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THIN FILM CHARACTERIZATION USING RESONANT ULTRASOUND SPECTROSCOPY

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ABSTRACT

With the development of mesoscopic and nanoscale electronic systems, there is currently great interest in the properties of the thin films which form the environment for the electrons. Diamond-like carbon films have also attracted attention for use as a protective coating against physical damage to delicate electronic components. As with bulk solids, important properties include elastic constants and acoustic attenuation, which may be related to the electron-lattice coupling and other effects. By using resonant ultrasound spectroscopy (RUS) and comparing the normal mode frequencies of a specimen before and after film deposition, the elements of the elastic tensor and attenuation coefficients of the thin film material may be determined. With the ability to perform RUS on samples as small as tens of micrograms, the possibility of examining the properties of thin films is feasible. In order to detect the properties of a thin film using RUS, it is necessary that the substrate supporting the film not dominate the measurement. Numerical estimates show that using substrates with sizes on the order of 500 x 400 x 100 microns enables the study of films as thin as 100 nm.

Ideally, the study of a film should be made by measuring the resonances of the bare substrate, then depositing the film while the sample remains in the RUS apparatus, and then measuring the frequencies shifted by no change other than the film deposition. Unfortunately, most film depositions require geometries or hostile conditions (e.g. heated substrates) which cannot be accommodated with the substrate still mounted in the RUS apparatus. Thus the substrate must be removed for the film deposition, and then replaced. In order to determine changes due to the film alone, it is necessary to demonstrate that simply removing and replacing the bare substrate produces no significant shifts in the measured frequencies.

We have performed numerous tests by measuring substrates before and after several removals. We have found that the frequencies for samples with only moderate quality factors, Q of ~1000, cannot be reproduced with accuracy sufficient for studying thin films; the problem is not just the width of the resonance peaks, but also the difficulty in fitting the lower level signals with a changing background. However, Q's of ~10,000 are reproducible with more than the factor of ten improvement because of the reduced effect of noise in fitting. We have found that our original choice of substrate, silicon, was unsatisfactory, and has been replaced with strontium titanate.

TRANSCRIPT

DR. MAYNARD: This is some research that was started by a graduate student, Jason White, and we are now getting a lot of help from a postdoc, Jin-Hyun So.

[Transparency 1]

The objective is to study the physical properties that are related to elastic constants and damping. We are doing this for thin films that are deposited on some substrate.

There are some important applications of thin films, of course. There are thin films in magnetic recording media. These can involve more exotic magnetic materials like materials that show colossal magneto-resistance, manganites, and so on.

Also, thin films are used for protective and lubricating coatings, for example, diamond coatings, even quasi-crystalline coatings, and carbon nanotube films (I will say more about carbon nanotubes later).

Also, some important films are superconducting films, in particular, high-temperature superconductors and, also, of course, there are micro- and now nanoelectronic applications.

[Transparency 2]

There are some important scientific issues. For example, the physics is changed by having a thin film, because, for one thing, you have reduced dimensionality. If the thickness of the film is less than some characteristic length, like a coherence length, then the system really does behave as though it were two-dimensional. Of course, in physics the dimension of the system is a very important parameter.

Also, you can have some influence from the substrate. For example, you can have strain or disorder induced into the film because of lattice mismatch with the substrate, and that is very important, and you can have magnetic interaction between atoms or magnetic ions in the film and magnetic atoms or ions in the substrate.

You can also study novel properties of unique systems -- here, once again, are the carbon nanotubes (they are a hot topic in physics these days). Also, you can determine properties for practical applications such as elastic constants and hardness of a film, also its effect on friction and damping.

[Transparency 3]

The approach that we use, of course, is resonant ultrasound spectroscopy to measure the elastic constants, all of the elastic constants, for the film and for the damping of the film, and we assume that the properties of the substrate are known. I guess I do not really have to describe how RUS works here.

[Transparency 4]

The measurement for films is a little different from just single samples. What you do is you make a measurement on the substrate and determine its natural frequencies. Then you put a film on the substrate, the same substrate, and then measure changes in the natural frequencies, and from the changes in the natural frequencies you can determine all the elastic constants for the film.

In order for this to work, the film had better occupy some substantial fraction of the size of the sample. Just based on our experience of determining the precision of measuring the natural frequencies, we figure we should be able to measure a film that is only one part in a thousand of the thickness of the substrate. For example, we should be able to measure a 100-nm film on a 100-micron substrate (in other units this is 1000 Å on 1/10-mm substrate).

It is not too hard to get thin substrates, but if you have a film whose elastic properties are anisotropic -- for example, a high-temperature superconductor has certain elastic constants in the planes but quite different properties perpendicular, which would be the thin dimension of the film

-- you want to try to measure these elastic constants over the thickness dimension of the film.

In order to do that you would like to have the lateral dimensions of the substrate to be small as well, and I will just elaborate on that.

[Transparency 5]

Here is the substrate that has lateral dimensions that are only a little bit larger than the thickness, but if you look at the modes, most of the modes are pretty much just plate-like modes. If you went to a mode where you were accelerating the thickness of the film in order to measure its elastic constants across the thickness of the film, you would have to go to very high frequencies.

If you did that, you would have such a high density of modes from these plate-like modes that it would be almost impossible to pinpoint the right frequency and measure the thickness modes of the film.

[Transparency 6]

What you need to do is to have a sample, like a normal RUS sample, where the dimensions are all comparable. In that case you can excite modes that have all the dimensions involved in the normal modes and in that case you will be accelerating the film across its thickness and you can measure the thickness elastic constants.

[Transparency 7]

Just by a lucky chance we happened to have an apparatus for measuring very small samples. You need to sample where all 3 dimensions are on the order of 100ths of microns.

This looks like just an ordinary RUS apparatus, except that the size of the sample here is just a few hundred microns. Key elements in this apparatus are the transducers. If you have a small sample, then you need small transducers.

[Transparency 8]

For transducers we used piezoelectric film (just a plastic film like Mylar) polyvinylidene fluoride, PVDF (the trade name is Kynar), and you get it commercially in sheets that are only 9 microns thick.

The way we make our transducers is we take a sheet of this PVDF that is a few centimeters on a side and we evaporate gold conducting coating up to a line on one side and then, on the opposite side, we will evaporate the conducting coating up to a line so that they overlap by about half a millimeter. Then we take a razor blade and cut off a strip that is about a half-millimeter wide.

If you look at the edge of this strip with the greatly exaggerated thickness (this is really only 9 microns thick), where the 2 conducting coatings come in they form the leads to the transducer and where the conducting coatings overlap they form a little capacitor with this piezoelectric film in-between. This little half-millimeter square is the active area.

The properties of the PVDF are very nice. It has quite high piezoelectric sensitivity, but, also, its Q is very low, which is good for resonant ultrasound applications; you want the sample to resonate and not the transducers.

[Return to Transparency 7]

In this picture these strips here are the strips of the piezoelectric film and the active area where the conducting coatings overlap is shown by this red area here.

To mount the samples -- our samples look like a speck of dust (in fact, we have lost a lot of samples) -- (Laughter)

In fact, we made this special white box that is all clean inside, with sides, and we have to work inside this box, and you have to mount the sample -- we have a fine hypodermic needle that we pull a little vacuum on and then we get the sample sucked down inside this hypodermic needle and this little micro-manipulator positions the sample.

One of the transducers is on a block with a lead screw, so then we just bring up the second transducer until we just catch the sample to hold it between the transducers, just support its weight. The smallest sample we have measured so far is one that weighed 70 microgram -- it got lost. (Laughter)

[Transparency 9]

Here is a picture of one sample. This is actually a very large sample for us. This is a ruler and these are the millimeter lines on a ruler, so one of the dimensions is almost a millimeter but the others are smaller.

[Transparency 10]

Here is a more typical sample. It is not much bigger than the actual millimeter markings on a ruler.

[Transparency 11]

Now we need to address the feasibility of being able to measure thin films. We can measure small samples, 70 mcgm, 100-micron-sized samples, but can you still measure a film on such a sample?

Here I let the elastic constants for the film be c_{ij}', and c_{ij} will be just the elastic constants for the substrate. We wanted to determine with what precision we could measure the elastic constants of just the film. That is given by this expression. It is just proportional to the precision with which you can measure the natural frequencies.

You divide by this factor, which is the rate of change of the frequencies with respect to the elastic constants for the film, and it is normalized this way. This is something you can calculate with a RUS program that is set up to do a layered sample.

How well you can measure the elastic constants of the film depends on the precision with which you can measure the frequency. Usually in RUS, with a good high-Q sample (Q of 100,000), you can measure to a part per million, so this looks as though it ought to be pretty easy.

However, in the process you need to measure the substrate without the film and then measure it with the film. There are some cases -- in fact, probably most cases -- where you cannot actually deposit the film while the sample is in the RUS apparatus, you have to take it out.

For example, for most of these films we are studying, high T_c superconductors and the colossal magneto-resistance materials, the substrate has to be heated up quite high before you can evaporate the film on it, so you have to take the substrate out and deposit the film and then put the substrate back in.

The precision with which you can measure the frequency is determined by how reproducible it is to take the substrate out and, say, just put the same substrate back in and see how well you can get the same frequencies. That was the first part of our research program.

[Transparency 12]

Here is one of our samples. These are the different modes and these are the resonant frequencies the first time the sample was mounted, the second time it was mounted, and so on. We actually mounted the silicon sample nine different times.

Here is the average of all the different mountings and the reproducibility of the frequencies in parts per million. You can see here that it is a couple hundred parts per million reproducibility from taking the sample out and putting it back in, which is actually a fairly involved process.

You might think a few hundred parts per million is pretty good if you were measuring the elastic properties of the silicon, but we need to measure a film that is only 1/1000 the size of the whole sample. In other words, you have to take these numbers in parts per million and multiply by 1000 to get the precision with which you can measure the film.

Then it becomes a few hundred parts per thousand, which is only 20 or 30%, which is not really good enough.

The silicon did not work very well. You notice the thickness of the silicon was 97 microns (it was normally a 100-micron-thick sample).

[Transparency 13]

It turns out that the substrate of choice for high-T_c conductors and the manganite films is actually strontium titanate. So we got one of those samples and put it in and the Q's were much higher than with the silicon. Now we are getting, for mounting and remounting this strontium titanate sample -- and we did 4 different samples, and these are typical data, namely, the best data we ever got (actually, it is typical) -- 10 parts per million.

We have now measured this for each one of the different modes and we can calculate this with our RUS program for films to find out what that precision is.

[Transparency 14]

This is a strontium titanate sample, which in this case was 400-and-some microns thick, and the film on it (which is actually one of these manganite films that is 450 nm thick, so it is about a part in a thousand).

Here are the different modes and their frequencies. We also take the rate of change of the frequencies with respect to the film thickness. You can see that for a film that is a part in a thousand of the sample this number is about 10^{-3}.

These numbers are from that formula. This is the precision with which you can determine C_{11}, given the different modes. This is taking the delta f/f that we measured and dividing by that derivative. What dominates here is the smallest number. We can measure C_{11} with just one mode to a couple of percent.

You are actually going to be taking a least-squares fit of the measured frequencies so, actually, you can determine these to better than these numbers, so just a few percent. In fact, you cannot measure thickness to much better accuracy than a few percent, so it seems as if it is feasible.

Now what I would like to do is to go over the modifications to the algorithm for doing films and I just want to do this kind of quickly, just to show you how easy it is to do any RUS program.

[Transparency 15]

No one has done the theory yet, so I will just review it here. You start off with the definition of strain involving the displacements in the solid in the coordinate directions (this i and j stand for x, y, and z coordinate directions). There is Hooke's law that relates the stress to the strain with the elastic constants. You take that and you put it in Newton's law, you get a differential equation and, to get a boundary-value problem, you need a boundary condition, which is just the stress-free boundary condition. You can get these 2 equations by minimizing a Lagrangian.

[Transparency 16]

To do that, you use the Rayleigh-Ritz approximation. You take the displacement field and write it as a finite combination of some basis functions. Then the Lagrangian takes this form, just a matrix, and you get a mass matrix (this has the mass density in it and an integral of the basis functions), and a stiffness matrix that has the elastic constants in it.

One of the important things in the RUS code is how you do the indexing. You let one index actually represent, like the $_p$ and the $_i$ here -- $_p$ is which of the basis functions you are talking about and $_i$ is the coordinate direction, but you can combine those in some clever way, which I will show in a minute.

When you minimize this Lagrangian, you get just a matrix eigenvalue problem.

[Transparency 17]

One of the new ideas, relatively new ideas, was in the early work by Harry Demarest when computers were not so fast, it was convenient to use an orthogonal set of basis functions so that this E-matrix came out to be diagonal. But Bill Visscher at Los Alamos pointed out that if you use a simpler set of basis functions that are not orthogonal but just linearly independent, then you can do those integrals. You get off-diagonal elements in the mass matrix but the integrals can be done analytically for a number of different shapes, including prisms, spheroids, ellipsoids, shells, bells, eggs, potatoes, sandwiches, and others.

Visscher published this code. In fact, our first programs were written by the graduate students and they just looked like a horrible mess to me, but then I saw Bill Visscher's paper and saw how easy it was to do this stuff and then I realized, gee, I could write a program like this myself, so that is what I did.

In this program we found out that if you scale the basis functions with this a, b, and c, which are half the edge lengths of the sample, you get orders of magnitude better conditioning for the matrix, so that is one modification we did to Visscher's program.

The integrals that you have to do are just between limits of -1 and 1. In any case, you get very simple expressions for the integrals that you have to do, analytic expressions, so you do not have to do any numerical integrals.

There are some important consequences of symmetry. It turns out that if the elastic tensor has orthorhombic or higher symmetry (better symmetry), then the matrix that you have to diagonalize becomes block diagonal. This is a consequence of the parity in these basis functions.

For example, if the power here is odd, then this function is odd for plus and minus x. If you have pairs of these functions, if the overall power is odd, then when you integrate from -1 to 1 you just get 0. Because of that parity symmetry in x, y, and z, it turns out that the matrix is 0 everywhere except for 8 matrices along the diagonal. So instead of having to diagonalize a big matrix, you just have to diagonalize a much smaller matrix 8 times and that gives you an almost 8-fold saving in computer time.

That is the basic RUS algorithm.

[Transparency 18]

If you have a film, I define alpha to be the film thickness divided by half the edge length. The zeta here is the film mass density minus the substrate mass density normalized to the substrate. Then we define an elastic constant tensor as the difference between the elastic constants, the 4 index elastic constants, of the film and the substrate. You will see why we do that in a minute.

If you do that, then the integrals that you have to do, the mass integral, the first term is just like an ordinary RUS sample, but then you have a second term that has the difference in mass and for the stiffness integral you have this expression. Again, this is just like the ordinary RUS sample, but there is another term that has the difference in the elastic constants.

These integrals here are done from -1 to 1 in x and y, but from 1- alpha to 1 in z. Because of this different integral in z for the film, it breaks the symmetry in the z-direction. Instead of having an 8-block diagonal matrix you have only 4 matrices on the diagonal and they are larger than the other matrices, but at least you still have a fourfold increase in computation speed.

The next couple of viewgraphs are going to be pictures of computer code.

[Transparency 19]

You are not supposed to see anything in the computer code. I just want to show you these to impress you with how really easy this stuff is. Albert is happy to give you computer code, but I am sure he will agree with me that it is better if you are in control of your own computer code.

This part right here is the only part you have to do yourself; everything else comes out of Numerical Recipes. It uses the Levenberg-Marquart routine to least-squares fit the data. This routine over here is Bill Visscher's routine that is published, the actual source code is published.

[Transparency 20]

Just a couple of things to notice: When we scaled our functions we had to add these lines of code here. When you do the 8-fold block diagonal matrix, that is done in these 3 loops here. The 1 and the 2 for each of these variables are just the odd-and-even parity for the x, y, and z coordinates.

When you change to a film, the only change is that instead of doing this 8-fold loop, you do only a 4-fold loop. This last line here winds up over here and you actually calculate the matrix. You get a matrix that is twice as big but you still get the 4-block diagonal matrices.

[Transparency 21]

The other change is that here is where you actually do the calculation with the index elastic tensor. For our modification of the program we just took this, did a cut and paste and reproduced it down here, changed the c's to d's (this is the difference in the elastic tensor), and then there is function, f, which changes to a g. The only difference there -

[Transparency 22]

Here is Bill Visscher's f function (one line, basically), and here is our one line, and here is the 1-alpha. That is the only change for doing a film. It is probably a total of 10 lines of code difference from Visscher's published program for doing films.

[Transparency 23]

I will just mention one of our applications, as I see time is running out. We are doing manganite materials, and that is working very well, we get nice high Q's for the substrate with the film. We are also having a lot of fun doing mats of carbon nanotubes.

If you remember Buckyballs, if you heat up carbon, when the atoms come back together in a partial vacuum, they form these nice geometric clusters. If you do this with metal ions present, then the metal ion will attach to some site so that the Buckeyball will not close, so you get part of the Buckeyball down here but then you get a cylinder that grows, and even though this is maybe a few nanometers in size, these cylinders will grow to maybe 100 microns in length. It is undoubtedly the strongest fiber ever made.

There is lots of good physics in the way you can roll up these cylinders, there are different ways the cylinders form. You can have a one-dimensional metal or a semiconductor, depending on how they roll up.

[Transparency 24]

They have interesting mechanical properties (there is an article in Physics Today on that).

[Transparency 25]

People have tried to measure elastic constants for single fibers. This is actually a resonant ultrasound spectroscopy measurement, but this was for a multi-walled fiber.

[Transparency 26]

What we are trying to do is to have these carbon nanotubes deposited on a substrate and then you use RUS to determine the elastic constants for a spaghetti of these carbon nanotubes.

We are finding that there are huge differences in damping. Damping can change from a Q of 17 to a Q of 1000 just depending on what kind of exposure this thing has had to air.

That is it. Thanks.

DR. MEHL: Are those nanotubes in some kind of matrix? What is holding them on the surface?

DR. MAYNARD: They have weak van der Waal's bonding forces to the substrate and to each other. You can actually get those mats that are as thick as a micron, which would be pretty thick for our measurements. You have to bake the samples very carefully and that is what we are doing now. We are trying a slow bake at a temperature that does not melt our PVDF transducers. We are also trying to take the sample out and baking it at 400 C, or something, to give it a good surface treatment.

DR. LEISURE: That was pretty much my question, was how those things are bonded to the surface, and are your results affected by how strongly the film is somehow attached to the surface?

DR. MAYNARD: I cannot answer that until we do a complete bake-out of the system. They were shipped to us through the mail -- they were supposed to come in a vacuum container, but they forgot to do that. With overnight express it gets exposed to air a bit.

DR. ISAAK: The bit about the precision with df/dt, did you play around with maximizing the contrast between the substrate and the expected elastic properties of the film? That would increase your df/dt.

DR. MAYNARD: No, in fact, that was for a real sample, that was for a strontium titanate substrate with a manganite film on it.

DR. ISAAK: Yes, but the contrast between those 2 materials.

DR. MAYNARD: I would have to look at the elastic constants.

DR. ISAAK: I mean, if you had a large df/dt, it would improve the precision.

You got at it by getting stuff that gave you really high Q's, so you could find the peaks very accurately, right? That would be another way, I think.

DR. MIGLIORI: What was the Q of the strontium titanate there?

DR. MAYNARD: I think there might have been some peaks that were 10^5. We do not quite understand why the silicon was as bad as it was.

DR. MIGLIORI: Was it glass?

DR. MAYNARD: No, these are single crystals. You have to remember that the Q goes like the surface to volume if you have surface microcracks and losses due to that. As the thing gets smaller and smaller, which our samples do, then the Q goes down, so it is not like a millimeter-size sample.

DR. MIGLIORI: We have had awful problems getting high-Q single-crystal silicon samples because of surface microcracking when you polish them.

DR. LEDBETTER: I think you said you measured oxide superconductor films?

DR. MAYNARD: We are going to. The person who was going to give us those films gave us the manganite films instead.

DR. LEDBETTER: If you had measured them, the question would be how do the measured results compare with the bulk properties. Have you made such a comparison for any materials?

DR. MAYNARD: No.

DR. GILBERT: If you do not get the shapes exactly right, those shapes in the pieces in the sample, how does that enter into your calculation, for example? Suppose your measurements are off, how does that affect what you get out of your calculation for the shifting of the resonances?

DR. MAYNARD: I am sorry?

DR. GILBERT: You are at very high frequencies, I would guess much bigger than some of the modes of the shape, and you showed the shapes twisting around, and that depends on having gross geometry of the pieces correct.

DR. LEVY: Do you mean dimensions?

DR. GILBERT: Dimensions.

DR. HARGROVE: Dimensions or parallel faces?

DR. GILBERT: I mean the gross geometry of the sample, how does that affect what you learn about the elastic constants?

DR. MAYNARD: You are not talking about films now, you are talking about --

DR. GILBERT: Just take the sample, for example.

DR. MAYNARD: A lot of this is in Phil Spoor's thesis. For his samples he did a very careful analysis of how parallel and perpendicular the sides were and he had a program where he could put that information in to see how it shifted the frequencies. This was getting absolute numbers out better than a 10th of a percent.

DR. MIGLIORI: But if you have the dimensions off by a 10th of a percent, you may not get a fit; that is, if your mathematical model does not correspond to the real sample, then you will fail. I think there is a straightforward correspondence between dimensional errors and how badly you do.

DR. GILBERT: I guess I could ask one more question. How is what you get from running these elastic constants affected by the shape of the sample? It should be independent of that, right? The elastic constants are a property of the crystal structure, not --

DR. MAYNARD: Oh, if you know the shape of the sample, you get the answer.

DR. GILBERT: Okay, so, in principle, the shape of the sample somehow does not matter if you do everything right.

DR. MAYNARD: Exactly, yes.

DR. SACHSE: It has to be pointed out that the resonant peaks will shift --

DR. MIGLIORI: In fact, a good way to tell whether you know what you are doing is to polish it and measure again to see if you get the same answers.

DR. MAYNARD: Right.

DR. BASS: Thank you, Jay.