passionate to develop a deep fundamental knowledge of the experimental techniques I wanted to master for my thesis work. So, when this project presented along with itself an opportunity to rebuild a sputtering machine (pictures of the system in Figure 7) needed for my experiments, I dived right in. This project turned out to be especially tough, but now that I am on the other side of it, I really prize my learnings and feel rewarded.



**Figure 6:** (a) Schematic of plasma species[12], (b) picture of the sun[13] and (c) picture of plasma from my experiments.

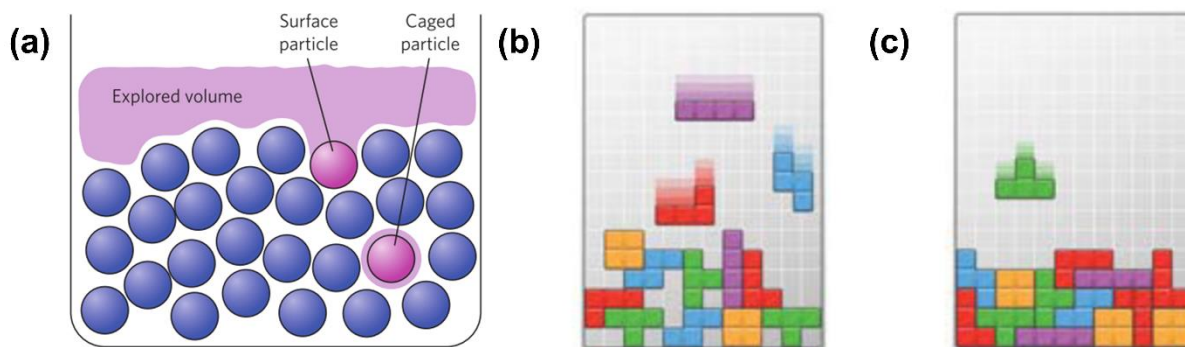
After I built my machine, I had to figure out the conditions to make glassy thin films of interest. Using the plasma state to vaporize and direct metal atoms to the substrate is a lot like playing pool: using the cue stick (the power supply controlling how the plasma is made), you aim the cue ball (plasma) at pool balls (source material) so they travel to the pockets (substrate). The first step was to evacuate all the air from a vessel to get to a pressure like that of outer space. I achieved this by using two types of special pumps: a rotary vane pump that sucks air out and a cryopump that gets very cold (approximately 470 Fahrenheit below water's freezing temperature) so it can trap most of the gas molecules. In the second step, I heated up the substrate and allowed a tiny quantity of pure argon gas into the vessel. Next, I used a "sputter gun" to generate a plasma, which can both spark a plasma and keep it alive using electric and magnetic fields. Plasma is very

energetic and when it contacts the source material, the material's atomic bonds break, vaporizing them. In my experiments, the starting material is a precisely controlled mixture of metal atoms (technically called an alloy), which is important to promote glass forming ability. Sputtering is a unique technique that can maintain the same atomic ratios in deposited thin films as the starting material.



**Figure 7:** (a) and (b) show two pictures from the outside of the sputtering system while (c) shows inside view.

The metal vapor transfers through vacuum, condenses into a thin liquid layer at the substrate and then solidifies. Atoms on the surface can move as much as 100 million times faster than atoms buried beneath several layers (also called film bulk), like cold, solid ice cream staying firm in the cone with the molten top running down the cone's sides on a hot summer day. This phenomenon is because each atom in the film bulk is surrounded by other atoms, but the surface layer has one side free of any neighbors as shown in Figure 8(a). Thus, surface atoms can move around and relax into preferred positions given enough time and energy. Therefore, a glass prepared by PVD likely has better organized atomic structure than glass made from fast cooling.



**Figure 8:** (a) Schematic compares limited mobility of a bulk atom versus enhanced mobility of surface atom[14]. (b) and (c) relate vapor deposition of metallic glasses to playing Tetris: (b) is deposition at fast rates/low temperatures while (c) is deposition at slow rates/high temperatures[15].

Next, how do we control the thin film formation process to promote better organized glass? Essentially, we have two controls on our experiment: deposition rate (or the rate at which vapor atoms arrive at the substrate) and substrate temperature. If we dial down the deposition rate to favor a layer-by-layer fashion, each atom gets a chance to be part of the “runny” surface layer. Therefore, a careful choice of slow deposition rate and optimally high substrate temperature can promote the time atoms stay at the surface and how much they move as part of this liquid layer. I would like to end this section by giving my favorite analogy about the effect of deposition rate on glass structure (borrowed from Drs. Bishop’s and Beasley’s WISL thesis chapters): making glasses by PVD is like playing Tetris (shown in Figure 8(b), (c)). PVD at fast deposition rates and low substrate temperatures is like playing with the difficult game settings: blocks (or atoms making up the glass) will fly down fast and you won’t have enough time to orient them well enough to fit tightly. PVD at slow deposition rates and high substrate temperatures is like switching Tetris to the easy setting: you have enough time to reorient the blocks for efficient packing.

### 1.5 How are groups of atoms organized in a better packed glass?

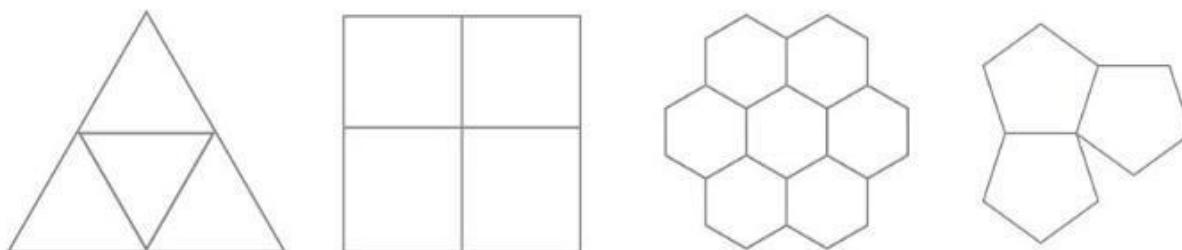
In an earlier section, I talked about how controlling the deposition conditions can result in a better organized glass. But what tells us that the glass is indeed better organized? Glasses don't have discernible repeating atomic arrangements, but they certainly have small clusters or groups of atoms (size can be  $\sim 20$  atoms) arranged in certain patterns. We can study the types of these atomic clusters by determining symmetries present in them. Regular polygons are polygons with all sides of equal length and are said to have rotational symmetry since they can be mapped onto themselves about a central point by less than a complete rotation as shown in Figure 9(c). For example, an equilateral triangle is a 3-sided polygon with equal lengths, thus showing 3-fold symmetry. More generally, where  $n$  is a number, an  $n$ -sided regular polygon is said to have  $n$ -fold symmetry and can be mapped onto itself by a rotation angle of  $360^\circ/n$ .



**Figure 9:** Five-fold symmetries in (a) starfish[16] and (b) okra slices[17]. (c) compares existence of 6-fold rotational symmetry in a regular hexagon versus none in a scalene triangle[18].

As glass scientists, we care a lot about promoting increased resistance to both, (1) crystallization when heated and (2) deformation: (1) indicates a glass that can survive against heating and (2) indicates a stronger glass. The key to a glass' response to external stimuli like heating or deformation resides in clusters or groups of atoms making up the glass. So, what are the different types of symmetries that exist in these atomic clusters and what can they tell us? A famous

mathematical theorem called crystallographic restriction (based on observing many actual crystals) states that only regular shapes with 2-, 3-, 4- and 6-fold symmetries can completely fill up a plane's space (also called tiling a plane). These symmetries mostly make up crystals with long range repeating structure. On the other hand, 5-fold symmetry cannot efficiently tile a plane, leaving behind unfilled space. Then, 5-fold symmetry is incompatible with forming repeating patterns of atomic arrangements and cannot form a crystal (except in one class of materials called quasicrystals, but we will not talk about those here). Five-fold symmetry is all around us, like starfish or okra slices. Some previous experiments and simulations have attributed a higher 5-fold or "icosahedral" atomic clusters to metallic glass structure as the reason for increased resistance to crystallization and deformation both.

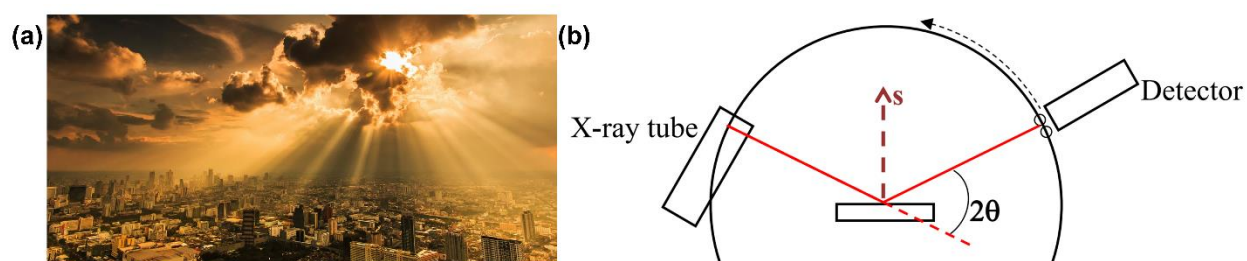


**Figure 10:** 3, 4 and 6 sided tiling shapes fill all space perfectly while 5 sided shapes leave gaps[19].

### 1.6 How do we study glass structure in the lab?

Once I made a new thin film material, I needed to find out what the structure was. To do that, we studied the glass structure by aiming either X-rays or high energy electron beams at our samples and detecting how they “diffract.” Similar to light, X-rays and electron beams usually travel in straight lines, but upon encountering a barrier, they bend around it and become spread out. This phenomenon, called diffraction, occurs when X-rays or electron beams are bent around atoms that are nearly the same order of magnitude or bigger in size than the beams’ wavelengths.

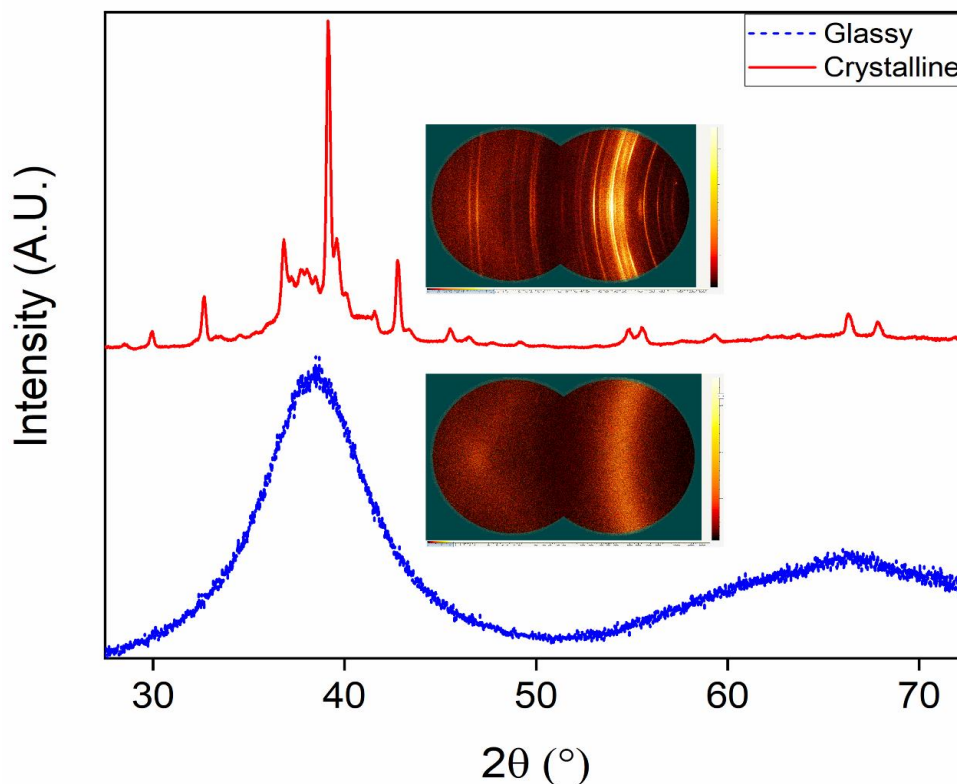
An everyday example of diffraction (although from sunlight rather than X-rays or electron beams) is diffraction of sunlight by clouds, which we call silver lining (Figure 11(a)). Diffraction from X-rays and electrons helps us understand how far apart the atoms are. Lab-grade X-ray diffraction informs us as to whether our thin films are crystalline or glassy. Figure 11(b) shows the instrument's measurement geometry and Figure 12 shows example X-ray diffraction results on glassy and crystalline thin films. While the crystalline data shows well-defined sharp peaks, the glassy data represents a broad peak. The sharp peak means there are crystals with atoms spaced regularly at the corresponding distance. On the other hand, the amorphous sample indicates a range of distances for the interatomic spacing, highlighting its non-repeating atomic structure.



**Figure 11:** (a) Picture of silver lining[20]. (b) Schematic shows geometry of incident X-ray beam originating at the X-ray tube aimed at the sample and detector detects the diffracted beam intensity[21].

While X-rays can tell us whether thin films are amorphous or crystalline, we need a much more sophisticated tool to perform something called electron beam diffraction so we can look at atomic clusters with five-fold and the other symmetries. We performed electron beam diffraction in a million-dollar machine called a scanning transmission electron microscope, shown in Figure 13(a). Figure 13(b) shows the measurement geometry of this technique. My colleague, Debaditya Chatterjee scanned a high energy, focused electron beam of a size  $\sim 10,000$  times smaller than hair diameter (the same size as atomic cluster features we are looking for) across a sample and collected

the diffraction signal resulting from transmission through the sample. Then, we analyzed this diffraction data to reveal dominant symmetries present in our atomic clusters.



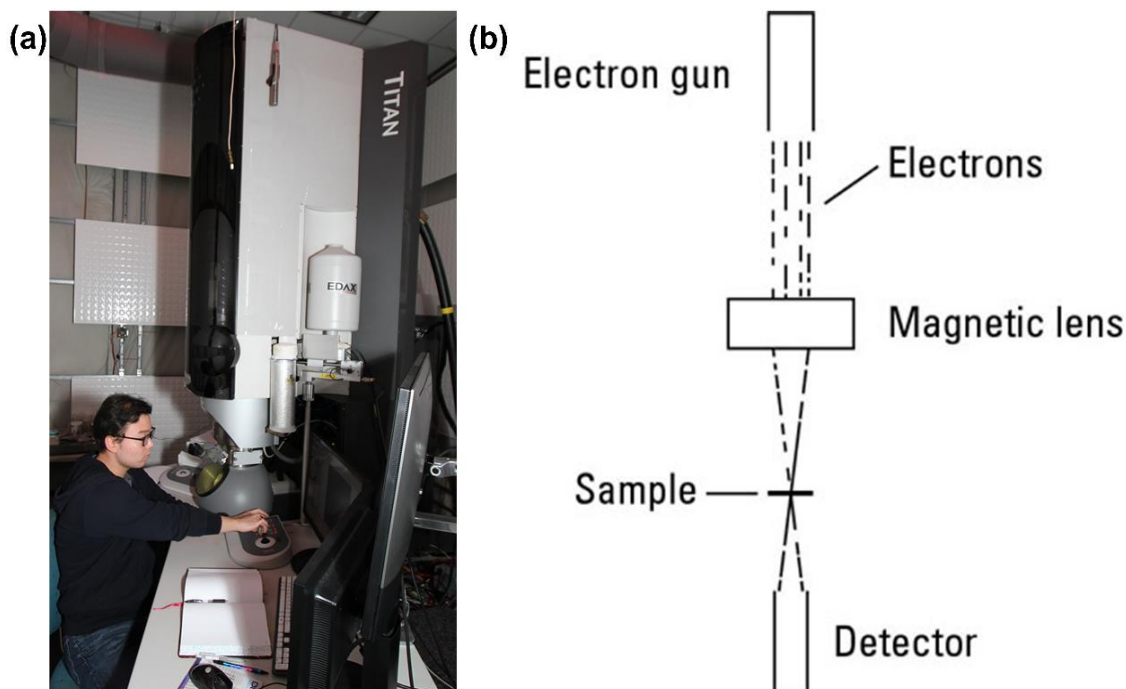
**Figure 12:** The curves represent example results from X-ray diffraction on a glassy (blue dotted curve) and a crystalline (red solid curve) thin film while the insets show detector signal acquired by the instrument.

### 1.7 My key results: shaking a martini of metal atoms to make harder glass

In this document, I want to focus on one main result from my experiments since I consider this piece of new knowledge I created very important to the glass community. Working together with a team of professors, other graduate students and postdocs, we discovered that slowing the deposition rate promotes the occurrence of “icosahedral-like” clusters (size ~20 atoms) in our metallic glasses, which makes their structure more resistant than fast-cooled glasses to breaking either by heating or mechanical deformation. Our work provides a novel understanding of the



deposition conditions required to make harder glass (~4% harder than fast cooled glass) and connect the improved glass properties to a structural origin.



**Figure 13:** (a) Picture shows my colleague, Dr. Chenyu Zhang driving the million-dollar microscope[22]. (b) Schematic shows geometry of electron diffraction measurements[23].

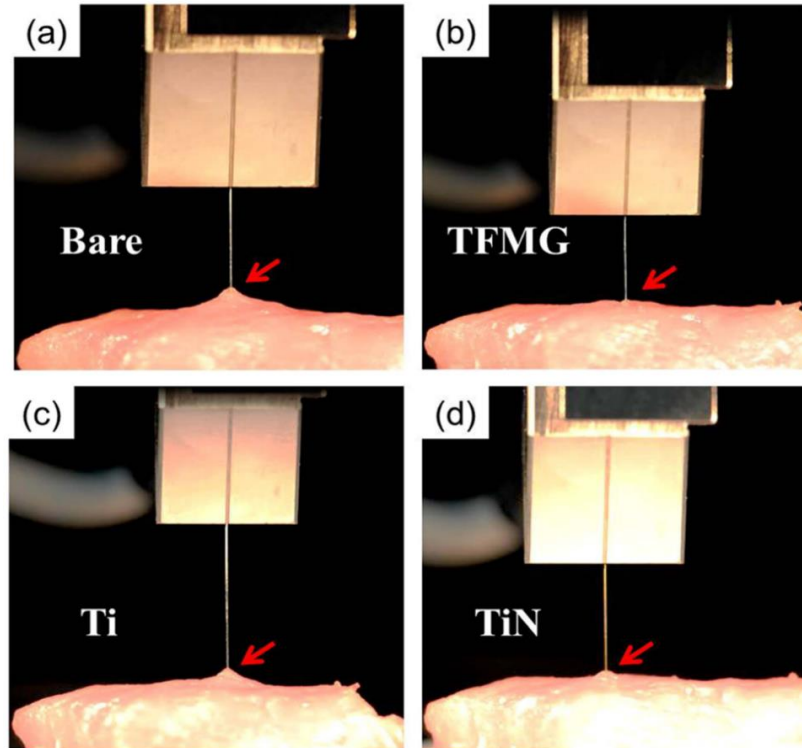
### 1.8 Potential uses: great things come in small packages

My PhD thesis has focused on preparing and promoting 5-fold ordered atom clusters in metallic glass thin films. By virtue of the novel metallic glass states and resulting properties my work could achieve, we think our glasses could have applications in protection of interacting surfaces in relative motion such as gear assemblies (also called tribological applications in the engineering community), and mechanical barrier coatings. Particularly, we think our glasses show promise as hard coatings in biomedical devices like scalpels, needles, and implants. My favorite application was developed in Prof. Jinn P. Chu's group in Taiwan, shown in Figure 14: the team compared interactions of a surgical needle with pig tissue. For the bare needles and those coated

with crystalline titanium and titanium nitride, the tissue stuck to the needles noticeably indicating damage as the needle was inserted and then retracted. Comparatively, the needle coated with thin film metallic glass by sputtering showed minimal tissue damage. The thin film metallic glass needle had a smooth surface and lesser friction, allowing it to easily pierce the skin and thus reduce the pain of receiving an injection. So, if vaccine syringes are made with these coatings, shots would hurt less.

### **1.9 Personal outlook**

My stay in the United States so far has exposed me to academic research in university and national lab settings, and industrial research. As I wrap up my PhD thesis and look back at the last six years of my life, I see the truly immense professional and personal growth graduate school has afforded me. As an international student originally from India, I came to an unfamiliar country with just two full suitcases and frankly, didn't know what to expect. Now having spent five plus years at Madison and one year in Berkeley pursuing research, I understand the scientific process much better and feel as much at home in the United States as I do in my home country. I want to acknowledge all the brilliant academic and industry mentors, colleagues and all my peers I had the pleasure of working with. Despite graduate school being full of ups and downs, I am deeply grateful for this opportunity since it allowed me to build lasting friendships, personal resolve, and grit. After my PhD, I will be starting as a Process Engineer at Intel Corporation, and I hope to leverage my hardware skills and fundamental understanding of physical phenomena, so I contribute to solving impactful problems. Nevertheless, no matter where I end up in the future, I endeavor to take with me the cultivated scientific attributes of rigorous inquiry and abject wonder.



**Figure 14:** Pictures of (a) bare, (b) metallic glass thin film-coated, (c) titanium-coated and (d) titanium nitride-coated needles during retraction from pork muscle. Arrows show needle does not stick to pork muscle in (b) but does so in (a), (c) and (d)[24].

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