Teacher's Preparatory Guide

Coffee Break with Nanoscience: Film Formation and "Coffee Rings"

Purpose: This lab is designed to help students understand some key phenomena exhibited by materials at the micro- and nanoscale. These phenomena play important roles in applied nanoscience and technology. In this activity, students will create thin layers composed of sub-micron particles using the technique of drop casting. They will explore two factors affecting the thin film deposition, film cracking and the formation of "coffee rings." The latter are the familiar patterns left when a droplet of liquid with suspended particles (like coffee) is allowed to dry, forming a distinct ring.

In addition to practicing their experimental technique, students will need to apply knowledge of unit conversions and scientific notation as they calculate film thicknesses. They will also develop thinking skills for laboratory work, develop their ability to apply knowledge in practice, and improve their ability to conduct independent observations, frame a research problem, draw conclusions, and generalize.

Time Required: Two 50-minute lab periods.

Level: Middle school physical science and general science
High school chemistry and physical science
Undergraduate chemistry

Big Ideas: Forces and Interactions; Structure of Matter

Teacher Background: Nanotechnology may be defined as a set of manufacturing technologies that can provide low-cost tools for complete control over the structure of matter. A number of remarkable technological innovations may be enabled by nanotechnology. There are also many everyday technological applications that rely on phenomena at nanoscale. One such technology is the deposition of thin films.

A thin film is a layer of material ranging from a few tenths of a nanometer to several micrometers in thickness. Examples of thin film applications include electronic semiconductors, optical coatings, computer memory, pharmaceutical uses (such as drug delivery systems), ceramic coatings, and advanced solar cells. Drop casting deposition is one technique for depositing a thin film of liquid material onto a substrate. This method is capable of creating good quality, uniform thin films for a variety of applications. In this laboratory we will explore forming thin films using drop casting, identify the potential problems that may occur during deposition, and test methods to improve the uniformity of the layer.

One such problem in film formation is known as the "coffee ring effect". It occurs when a liquid suspension of particles (for example, coffee) is allowed to dry on a flat surface. During the

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drying process, the particles are not uniformly spread over the surface of the drop, but tend to be transported to the outside edge of the drying droplet. This results in a non-uniform coating with much of the particulate material depositing in an outer ring. This effect must be taken into account, for example, when using conventional inks in ink-jet printers.

When a drop of coffee begins to dry, it does so first at its outer edges where the drop is spread most thinly. This pins the outer edges of the drop, so its diameter does not change even as the amount of liquid shrinks. As the drop continues to dry, liquid flows from the center to the edges of the drop under the force of surface tension. The water carries along the insoluble particles, and they gather at the edge of the droplet, which leads to the formation of a dark border around the edges. Multiple concentric "coffee rings" can be observed during the drying of droplets of almost all types of suspensions containing microscopic solids. You can see a video of the coffee ring phenomena in "Scientists crack the physics of coffee rings", viewable at www.npr.org/2011/08/17/139681851/scientists-crack-the-physics-of-coffee-rings .

The patterned deposition of particles can be controlled by altering physical parameters such as evaporation and surface tension, and perhaps one day these phenomena will be manipulated to create small-particle tools. When the liquid evaporates much faster than the particle movement near a three-phase contact line, coffee rings cannot be formed successfully.

A second problem encountered with thin films is cracking. When a liquid film covers a solid substrate and begins to dry, the difference in chemical composition between the substrate and drying film creates mechanical stress, i.e., forces that push and pull on the film and the interface. In many cases this stress causes unwanted cracking of the film. Common thick films used for practical applications, such as clays, paints, and many other types of coatings often crack under drying. The maximum crack-free film thickness depends on particle size, film rigidity, the thickness of the deposition, materials, and drying time. Thinner films are able to sustain larger tensile (stretching) stresses before cracking. The stress at cracking varies inversely with the square root of the film's thickness.

Equipment: per group

- bubble level
- digital scale
- ruler (metric, of course)
- optical microscope, with 50 to 100X capability
- small glass bottles
- micropipette capable of dispensing droplets 100 to 350 microliters (μl)

Materials: per group

- nanoparticle suspensions (see source list below)
- instant coffee
- distilled or deionized water
- glass microscope slides
- flat rubber faucet washers, with an opening of about 18-20 mm; these can be obtained at any hardware store (10 per group)
- metal binder clips, medium size (20 per group)
- micropipette with tips

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- gloves
- safety glasses

Source/Website	Material
Sigma Aldrich	• TiO_2 nanoparticles (diameter <150 nm) 35 wt% particles in water; catalog #700347 • ZnO nanoparticles (avg diameter 35 nm), 50 wt% particles in water; catalog #721077
Alfa Aesar (http://www. aesar.com)	• Polystyrene latex microspheres (e.g. 42711 and 42744); Different sizes available

Nanoparticle suspensions:

Several nanoparticle suspensions with different size particles and/or different concentrations may be used. The following suspensions are recommended because they are safe to use and relatively inexpensive.

Safety equipment: The suspensions are all non-toxic, but may be at low or high pH values, so they should be treated as weak acids or bases. Wear latex gloves and wear safety glasses/ goggles when handling. Review the Material Safety Data Sheets (MSDS) for the materials before the lab.

Instructional Procedure:

A. Advanced Preparation

1. Dilute the ZnO suspension by a factor of 10 with distilled or deionized water, to make a suspension of approximately 5 wt% nanoparticles.
2. Dilute the TiO_2 suspension by a factor of 10 with distilled or deionized water, to make a suspension of approximately 3.5 wt% nanoparticles.
3. Prepare enough diluted suspensions to allow 10 ml per student.

B. Overview of Activity Procedure

1. Students first make the sample holders: place a flat rubber washer on the front of a microscope slide and clip the sides of the washer with the binder clips. Each team repeats for 10 sample holders. Two samples can be placed on each microscope slide.
2. Students then prepare their coating mixtures:
   a. Suspension A: use as prepared in part A.
   b. Suspension B (coffee): Measure 50mg of instant coffee, put in a glass bottle, add 5ml of water, and label the bottle Suspension B.

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3. Assign a group number for each group. As an example for the date of the experiment 07.15.2012; the first group number is 071512_1.
4. Students then proceed to apply different quantities of coating liquid to the sample holders to make films of differing thickness.
5. After the films dry, students will calculate the film thickness for each sample, using information on film area and the fraction of solids in the original suspension.
6. Students microscopically observe the films for cracking. The different thicknesses will be examined for their tendency to form cracks, with thicker films expected to form cracks more readily.
7. Students will also form small films by drop casting suspensions onto a microscope slide with no washer, allowing it to spread and dry. After the film has dried, students will examine it for the coffee ring effect.

Time	Activity	Goal
Day 1		
30 min	Introduce students to the topics of nanoparticles, thin films, and film deposition. Review and discuss the coffee ring and cracks effects. Review the mechanics of unit conversions and scientific notation.	To prepare students for the experiment
5 min	Students answer warm-up questions.	To ensure students understand the material to start the experiment.
15 min	Distribute *Student Worksheets* to students. Students follow procedures as instructed and start the first part of the laboratory work.	To form dried samples for analysis on Day 2.
Day 2		
20 min	Students do measurement and calculation.	To ensure students develop thinking skills in academic work, and create the ability to apply knowledge in practice.
25 min	Observation and conclusions.	To allow students to improve the ability to conduct independent observations, continue to form part of the search abilities of cognitive activity to understand the problem, draw conclusions, and generalize
5 min	Clean up.	To prepare the workspace for the next class.

Teaching Strategies: Options include the following.

1. Discuss with students how important nanotechnology is in real life and what products have been introduced that make use of nanotechnology. (see Resource section)

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2. Review the concepts of size and scale. In particular, focus on small particles. Start with everyday small particles like sand or salt. How do these compare in scale with the particles used in this activity?
Coarse sand has particles a few hundred micrometers (1/1000th of a millimeter, abbreviated as μm) in diameter; fine beach sand may be as small as 50 μm. The coating particles we'll be using are about 0.02μm (or 20 nanometers) in size.
3. Discuss the concept of a thin film. What is it? Where are thin film technologies used?
A thin film is a layer of material ranging from fractions of a nanometer to several micrometers. Solar cells, fuel cells, DNA identification technologies are some examples.
4. Review the measurement units involved with the lesson:
    - Volume: micro liters (μl), milliliters (ml), cubic centimeters (cm^3)
    - Mass: grams (g)
    - Distance: micrometers (μm), centimeters (cm)
    - Density: grams per cubic centimeter (g/cm^3)
5. Review procedure for unit conversions:
    - $1\ \mu l = 10^{-3}\ ml = 10^{-3}\ cm^3$
    - $1\ \mu m = 10^{-3}\ mm = 10^{-4}\ cm$

   Do some practice unit conversions with the class prior to doing the activity.
6. Discuss the research goals of designing and developing new efficient, low cost thin films.
7. Discuss and define the coffee ring effect.
8. Explore the process of cracking. What is stress in a film?

Cleanup: The particle suspensions used in this activity are non-toxic and can be disposed of down the drain. Clean-up spills with soap and water. Discard dried films in the regular trash.

Assessment: The resultant calculations will provide the primary assessment tool. Students will write a lab report summarizing their work; hypotheses and result are required. The reports can be evaluated upon a lab rubric.

Resources:

1. Peter J. Yunker, Tim Still, Matthew A. Lohr and A. G. Yodh. " Suppression of the coffee-ring effect by shape-dependent capillary interactions". Vol. 476, Pg. 308–311, Aug 18, 2011.
2. Mahesh S. Tirumkudulu and William B. Russel. "Role of Capillary Stresses in Film Formation." *Langmuir* 20(7), p2947, March 2004.
3. Kamail B. Singh and Mahesh S. Tirumkudulu. " Cracking in Drying Colloidal Films", *Physical Review Letters* 98, p. 218302, May 2007.
4. Web site of the National nanotechnology Infrastructure Network (www.education.nnin.org) **–** concept of size and scale
5. Video: **"**Scientists Crack the Physics of Coffee Rings", at www.npr.org/2011/08/17/139681851/scientists-crack-the-physics-of-coffee-rings
6. General resource for nanotechnology: www.nano.gov

National Science Education Standards (Grades 10-12)

Standard A: Science as Inquiry

- Abilities necessary to do scientific inquiry

- Understanding scientific inquiry

Standard B: Physical Science

- Structure and properties of matter
- Mechanical properties of liquid

Standard C: Science and Technology

- Abilities of technological design
- Understanding about science and technology

Standard G: Science and Technology

- Nature of scientific knowledge

Next Generation Science Standards

MS-PS1-2 Analyze and interpret data on the properties of substances before and afer tahe substances interact to determine if a chemical reaction has occurred.
MS-PS1.B: Chemical reactions
MS-PS-2.B: Types of interactions
HS-PS1.A: Structure and properties of matter
HS-PS1.B: Chemical reactionsHS-PS2.B: Types of interactions

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Name:_______________________________Date:_______________Class:________________

Student Worksheet

(Teacher comments are in red)

Coffee Break with Nanoscience: Film Formation and "Coffee Rings"

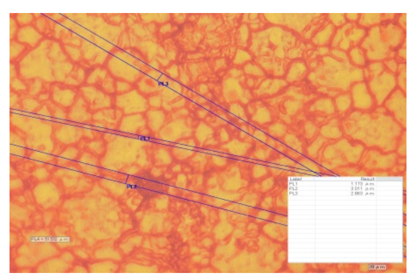
"The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom."
Richard Feynman 1959 "There's plenty of Room at the Bottom"

Introduction

Nano is a prefix meaning "extremely small." Nano comes from the Greek word "nanos" meaning "dwarf". Nanotechnology may be defined as a set of manufacturing technologies that can provide low-cost tools for complete control over the structure of matter. A number of remarkable technological innovations may be enabled by nanotechnology. There are also many everyday technological applications that rely on phenomena at nanoscale. One such technology is the deposition of thin films.

A major tool of nanotechnology products and research is metal or semiconductor nanoparticles. A nanoparticle is any material with at least one dimension of 100 nanometers (nm) or less. Materials at these dimensions may exhibit properties that deviate from the properties of the same material in bulk (that is, at conventional size scales). For example, gold particles less than 100 nm in diameter will have an intense red color, rather than the usual yellow-gold color of macroscopic quantities of gold. Similarly, the electronic properties of materials may change at the nanometer scale.

There are many phenomena that scientists study using nanotechnology. Some of the problems or questions that scientists face when doing nanotechnology research are the same issues that you may observe in everyday life. A good example is the process of coating a surface with a film, like paint or varnish. Paint is a mixture of pigments (colored particles), a vehicle (water or solvents), and a material that dries to form a thin, tough film (usually a polymer of some kind). Once applied to a surface, the paint film protects it from moisture, sun damage, and wear.



Engineers and scientists working with thin films of all kinds must confront two phenomena working against them: cracking and the coffee ring effect. When a liquid film covers a solid substrate and begins to dry, the difference in chemical composition between the substrate and drying film creates mechanical stress, i.e., forces that push and pull on the film. As the film dries, it can no longer stretch or shrink freely, so in many cases this stress causes unwanted cracking of the film.

In addition to cracking, another problem encountered with thin films is known as the coffee ring effect. It occurs when a liquid suspension of particles (for example, coffee) is allowed to dry on

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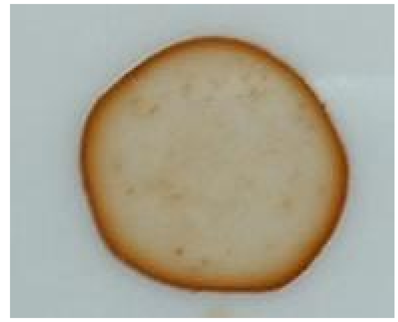
a flat surface. During the drying process, the particles are not uniformly spread over the surface of the drop, but tend to be transported to the outside edge of the drying droplet. This results in a non-uniform coating with much of the particulate material depositing in an outer ring. This effect must be taken into account, for example, when using conventional inks in ink-jet printers.



Some types of solar cells are made using thin films of particles called nanocrystals suspended in a liquid. When making films from nanocrystals, scientists and engineers must try to solve the problems of film cracking and coffee rings, both of which will destroy solar cell performance. In fact, the real-life problem of peeling paint is being solved by scientists using nanotechnology, too (modern paints contain nanoparticles)!

This lab will explore the phenomena involved in coating. You will explore the problems that crop up in real- life coating applications, and see how to avoid coffee rings and reduce cracking during the drop-casting deposition of a thin film.

Equipment

- bubble level
- ruler
- metal binder clips, medium size
- Optical microscope, with 100 to 200X capability
- Small glass bottles or beakers
- Marking pen
- Micropipettes and tips

Materials

- Nanoparticle suspensions, 3 - 5wt% solids
- Instant coffee
- Distilled water
- 12 glass microscope slides
- 12 flat rubber faucet washers
- Gloves
- Safety glasses

Procedure: Day 1

1. Put on gloves and safety glasses
2. Transfer about 10 mL of the nanoparticle suspension to a small beaker, and label as suspension A
3. Measure 50mg of instant coffee, put in glass beaker, add 5ml of water, and mix well. Label the bottle suspension B.
4. Make twelve sample holders by placing a faucet washer on the front of a microscope slide and clip it with 2-3 binder clips.
5. On the back of your samples write down the number of your group. For half of your sample holders, also label them as follows: 100, 200, 250, 300, and 350. Add extension A for suspension A.

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6. For the other half of your sample holders, label them with 100, 200, 250, 300, and 350, and add extension B for suspension B.
7. Label one plain microscope slide (no washers) as CR-A. Label a second plain microscope slide as CR-B.
8. Place all sample holders on a flat surface that you can move when you are done (like a book or a tray). Use the bubble level to ensure that the surface is level.
9. Use a micropipette to drop 100µl of suspension A on the surface of the sample holder marked 100-A.
10. Use the micropipette to drop 200µl of suspension A on the surface of the sample holder marked 200-A, 250µl of suspension A on the sample holder marked 250-A, etc--repeat for the 300µl and 350µl sample holders.
11. For the sample number CR-A, drop 1-2 drops of suspension A on the surface of the microscope slide. Let the drop spread out, but avoid letting it run off the slide.
12. Repeat steps 9-11 for suspension B, including CR-B.
13. Carefully move the sample holders to a place where they can dry overnight.

Procedure: Day 2

1. Gently remove the metal binder clips.
2. Measure the diameter of the inside of the faucet washers. This is your drop diameter, unless the liquid leaked under the washer.
3. Enter your measurements in scientific notation format in Table 1 for Suspension A and in Table 2 for Suspension B.
4. Now we need to determine how thick the films are, but they are far too thin to measure with a ruler. Instead, we will calculate the thickness based on things we can measure.
5. Calculation procedure for suspension A (titanium dioxide or zinc oxide suspension):
   a. Convert the volume of particle suspension to mass.

$$mass\ of\ suspension\ = \frac{volume\ of\ suspension}{suspension\ density}$$

   The volumes you used were 100µl, 200µl, 250µl, 300µl, and 350µl. Convert these volumes from µl to cm^3 (hint: convert them first to ml, which is the same unit as cm^3). Use 1.02 g/cm^3 as the density of the titanium dioxide suspension and 1.04 g/cm^3 as the density of the zinc oxide suspension. Your answer should be in grams--remember to convert the volume units as needed!

   b. Use the result in part (a) to calculate the total mass of particles in each dried film. The mass of the particles in the dried film is given by

$$mass\ of\ particles\ = mass\ of\ suspension\ \times particle\ fraction\ of\ suspension$$

   The particle fraction of the titanium dioxide suspension was 3.5 wt% (multiply by 0.035) and the zinc oxide suspension was 5 wt% (multiply by 0.05).

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c. Use the result in part (b) to calculate the total volume of particles in each film.

$$volume\ of\ particles\ = \frac{mass\ of\ particles}{particle\ density}$$

Use 4.23 g/cm^3 as the density of the titanium dioxide particles and 5.6 g/cm^3 as the density of the zinc oxide particles.

d. Calculate film thickness. Treat the films you made as very thin cylinders with area *A* and thickness *T*. The volume of a cylinder *V* is given by $V = A \times T$.

Using algebra, we can get the film thickness *T*: $T = \frac{V}{A} = \frac{volume\ of\ particles}{measured\ area}$

So the film thickness is calculated by taking the particle volume (from part (c)) and dividing by the area of the film. Since the film is (or should be) circular, its area is given by

$area\ = \ \pi \frac{D^2}{4}$ where *D* is the measured diameter of the circle.

6. Do this for each of your nanoparticle films made with suspension A, and enter the results in Table 1. Convert the thickness of your film from centimeters to micrometers.

NOTE TO INSTRUCTOR: These calculations have been developed in an Excel spreadsheet, which is available for download with this lesson from NNIN. You can use the spreadsheet to check student calculations, or share the spreadsheet with them.

7. Repeat step 5 for your nanoparticle films made with suspension B, and enter the results in Table 2. The values you will need for suspension B (the coffee) are:

   Density of liquid coffee = 1.0 g/cm^3

   Density of solid coffee particles = 0.40 g/cm^3

   Particle fraction of coffee = 1% (=0.01).

Observations and measurements:

1. Under a microscope, examine the films for cracking, as follows: pick three places on each sample, focus in on each spot at a higher power (50 - 100X), and count the number of individual cracks visible. Enter this number in Table 3 for samples with extension A and in Table 4 for samples with extension B.
2. If you microscope has digital imaging, save some pictures of your deposited layers.
3. Draw a graph using data from Table 1 and Table 3 showing the relation between the thickness and the number of the cracks in the film.

Observations and measurements: coffee rings

1. Observe the coffee ring pattern made by both the nanoparticle suspension (CR-A) and the dried coffee (CR-B).

2. Do you see a non-uniform distribution of the particles?
3. How do the CR-A and CR-B patterns differ?

Cleanup:

1. Put the rest of your Suspensions (A&B) into a container designed for inorganic waste.
2. The rest of the coffee can be poured down a sink.
3. The microscope slides may be washed and reused.
4. Clean your experiment table.

Table 1—Suspension A

Note to Instructor: typical values for titanium dioxide are given.

	Diameter (cm)	Area $(cm)^2$	Liquid Volume (μl)	Liquid Volume (cm^3)	Particle Volume (cm^3)	Film thickness (cm)	Film thickness (μm)
Sample #1B	*1.5*	*1.8*	*100*	*0.1*	$7.0x10^{-4}$	$3.9\ x10^{-4}$	*3.9*
Sample #2B	*1.5*	*1.8*	*200*	*0.2*	$1.4\ x10^{-3}$	$7.9\ x10^{-4}$	*7.9*
Sample #3B	*1.5*	*1.8*	*250*	*0.25*	$1.7\ x10^{-3}$	$9.8\ x10^{-4}$	*9.8*
Sample #4B	*1.5*	*1.8*	*300*	*0.3*	$2.1\ x10^{-3}$	$1.2\ x10^{-3}$	*11.8*
Sample #5B	*1.5*	*1.8*	*350*	*0.35*	$2.4\ x10^{-3}$	$1.4\ x10^{-}$	*13.8*

Table 2—suspension B (Coffee)

	Diameter (cm)	Area $(cm)^2$	Liquid Volume (μl)	Liquid Volume (cm^3)	Particle Volume (cm^3)	Film thickness (cm)	Film thickness (μm)
Sample #1A	*1.5*	*1.8*	*100*	*0.1*	$2.5x10^{-3}$	$1.4\ x10^{-3}$	*14*
Sample #2A	*1.5*	*1.8*	*200*	*0.2*	$5.0x10^{-3}$	$2.8\ x10^{-3}$	*28*
Sample #3A	*1.5*	*1.8*	*250*	*0.25*	$6.3x10^{-3}$	$3.5\ x10^{-3}$	*35*
Sample #4A	*1.5*	*1.8*	*300*	*0.3*	$7.5x10^{-3}$	$4.2\ x10^{-3}$	*42*
Sample #5A	*1.5*	*1.8*	*350*	*0.35*	$8.8x10^{-3}$	$5.0\ x10^{-3}$	*50*

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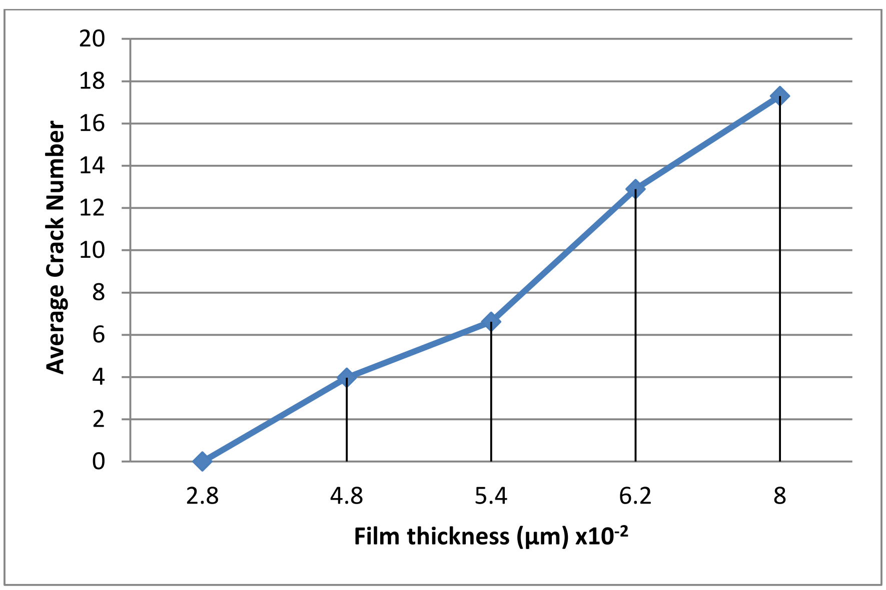
Table 3. Cracks in films made with suspension A.

	No. of Cracks	No. of Cracks	No. of Cracks	Average No. of Cracks
Sample #1A	*1*	*0*	*2*	*1.0*
Sample #2A	*12*	*14*	*17*	*14.3*
Sample #3A	*33*	*43*	*55*	*43.7*
Sample #4A	*56*	*78*	*54*	*62.7*
Sample #5A	*99*	*103*	*89*	*97.0*

Table 4. Cracks in films made with suspension B

	No. of Cracks	No. of Cracks	No. of Cracks	Average No. of Cracks
Sample #1B	*0*	*0*	*0*	*0.0*
Sample #2B	*12*	*14*	*17*	*14.3*
Sample #3B	*33*	*43*	*55*	*43.7*
Sample #4B	*56*	*78*	*54*	*62.7*
Sample #5B	*99*	*103*	*89*	*97.0*

Example Graph:



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Draw Conclusions

1. Did you observe what you expected?

   ____

   If not, how were your observations different from your prediction?

   ___*Answers can vary*

   ____

   ____

2. What natural effects make the thin films non-uniform?

   _________*"Coffee rings" and cracks*__________________________________

   ____

3. How did Suspension A and Suspension B differ in their cracking behavior?

   _________*Answers can vary*

   ____

   ____

4. From your observation, how can you prevent the coffee ring effect during deposition of the suspension?

   *Using a frame around the film prevents the formation of coffee rings*___________________

   ____

   ____

5. From your experiment what parameters can reduce the cracks during the deposition?

   *The amount and size of the crack depends on the film's thickness*______________________

   ____

   ____

   ____

6. Why is it convenient to use an optical microscope to analyze thin films?

   The thickness of the film is very small; viewing it under the microscope with high resolution allows us to take measurements and the analyze surface morphologies of the thin film

   ____

   ____

7. Please describe the result of the experiment in one paragraph and how it relates to nanotechnology. Give your opinion of your experience.

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Answers can vary

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