Materials Chemistry

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Module - 2
Lecture - 1
Molecular Beam Epitaxy Monolayers to Multilayers

We have come now to the second module of our course, and in the first module we have seen how chemical approaches are fundamental to making solids and inorganic structures. So, we have seen the power of chemical methods, how they can be cost effective and we can make molecular solids into inorganic solids. And what are the fundamental approaches from chemistry point of view to make such three dimensional inorganic solids.

In the second module, I am going to take you through a totally different approach, which is predominantly a physical approach. In physical approach, I am going to tell you, how using physical vapor deposition techniques, which is not traditionally the chemistry routes, but these are involving high vacuum or medium vacuum level and using vacuum, how you can make solids. There are different techniques by which one can make inorganic solids of different varieties. It is not confined only to metallic materials, you can make materials as oxides, you can make materials as nitrides, you can make materials of alloys, all these are possible using physical vapor deposition routes.

And in today’s talk, I am going to emphasize on the same theme of building solids from monolayers to multilayers. In other words, we are going to start from basic atomic level growth to building up a three dimensional growth. So, making a atomic level deposition or just putting one atomic layer over the other is the fundamental way to build inorganic solids or three dimensional lattices.

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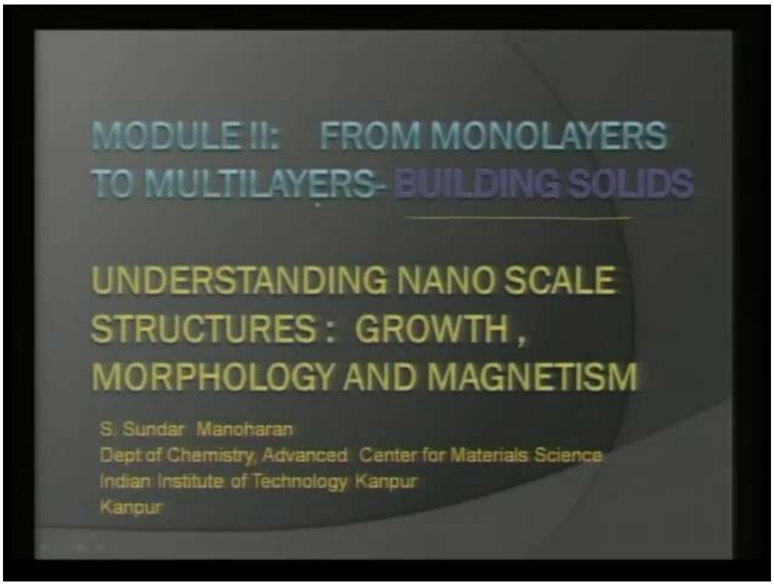

MODULE II: FROM MONOLAYERS TO MULTILAYERS- BUILDING SOLIDS

UNDERSTANDING NANO SCALE STRUCTURES : GROWTH , MORPHOLOGY AND MAGNETISM

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So, this is the state of art approach as far as making materials and in this, we are actually going to stumble on another important feature, that we all keep hearing now and then, which is called nanotechnology or nanoscience. Nanoscience is to study the fundamental properties in nanoscale, when you confine any material in nanoscale, the basic property such as structural, electronic, magnetic or optical properties they vary, because you have the confinement in nanoscale.

This is quite a departure from understanding a bulk material and it is related properties. So, if we want to make materials starting from the scratch that is, from atomic plane to three dimension, now we need to understand that, as we grow, the way we grow a atomic plane will also determine the magnetic property. And in other words, the magnetic property will affect the electronic property, so fundamental to the growth and morphology is the way we build these atomic planes.

So, I am going to take you in the next 50 minutes, I am going to tell you how we can make the solids starting from the basic aspects or the minimum thickness, that is called a monolayer. Monolayer is nothing but a atomic plane usually of the order of 0.2 nanometers, so if you have 0.2 nanometer thick atomic plane, can we put one atomic plane over the other to drive home the pointer. So, in today’s lecture, I am going to talk to you about, how to understand this nanoscale growth and how to, we can correlate that to some property for example, with reference to magnetic property.

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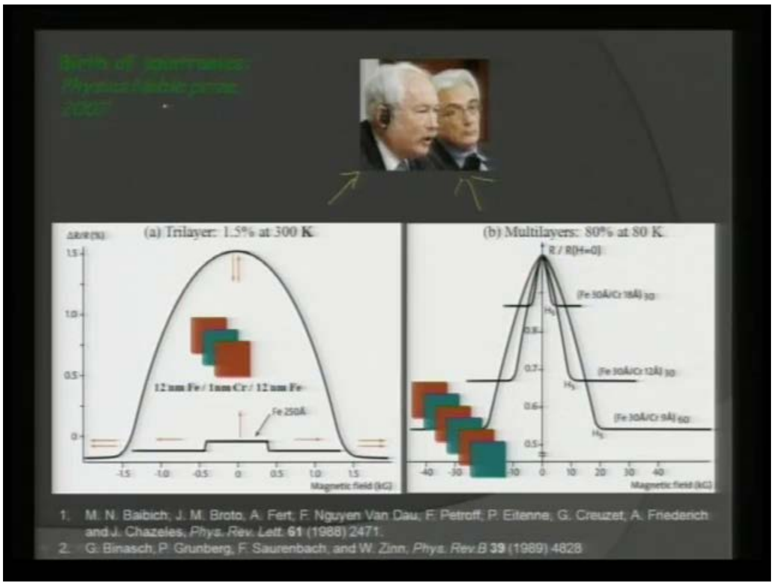

Birth of spintronics: Physics Nobel prize: 2007

1. M. N. Baibich, J. M. Broto, A. Fert, F. Nguyen Van Dau, F. Petroff, P. Eitenne, G. Creuzet, A. Friederich and J. Chazeles, *Phys. Rev. Lett.* **61** (1988) 2471.
2. G. Binasch, P. Grunberg, F. Saurenbach, and W. Zinn, *Phys. Rev.B* **39** (1989) 4828

But, I have to tell you that, the interest in going down to such nanometer thickness actually comes from the noble prize winning work of Peter Grunberg and Albert Fert, who won the noble prize in physics in year 2007 and they came out with very interesting results, which involves nanoscale thicknesses. Now, this is the work of Peter Grunberg which shows that, if you deposit a material which is a trilayer where, the bottom layer is actually 12 nanometer thickness, in other words 120 angstrom thick and film.

And then, you put in between a 10 angstrom or 1 nanometer thick chromium and then, if you again put on the top layer 12 nanometer thick iron. Now, you can look at the basic property of this material in terms of it is magneto resistance. Now, you can see here for a layer like chromium iron, now for having just 1 nanometer thick separation, you can clearly see that the resistance varies with field in this fashion. Whereas, if there is no separation of iron by such a thin film like chromium then, you can see the magneto resistance is only of this order.

So, this is not a spectacular change in resistance as a function of magnetic field whereas, the moment I put 1 nanometer thick chromium, immediately the response is something like this. So, what is the feature that is responsible for such a change in resistance, is what we are going to see. Now, before we go into those aspects, which I will discuss in detail in module 5, when I talk about magneto resistive properties. I want to draw your attention to this fact that, 1 nanometer thin chromium film can bring about a pronounced change.

Now, the same thing was carried out by Albert Fert and he also made this sort of bilayers with different repeats. For example, iron chromium, iron chromium like that you can have 30 repeats or iron chromium iron chromium like that as another 30 repeats or you can go for 60 repeats of this bilayers. But, you should notice that, the resistance varies in a different way as a function of magnetic field depending on the thickness of the chromium layer.

The chromium layer actually here is 1.8 nanometer, in this case it is 1.2 nanometer, in this case it is just 0.9 nanometer. So, you are actually talking about just three or four or five or six atomic plane separations between thick layers of iron. And with respect to the chromium thickness, you can see the magnitude of this magneto resistance or change in resistance is varying by orders. So, the thickness of the spacer layer which we call it, this is a spacer layer or we can even call this a non magnetic layers.

And if this non magnetic layers which are alternated to iron layers, if they are made very, very thin then there is a pronounced activity in this one, smallest the thickness I can make and in one sense, that is the birth for nanotechnology. Since then, many groups have worked on making thin films, not only in such alloy structures, but also in oxides, nitrates, say everywhere. People have made thicknesses, which are of a very low dimension and to see when you confine to low dimensions, whether you can bring about a pronounced activity in the properties that you are studying. So, this is a classic example for, how a rush to nanotechnology has originated, now the next slide.

I want to show professor Peter Grunberg’s noble prize winning moment, because he was the one who was actually responsible to say that, if I put 1 nanometer thin chromium between two iron layers then, you can see a magneto resistance of a pronounced nature. And therefore, I just want to recognize his contribution, which has actually provided a pathway for many people to study different materials in nanodimensions. Now, we are all working, most of us who are listening to this module must be working on nanomaterials at least in bulk form, some of you may be working in nano thin films, some of you may be working on nanostructuring. But, there is a mass confusion as to, what is nanostructuring and what is nanomaterials.

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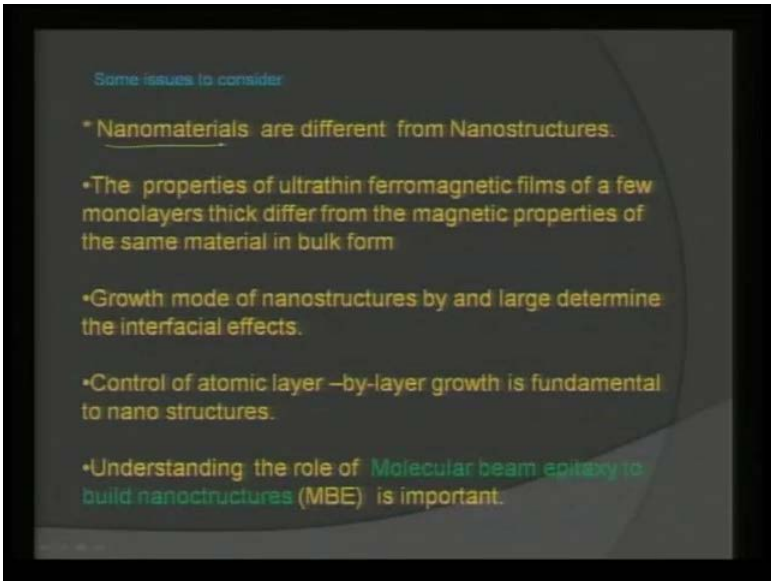

Some issues to consider

- Nanomaterials are different from Nanostructures.
- The properties of ultrathin ferromagnetic films of a few monolayers thick differ from the magnetic properties of the same material in bulk form
- Growth mode of nanostructures by and large determine the interfacial effects.
- Control of atomic layer –by-layer growth is fundamental to nano structures.
- Understanding the role of Molecular beam epitaxy to build nanoctructures (MBE) is important.

Fundamentally, there is a difference between nanomaterials and nanostructures, nanostructures are intentionally built or you can start from a bulk and you can go down to a two dimension or a one dimensional stripes where, you can confine the material in nano form or you can make nanomaterials, which are of bulk in nature. And predominantly, this nanomaterials are three dimensional whereas, nanostructures can be either one dimensional, two dimensional or it can even be three dimensional.

Therefore, there is a fundamental difference between nanostructuring and nanomaterials, predominantly chemical routes takes care of nanomaterials, while nanostructuring is taken care by physical approaches. Another thing that we need to consider, the properties of ultrathin ferromagnetic films of a few monolayers thick differ from the magnetic properties of the same material in bulk form. So, when you confine any material in nano size, there is a fundamental difference in the property.

Another issue that we need to bear in mind is, the growth mode or the way we grow this nanostructures by and large depend, determine the interfacial effects. Suppose, you are making a bilayer of two different metals, we need to understand that, the interface between two materials has to be very very sensitive or very very sharp, otherwise that will be mix up of the properties. Therefore, interfacial effects are dominant and as a result the growth mode, how you grow this nanostructures are important.

And second, if you want to make a atomic layer by layer growth then, we need to have a control over it, because you cannot make a island like shape and then, call that as a nanostructure, because it has to be extremely flat in order to give such sharp interfaces. Now, how do we achieve this nanostructures, one of the most predominantly refined and the most expensive way of realizing nanostructures is to use molecular beam epitaxy to build nanostructures. Molecular beam epitaxy is usually referred to MBE growth and therefore, this is one of the state of art method, by which any one can make nanostructures.

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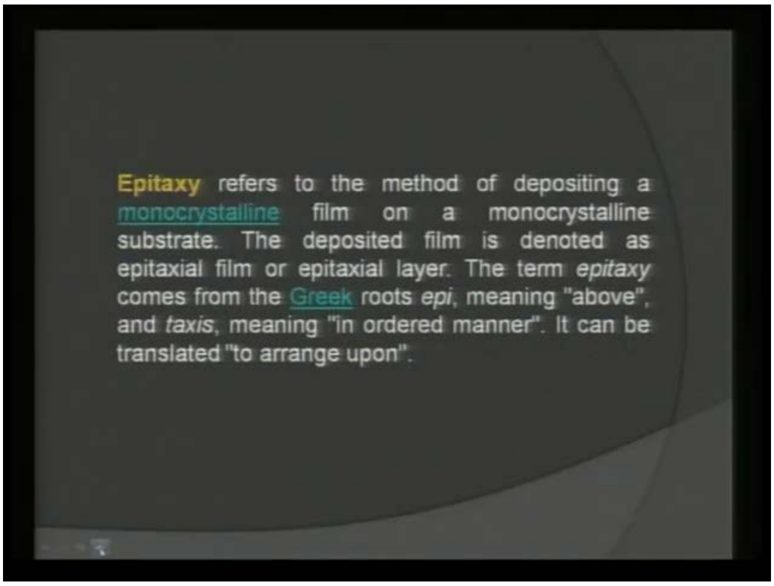

Epitaxy refers to the method of depositing a monocrystalline film on a monocrystalline substrate. The deposited film is denoted as epitaxial film or epitaxial layer. The term *epitaxy* comes from the Greek roots *epi*, meaning "above", and *taxis*, meaning "in ordered manner". It can be translated "to arrange upon".

Now, I want to start with some basic definitions, which are very important for understanding this. One is the word epitaxy, what is epitaxy, molecular beam epitaxy to grow films. So, what this epitaxy means, it refers to the method of depositing a monocrystalline film on a monocrystalline substrate. We can even call that as a single crystalline film on a single crystalline substrate, the deposited film is denoted as epitaxial film or epitaxial layer, if it is growing on the same geometry and on the same orientation as that of the substrate.

The term epitaxy comes from the Greek word epi, meaning above and taxis meaning in ordered manner. So, if you can order some atomic planes over on the top of a substrate then, you can call such a growth layer as epitaxial growth, it can be translated as to arrange upon. So, if you have a c axis oriental substrate then, if it is epitaxial film, it has to grow in c axis. So, this is of fundamental importance, the next definition is homoepitaxy.

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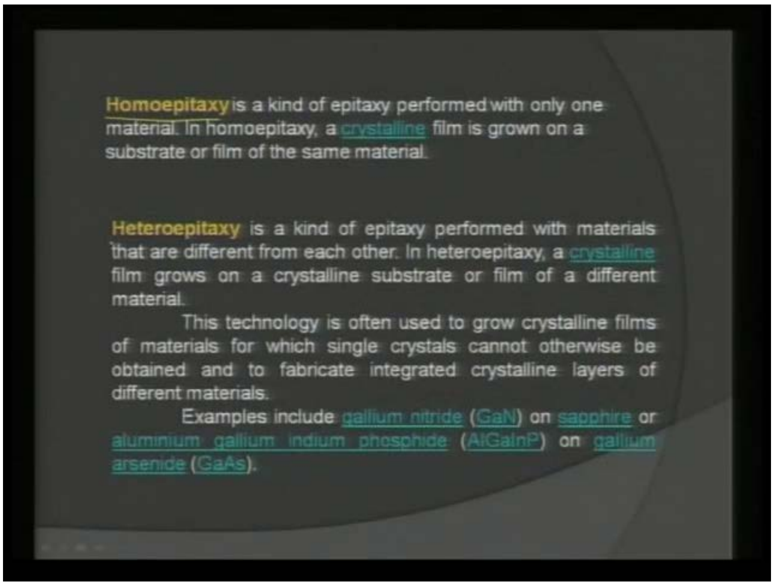

Homoepitaxy is a kind of epitaxy performed with only one material. In homoepitaxy, a crystalline film is grown on a substrate or film of the same material.

Heteroepitaxy is a kind of epitaxy performed with materials that are different from each other. In heteroepitaxy, a crystalline film grows on a crystalline substrate or film of a different material.

This technology is often used to grow crystalline films of materials for which single crystals cannot otherwise be obtained and to fabricate integrated crystalline layers of different materials.

Examples include gallium nitride (GaN) on sapphire or aluminium gallium indium phosphide (AlGaInP) on gallium arsenide (GaAs).

There is a term called homoepitaxy, there is a term called heteroepitaxy, now homo and heteroepitaxy is very important, because there are fundamental differences or ease with which you can make such solids. Now, in homoepitaxy, it is a kind of epitaxy performed with only one material, in homoepitaxy a crystalline film is grown on a substrate or film of the same material. For example, if I want to grow copper atoms on copper 1 0 0 substrate, now this is called as homoepitaxy. And as you would guess, building copper atoms on copper is going to be very easy, because both of them share the same crystal symmetry, both of them share the same surface energy.

Therefore, to grow a purest form of atomic layer on the same material, which is single crystalline is a fairly easy method and therefore, this is called as a homoepitaxy. Whereas, if you think of heteroepitaxy, it is a kind of epitaxy performed with materials that are different from each other. In heteroepitaxy, a crystalline film grows on a crystalline substrate or film of a different material. This technology is often used to grow crystalline films of materials, for which single crystals cannot otherwise be obtained and to fabricate integrated crystalline layers of different materials. For example, gallium nitride you can grow it on sapphire, sapphire is nothing but iron doped alumina or you can try to dope aluminium gallium indium phosphide on gallium arsenide substrate. So, this is an example of heteroepitaxy, this is an example of homoepitaxy, so growing heteroepitaxy is much more challenging than growing homoepitaxy.

So, I want to draw all these fundamental definitions about growing nanostructures, but I should also tell you, because molecular beam epitaxy is a more refined technique. It is impossible to have this facility all over the world and almost in every laboratory, but now we have another sophisticated machine, which is coming which is called as focused ion beam.

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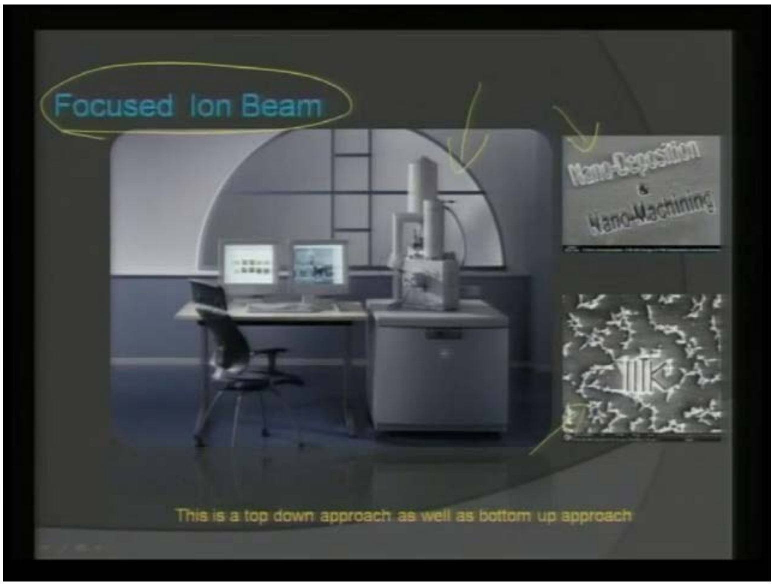

Focused Ion Beam

This is a top down approach as well as bottom up approach

And this is more affordable, because the way focused ion beam looks like, it looks like a ordinary SEM, but it has special facility not only to look at surfaces, you can also try to do variety of things. So, this is a SEM image of polymeric film, which is deposited by another technique, but you can actually look at the SEM picture of this and you can also write IITK as a nanostructure. Because, the thickness of this letter is just 20 nanometers, you can try to write such nanostructures on a film.

Same way, you can also write nano deposition, nano machining which is possible to write using this focus ion beam. The advantage of focus ion beam is, you can actually have a top down approach to make nanostructures meaning, you start from bulk and you can reduce it to nanostructure or you can even do some limited depositions to grow some nanostructures, as you are trying to do this sort of machining. So, you can actually try to either scale it down to nanostructure or you can build upon, both are possible using this FIB. And therefore, this is the most sophisticated instrument as of now, which can nearly substitute for molecular beam epitaxy. In the next slide, I want to tell you what is this molecular beam epitaxy and why this is very important to make nanomaterials.

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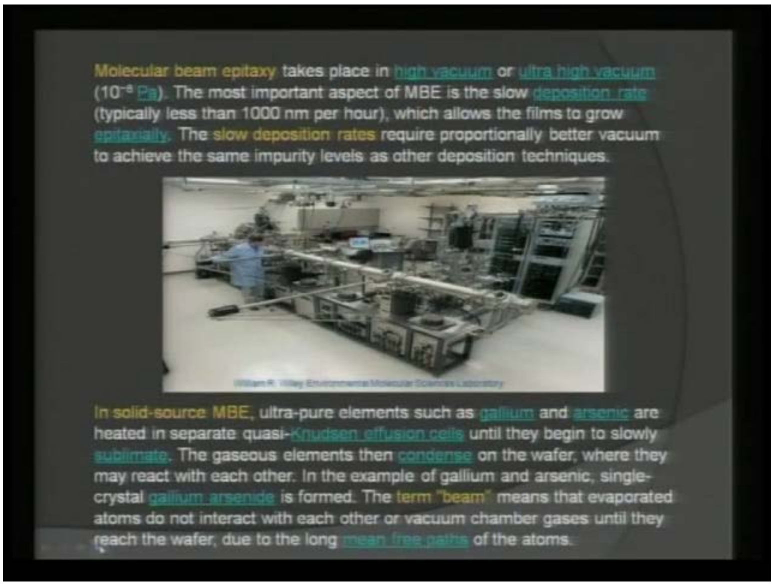

Molecular beam epitaxy takes place in high vacuum or ultra high vacuum (10^{-8} Pa). The most important aspect of MBE is the slow deposition rate (typically less than 1000 nm per hour), which allows the films to grow epitaxially. The slow deposition rates require proportionally better vacuum to achieve the same impurity levels as other deposition techniques.

William R. Wiley Environmental Molecular Sciences Laboratory

In solid-source MBE, ultra-pure elements such as gallium and arsenic are heated in separate quasi-Knudsen effusion cells until they begin to slowly sublimate. The gaseous elements then condense on the wafer, where they may react with each other. In the example of gallium and arsenic, single-crystal gallium arsenide is formed. The term "beam" means that evaporated atoms do not interact with each other or vacuum chamber gases until they reach the wafer, due to the long mean free paths of the atoms.

Molecular beam epitaxy for example, a machine can be as big as this, we should not get discouraged looking at the machine, but typically if you want to have all the characterization facilities attached to a single instrument then, the machine will be of the order of this size. And this is a picture view of a William. R. Wiley environmental molecular sciences laboratory in USA and this is not scare you, but to tell you that molecular beam epitaxy is actually the most sophisticated instrument and the most costliest deposition technique in the world as of now.

Now, I want to also say, what this molecular beam epitaxy is, it takes place in high vacuum, high vacuum of the order of 10 power minus 8 Pascal or it can even go up to 10 power minus 11 torr and therefore, it is called as high vacuum or ultra high vacuum. The most important aspect of MBE is the slow deposition rate, the atomic layers grow one over the top in a very slow fashion, typically less than 100 nanometer per hour. In other words, the 10000 angstrom thick layer can be deposited in 1 hour time, which allows the films to grow epitaxially. This slow deposition rates requires proportionally better vacuum to achieve the same impurity levels as the other deposition techniques. In solid source m MBE, ultra pure elements like gallium, arsenic or even iron, copper, cobalt, any metallic substrates that you want to chose, you can have it in sort of effusion cells and until they begin to slowly sublimate.

You can keep heating this substrates, now they will sort of sublimate, the gaseous elements then condense on the wafer or the single crystal or the substrate where, they may react with each other. In the example of gallium and arsenic, single crystalline gallium arsenide is formed if two things are parallely evaporated. Same way, you can also make metallic films like iron chromium, which I showed you, you can have iron and then, you can have chromium. Whenever you want iron you can open the shutter, whenever you want chromium you can open the shutter, by this way you can keep alternating such nanostructures.

In the term beam, what is this term molecular beam means that, the evaporated atoms do not interact with each other or vacuum chamber gases until they reach the wafer due to the long mean free paths of the atom. So, it is like a study stream of atoms, which are going without any interaction, therefore they all carry the same kinetic energy, therefore the growth is going to be exactly homogeneous at the interface. There would not be a Gaussian distribution of the kinetic energy of the arriving atoms, which might moderate or manipulate the growth mode. So, all the atoms reach with same kinetic energy to the surface, as a result you have a very beautiful growth atomic growth that is ensured, that is why it is called molecular beam epitaxy and this is expensive that way.

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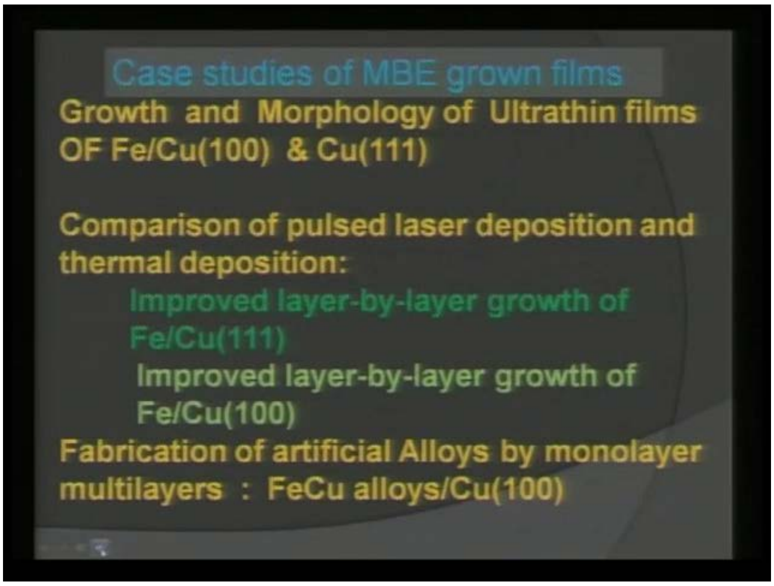

Case studies of MBE grown films

Growth and Morphology of Ultrathin films OF Fe/Cu(100) & Cu(111)

Comparison of pulsed laser deposition and thermal deposition:

- Improved layer-by-layer growth of Fe/Cu(111)
- Improved layer-by-layer growth of Fe/Cu(100)

Fabrication of artificial Alloys by monolayer multilayers : FeCu alloys/Cu(100)

In today’s talk, I am going to confine and show some examples, how small this atomic layers can be and how we can make such layers. As case studies of MBE grown films, I will talk about how to grow monolayers or ultrathin films of iron on copper and iron on copper 1 1 1. See, if you chose copper 1 0 0 as a substrate or copper 1 1 1 as a substrate, I will show in the next few slides, how the whole pattern of iron growing on copper will be modified.

Next, I will also tell you, if we take pulsed laser deposition and thermal deposition as two different approaches in the same MBE then, you can try to improve or you can modify the growth mode in a very, very characteristic way. So, in the first example, I will show you how iron grows on two different substrates and I will show you in the next example, how iron grows based on two different methods. And lastly, I will also give you a classic example, if you have control over this monolayer growth then, you can even make adventure into making new artificial alloys, which are not present in mother nature, so three examples I will give before I conclude this talk.

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In a typical molecular beam epitaxy chamber, you have several such gadgets attached, what you see here is a instrument attached to the deposition chamber of your MBE, which can be used for magnetic measurements. You can also use instruments, which are for auger and you can also have facilities for STM. So, you can study the structure, you can study the elemental purity, you can study magnetic property all, without exposing the atomic layers or nanostructures to atmosphere, which means you are actually doing all the studies in the same condition where it is deposited, which we call it as insitu characterization.

Because, we are not breaking the vacuum, you are keeping the film in the same high vacuum condition, but you are ensuring that the material is not contaminated by exposing it to air or to even low vacuum. Therefore, whatever property you see in auger or magnetic or STM, will be the virgin property of the material, before it is exposed to atmosphere. That is the state of art or the most big emphasis of MBE growth, that you do not break vacuum, that you conduct all the studies in high vacuum.

Now, to understand this machine in a simpler form, this is the machine whose deposition chamber is the biggest in size and it is attached to a facility called RHEED. Because, if you want to know, whether you are making a atomic layer growth, you need to have some idea, whether you are in the right track. Therefore, you use a expensive characterization tool called RHEED, which is Reflection High Energy Electron

Diffraction.

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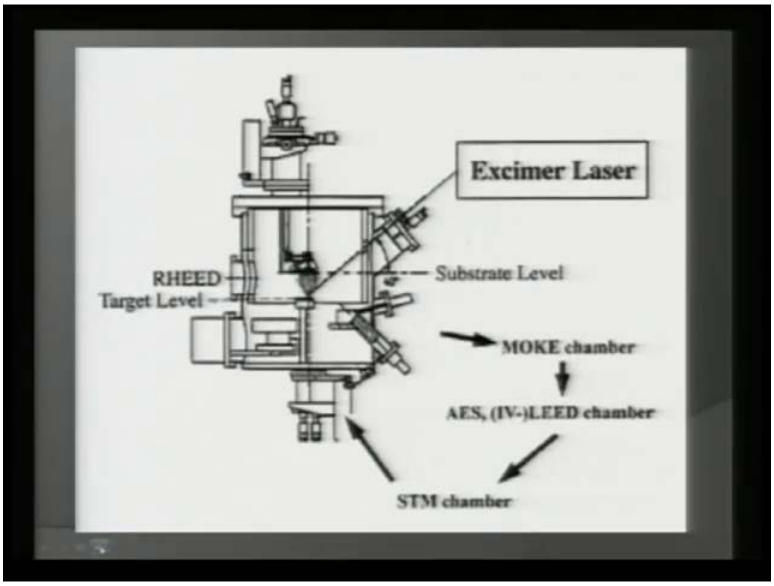

And you can actually ablate the material and make this thin films using excimer layer, as I told you or you can actually use thermal evaporation. So, either way in a MBE system, you can actually try to make films using different evaporation source and as I told you, you have this magnet which can be used for measuring the magnetic signal. Then, you have the LEED chamber to study the structural property and to know the morphology of your nanostructures, you use scanning tunneling microscopy. STM stands for Scanning Tunneling Microscopy, so all the characterization tools are combined to the basic deposition chamber.

Now, before I start showing some of the examples of, how this nanostructures look and what are the properties, I will stress on the different growth mode which is fundamental to growth of nanostructures. What you see here is a cross section views of three primary modes of thin film growth including Volmer Weber island formation, which is a and Frank van der merwe layer by layer growth, which is called as b and the Stranski krastanov layer plus island growth, which is categorized as c.

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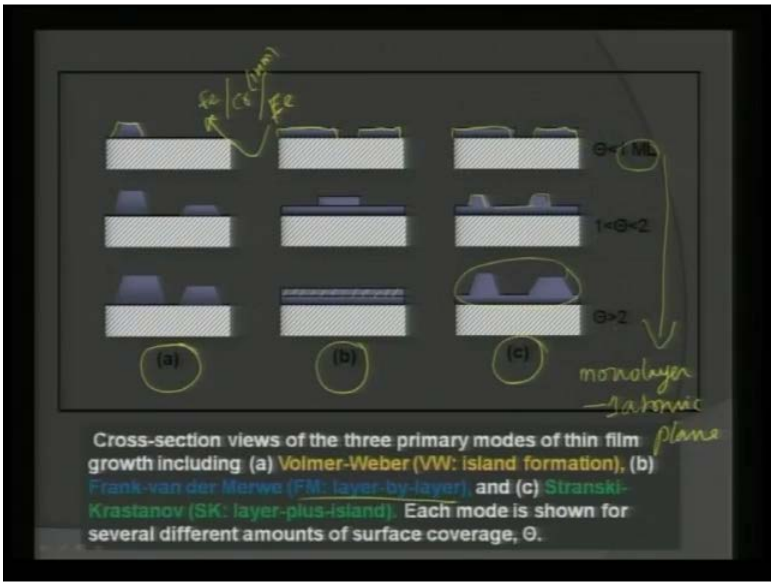

Cross-section views of the three primary modes of thin film growth including (a) Volmer-Weber (VW: island formation), (b) Frank-van der Merwe (FM: layer-by-layer), and (c) Stranski-Krastanov (SK: layer-plus-island). Each mode is shown for several different amounts of surface coverage, Θ.

What you see here is the development of this nanostructure as a function of coverage, this theta is nothing but coverage and it is expressed in one monolayer. Here, it is expressed in between one to two monolayers, here it is greater than three monolayers, monolayer the definition is one atomic plane, it is one atomic plane. So, if it is less than one atomic plane that means, few atoms you are going to throw on the substrate then, this is the way it will proceed, if it is island growth you will see the pattern of island that is forming.

But, if it is going to spread uniformly throughout, which we call it as a two dimension then, it will go as a flat terrace. Now, if it is going to be island plus layer growth, first it might proceed just as a flat growth and then, as you increase the coverage, you can actually top up with some islands and it can grow in this fashion. Now, perfectly one who desire to have very sharp interfaces in structures, as I discussed like iron chromium iron where, you have the chromium in 1 nanometer thickness.

If you want such a crucial separation then, you would actually go for a ideal growth of chromium in this fashion where, you would have a very sharp interface. In other words, this iron layer will not coupled with this iron layer, there will be a perfect separation between these two layers, otherwise you will not see such sharp variation in the presence of the magnetic field. So, what one desires is actually a two dimensional growth, this we need to register in our mind, because if you are thinking of a nanostructure then, always you should ensure a two dimensional growth.

Now, each mode is shown with several different amounts of surface coverage, now as you proceed further you will see, this can translate even into a two dimension or this can translate into something like this. Therefore, anything can happen as you keep growing the structure, but if you are going to play with the nanostructures, what is more decide or the ideal growth is two dimensional growth.

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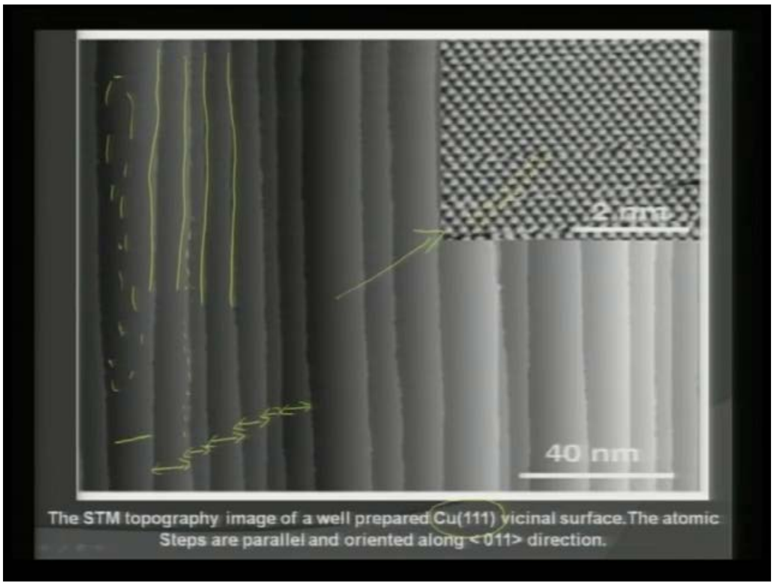

The STM topography image of a well prepared Cu(111) vicinal surface.The atomic Steps are parallel and oriented along <011> direction.

Now, this is a classic example of a clean surface of copper 1 1 1, which is a single crystal and this crystal, if it is very carefully prepared, this copper 1 1 1 crystal will actually have your step, with which is approximately of 20 to 40 nanometer. This may be different, but each one is a step and each one has a step edge like this. This is the way a crystal grows to relive its energy, so these are all step edges and these are all step terraces.

Now, when you try to put some atoms, this atoms can either come and fall here or the atoms can occupy the step edges, both can be possible. Now, the way you adopt the technique, you can try to modify it, I will come to that in a few minutes time, but what you should understand is, that these are all highly pure single crystals. This is the atomic resolution of the copper 1 1 1 terrace which clearly shows that, each one is a copper atom and it is highly ordered.

Now, when I am going to put iron, actually each of this iron atom has to sit on each of this copper and that is what we call it as epitaxy. If they are not going to form like this then, it is not a epitaxy layer. So, by molecular beam epitaxy, you are actually making a dissimilar element to actually sit on each of this copper atoms, therefore you call this as epitaxial films, they are growing. One more thing that we should understand, if you try to grow iron, iron in bulk is alpha BCC iron. But what you would see, if you take a FCC lattice in molecular beam epitaxy condition, it is possible to force a BCC element to grow in a FCC lattice until the stress strain issues are not coming into focus. So, it is possible to enforce a two dimensional growth with the different crystal structure for even a material in bulk, which is known to have a different crystal symmetry and that is the power of molecular beam epitaxy.

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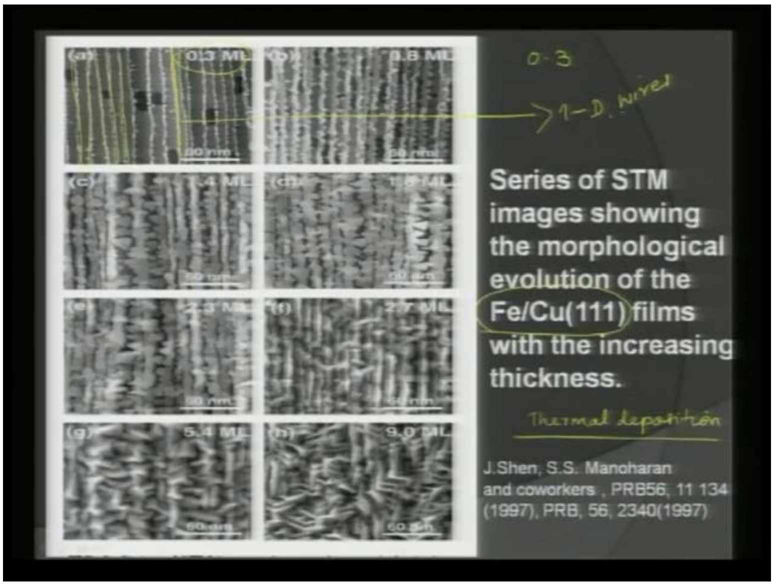

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1-D wires

Series of STM images showing the morphological evolution of the Fe/Cu(111) films with the increasing thickness.

Thermal deposition

J.Shen, S.S. Manoharan and coworkers , PRB56, 11 134 (1997), PRB, 56, 2340(1997)

Now, this is a classic example of, what really happens to iron grown on copper 1 1 1 using a thermal deposition technique. This is different from pulsed laser deposition technique, I will come to this comparisons later, but just have this in mind. If you thermally grow this film iron on copper 1 1 1, initially we are talking now about 0.3 monolayers that is, less than one atomic plane. So, if you try to give 0.3 monolayer coverage, you can see the stripes are growing in this fashion and atoms are not occupying the terraces of the steps, but they are occupying the step edges.

Therefore, this growth is called as one dimensional growth, because they are growing in one dimension or we can call them as one dimensional wires. Because, the length of this wire, if all the islands here, they are all connected nicely then, they can be called as one dimensional wires typically of the order of 800 angstrom or so you can make long wires or this is also called as one dimensional stripes. So, you can actually make such one dimensional magnetic wires and one dimensional stripes by decorating this preferentially along this step edges.

But, note that, in the next few slides I will show to you, the same deposition technique of iron, but if is grown on copper 1 0 0 instead of 1 1 1, the growth mode will be completely different. It would not grow on the step edges, that is unique of the substrate as well as the deposition mode. Now, if you proceed further to nearly to 0.8 monolayer, which is nearly to one atomic layer growth, you can see that it has grown and some of the islands are now growing on the top of the first island and also, some of the islands are sort of cress crossing now, it is growing along the stripes of the next step edge.

Now, if you go further, this is for 1.4 monolayer, you can clearly see that there is lot of cress crossing talking between the islands of adjacent layers and you call this as a two dimensional progression. So, from one dimensional, if you keep on depositing this layers, you transform to two dimensional growth. Now, if you proceed further, this is for 1.8 monolayer, now if you go to 2.3 monolayer, it is nearly complete. So, it is a flat growth of a two dimensional film and you can achieve such a growth around one point 2.3.

So, the dimensionality changes with the same growth for critical thicknesses, first you start with one dimension then, you go to two dimension. But, if you go from there to 9 monolayers you see, this is not looking flat at all, this is showing lot of bumpy surface, in other words this is nothing but three dimensional growth. So, within one system, as you proceed from 0.3 monolayers, if you go to just nine atomic planes, you see there is a change in the dimensionality of the growth mode from one dimension to two dimension and to three dimension.

Now, when such a transformation occurs linearly, you will also understand that, there is a problem that is associated with other transformations. When dimensionality changes, there is also change in the lattice or from FCC to a BCC and from the magnetic point of view, from in plane to out of plane geometry. So, in the next few slides, I will show you how this dimensionality changes the magnetic property as well as the structural property.

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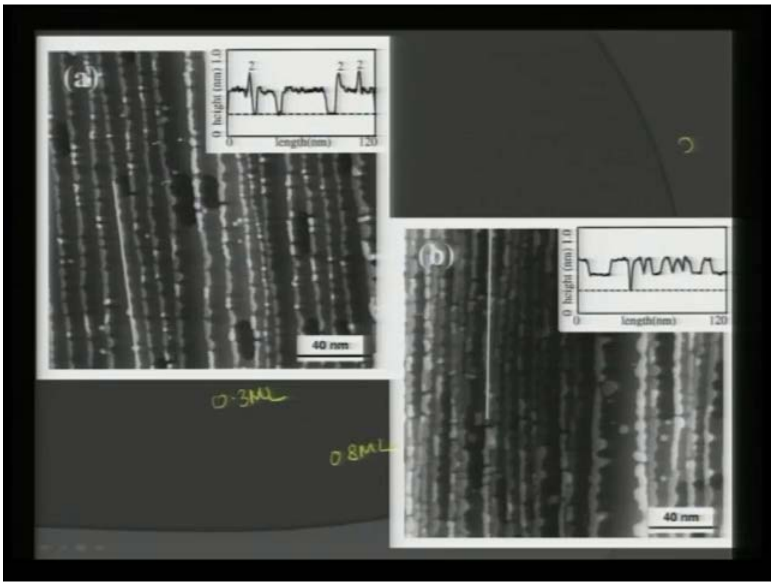

So, I will try to show a closer image of the first few monolayer growth say, 0.3 monolayers and 0.89 monolayers. You can see the growth mode is slowly transforming to a continuous stripe here, but here in this case you can see, there is some discontinuity between the atomic islands.

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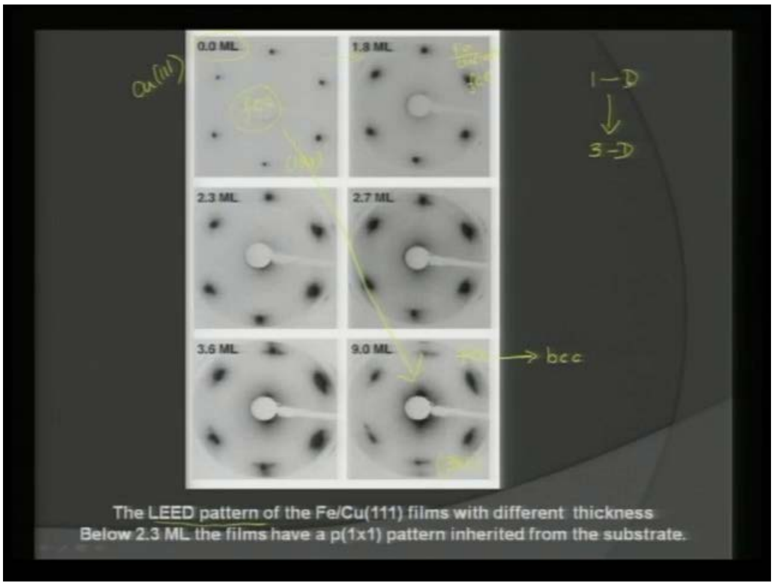

The LEED pattern of the Fe/Cu(111) films with different thickness
Below 2.3 ML the films have a p(1x1) pattern inherited from the substrate.

Now, if you go further, you can see from the LEED that is, LEED this is Low Energy Electron Diffraction pattern. We can get clue about, what is the structural transformation that is happening, we have already seen there is a transformation from one dimensional to three dimensional growth. Now, if you carefully monitor the LEED pattern, this is the situation of your copper 1 1 1 surface, it shows a electron diffraction pattern like this. So, this is typical for a FCC lattice, this is called p 1 cross 1 pattern, which is typical for a FCC.

Now, if you progress along the line say iron on copper, if you keep depositing 1.8 monolayer, you typically see the same. In other words, you can say this is still in FCC, because the electron pattern is still the same. Now, if you go to 2.3, you see this dots are smearing out and it is more smeared here and when you come here to 9 monolayer, you see a 3 cross 1 pattern. In this case, this is p 1 cross 1 pattern, in this case it is 3 cross 1 pattern, therefore when you go from a clean substrate to 9 monolayer, there is a transformation from FCC to BCC. So, along with the dimensionality change, there is also a change in the structure, structural transformation is there which is FCC to BCC.

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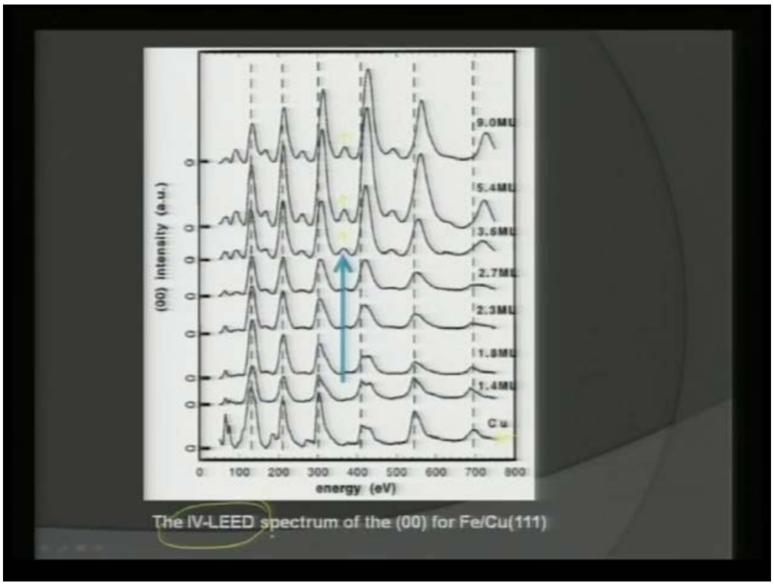

The IV-LEED spectrum of the (00) for Fe/Cu(111)

Now, if you go further, we can correlate that to magnetic property, but this is a IV LEED spectrum of the 0 0 spot for iron on copper 1 1 1, which gives you idea about the new pics that are coming here, which is typically due to the BCC transformation. So, as you go from a pure FCC lattice of copper, you do not see this a signature of BCC there, but as the system is transforming somewhere around 3.6, you can see this new pics coming. So, if you have a IV LEED spectrum recorded, that will also clearly show you where the transition onset is and therefore, you can clearly map the structural transition.

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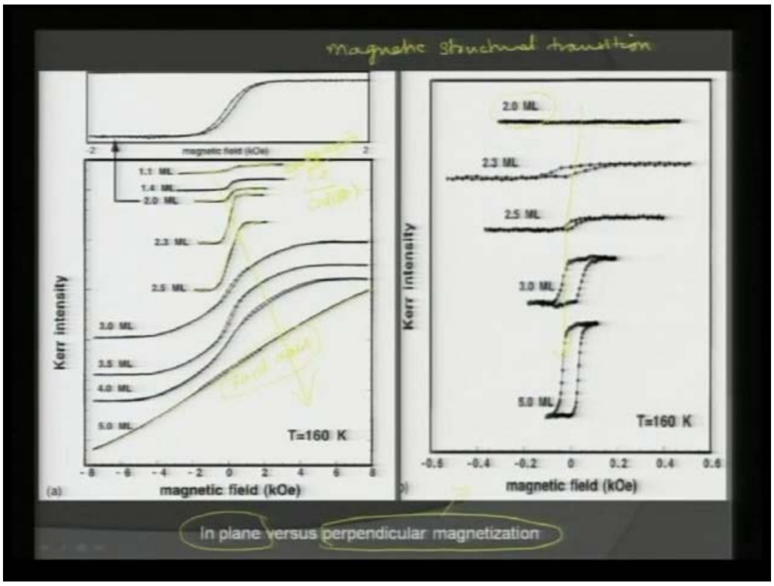

magnetic structural transition

In plane versus perpendicular magnetization

This is the magnetic transition, we can try to quantify magnetic structural transition, which shows how as a function of layer coverage, you can see the magnetic axis rotating. Now, this is nothing but in plane magnetization and this is called perpendicular magnetization. For your kind information, for most of the applications, it is the perpendicular magnetization, which is preferred over in plane magnetization. Nevertheless, for understanding the structure and the related transitions, let us see how it originates.

For example, if you take copper 1 1 1 then, for 1.1 monolayer, you can see a small hysteresis there which means, it is ferromagnetic. Now, if you go for further higher thicknesses, you can see this magnetic hysteresis more pronounced and it is more pronounced this way. And as you go through 3 monolayers, you can see slowly the nature of this magnetic signal is changing and as it goes to 5 monolayer or so it is nearly paramagnetic.

In other words, it is not magnetic along this direction or it is showing a hard axis of magnetization, this is called as easy axis of magnetization. So, in inplane you see, there is a change from easy axis of magnetization to hard axis of magnetization whereas, if you go to the perpendicular geometry, in the perpendicular geometry upto 2 monolayer… Here, in inplane it is magnetic whereas, in out of plane that is, perpendicular it is not showing any magnetic signature. But, you can see, as it proceeds through this layer thickness, it is slowly transforming from a non magnetic or to a magnetic situation. In other words, there is a rotation in the magnetic axis, wherever it is easy it is hard here, wherever it is hard here it becomes easy axis of magnetization.

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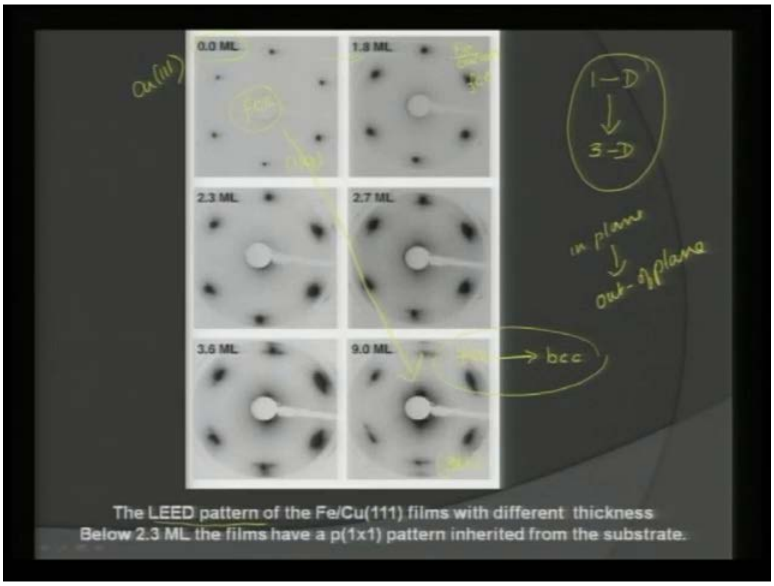

The LEED pattern of the Fe/Cu(111) films with different thickness
Below 2.3 ML the films have a p(1x1) pattern inherited from the substrate.

As you would see, now in the last slide I tried to show you one dimensional to three dimensional transformation occurs along this progression where, FCC to BCC also occurs. Now, I also told you from the magnetic signature, that there is a in plane to out of plane transition, that is a happening and all are going hand in hand. If you see the transition limits exactly where the FCC is transforming to BCC, you also see the change from in plane to out of plane. So, what we understand from here, that growth mode is important number 1, second thing when you affect the growth mode, it affects the crystal symmetry and it also affects the magnetic signature. Therefore, this is very important as we understand the nanostructures.

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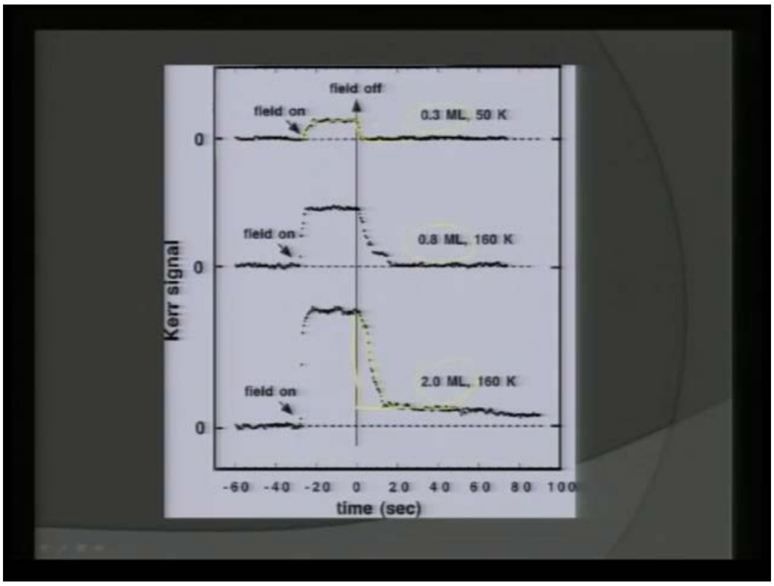

So, let me go back to the place where I left, we can also be very careful to understand this magnetic signatures in such low nanostructures, because it can even be paramagnetic. The hysteresis loop has to be verified and the best way to verify is time dependent magnetization, you try to magnetize a compound. You put the field on here that means, it will get magnetized and if you put the field off you see here, for lower thicknesses, immediately it falls down. So, we cannot be very sure if they are ferromagnetic whereas, if you grow thicker films, you can see that it takes a long time to decay, this area is building up. So that means, it is authentically ferromagnetic upto say 2 monolayers whereas at 0.3 monolayers, we need to be more cautious, whether to call it ferromagnetic or paramagnetic.

So, time dependent magnetization can tell us that fact, now if you actually plug the saturation magnetization as a function of coverage layer, you can see here, as you go from 1 to 2.2 monolayer, the magnetization actually linearly varies, which has to be the case. But, once your FCC to BCC transformation is onset and one dimension to three dimensional stripes are forming, you can clearly see there is a jump and then, it goes now to a different magnetization mode.

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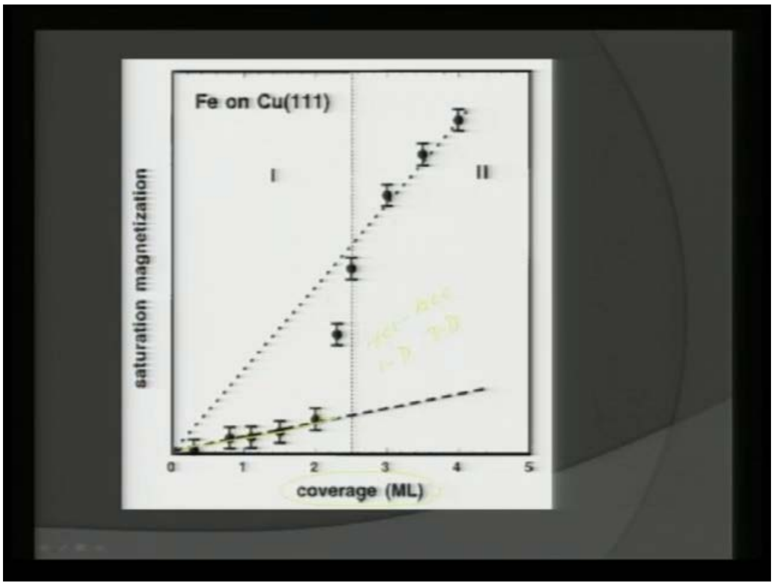

So, here the growth certainly affects the morphology and the morphology affects the crystal symmetry and the crystal symmetry affects the magnetization, so this goes hand in hand. Therefore, when you are dreaming of making a nanostructure, you should know in your mind that, with every additional thickness that you are adding to your film, something could be happening to it is structure or to the magnetic property.

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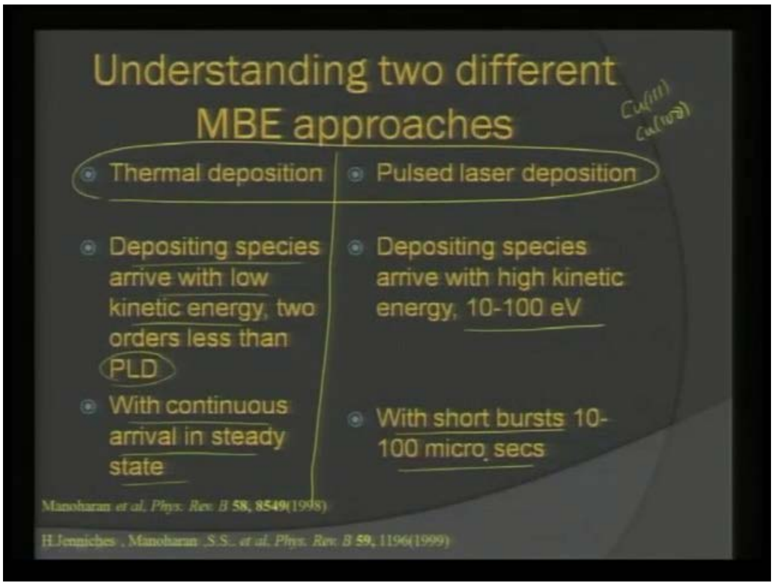

Understanding two different MBE approaches

Cu(111)
Cu(100)

- Thermal deposition
- Depositing species arrive with low kinetic energy, two orders less than PLD
- With continuous arrival in steady state

- Pulsed laser deposition
- Depositing species arrive with high kinetic energy, 10-100 eV
- With short bursts 10-100 micro secs

Manoharan *et al*, *Phys. Rev. B* **58**, **8549**(1998)

H.Jenniches , Manoharan .S.S., *et al*. *Phys. Rev. B* **59**, 1196(1999)

Now, I want to come to the second part of this story, where I will try to show you, instead of taking copper 1 1 1 or copper 1 0 0, if you suppose use two different techniques, how you can change the morphology. Now, what is the fundamental difference between thermal deposition and pulsed laser deposition. In thermal deposition, you have the depositing species arrive with low kinetic energy, nearly 2 orders less than the kinetic energy of the PLD grown films.

Whereas, in this case, the ions carry very high kinetic energy and in this case, with continuous arrival in steady state, but it comes as a short bursts of 10 to 100 microseconds. Now, this is the fundamental difference between this, so in one sense you are using a soft route, in other sense, in another approach, you are using a harder route, now we can see how you can modify the growth mode.

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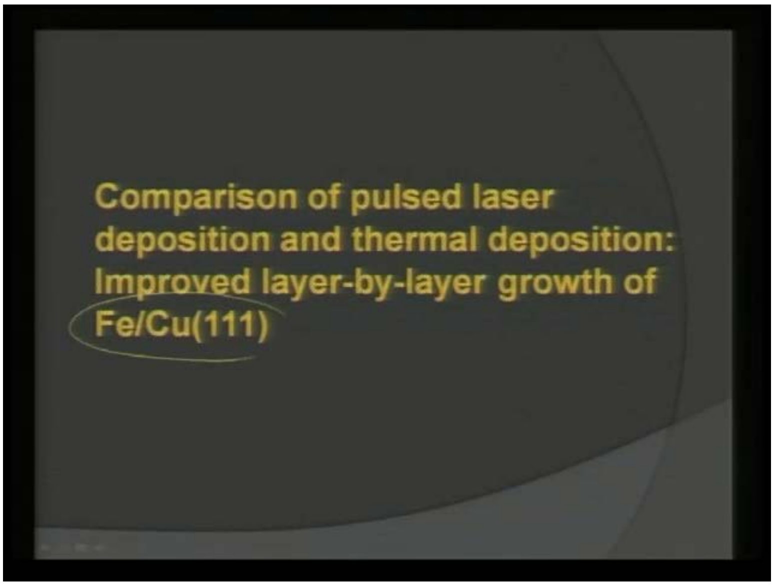

Comparison of pulsed laser deposition and thermal deposition: Improved layer-by-layer growth of Fe/Cu(111)

For example, if we take the same example which we have seen, you are already familiar. Now, with this STM micrographs of iron grown on copper 1 1 1 where, we have seen this stripes are forming, if you are going to use thermal evaporation at 300 K.

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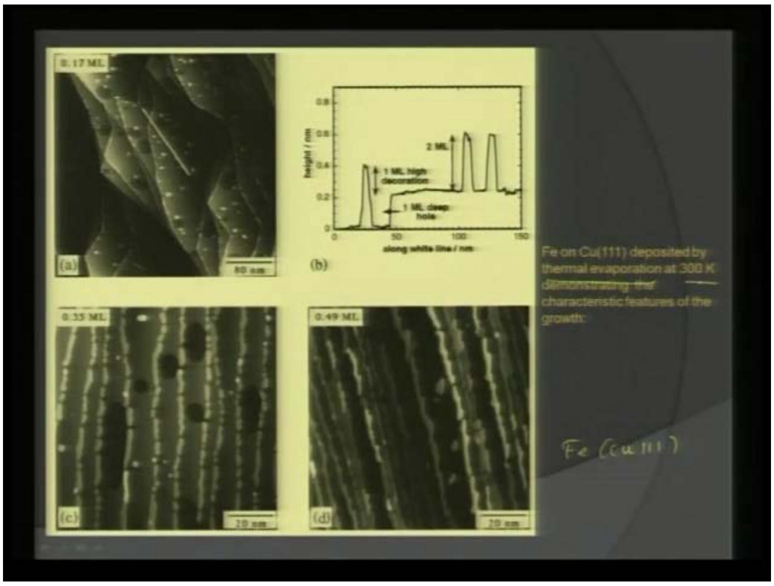

Fe on Cu(111) deposited by thermal evaporation at 300 K ~~demonstrating the~~ characteristic features of the growth:

Fe (Cu 111)

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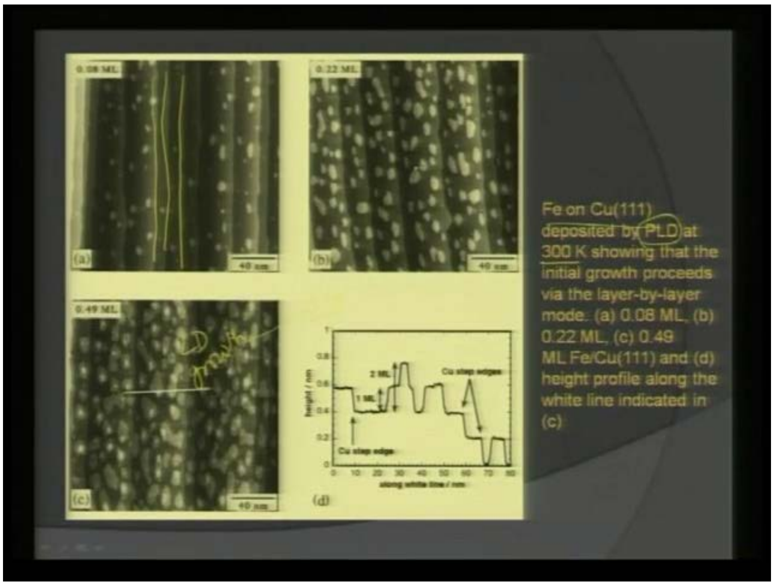

Fe on Cu(111) deposited by PLD at 300 K showing that the initial growth proceeds via the layer-by-layer mode. (a) 0.08 ML, (b) 0.22 ML, (c) 0.49 ML Fe/Cu(111) and (d) height profile along the white line indicated in (c)

But, if you are going to use the same one, using PLD Pulsed Laser Deposition at 300 K, you can see the growth mode is completely modified, there are no decorations along the step edges, which was the case in thermally grown film. Whereas, in the pulsed laser deposited films, you see the kinetic energy of the incoming ions are going to be very rapid and they would actually form islands to coverless. As a result, you have two dimensional growth, even from 0.08 monolayer. So, even before you cover one full atomic plane, you can enforce a two dimensional growth and that is the case.

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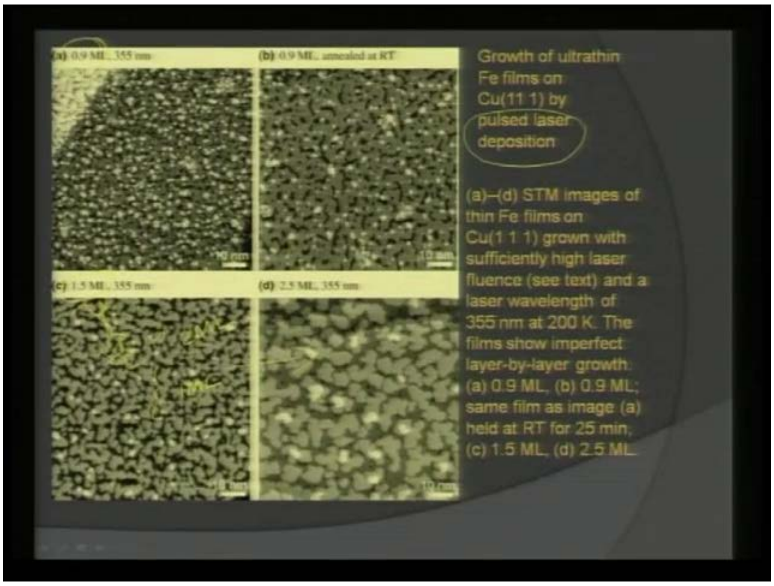

Growth of ultrathin Fe films on Cu(11 1) by pulsed laser deposition

(a)–(d) STM images of thin Fe films on Cu(1 1 1) grown with sufficiently high laser fluence (see text) and a laser wavelength of 355 nm at 200 K. The films show imperfect layer-by-layer growth: (a) 0.9 ML, (b) 0.9 ML; same film as image (a) held at RT for 25 min, (c) 1.5 ML, (d) 2.5 ML.

If you go nearly to 0.9 monolayer, you see it is a flat growth, there is no island growth, it is nearly flat, this is annealed at room temperature. Now, if you go to 1.5 monolayer, you can clearly see this white patches, whatever you see is the second layer, is the second monolayer which is growing and this black regions whatever you see is nothing but your first monolayer, which is already grown. So, first monolayer is fully covered and the patches are the second monolayer and you can see at 1.5 monolayer, all the islands are invariably percolated here.

So, they have a connectivity, this is called the threshold of percolation and that is exactly happening at 1.5 monolayer. Now, if you go further, you can still see that this two dimensional growth is maintained as long as your growing it in pulsed laser deposition. But, I want to again refer you back, if it is iron grown on thermal deposition, we already saw for say 2.5 monolayer, it is transformed from one dimensional to two dimensional growth.

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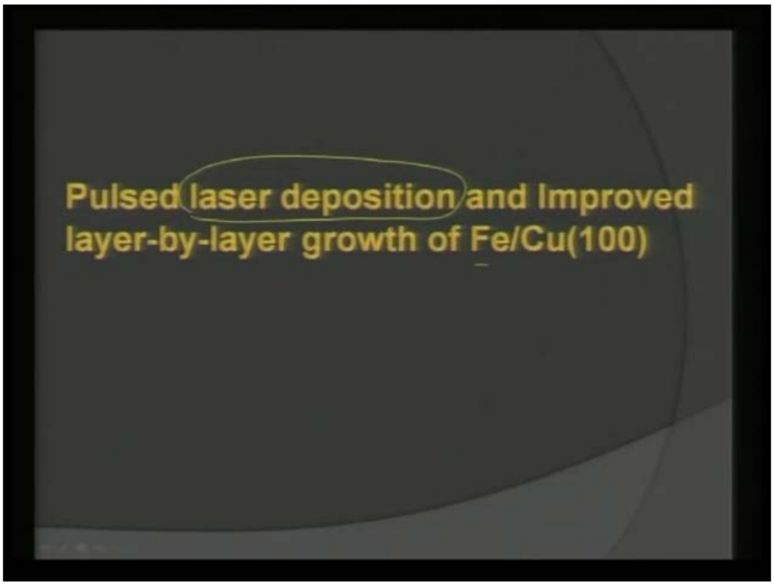

Pulsed laser deposition and Improved layer-by-layer growth of Fe/Cu(100)

I will also take you now through this route where, I will try to show you, if I grow PLD grown films on iron on copper 1 0 0, what would happen?

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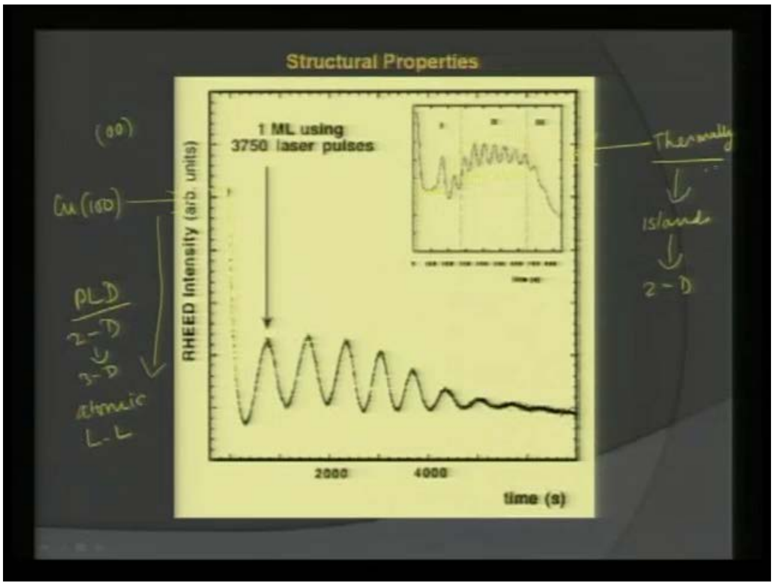

Structural Properties

Now, how do I know that, I am growing such a layer, we can use this sort of RHEED oscillations which I told you. This RHEED oscillations are very critical, because you start at this point where, the substrate is very very clean. So, you have a RHEED spot if you map the 0 0 spot of your copper 1 0 0 crystal. Now, this will show the intensity here, but as you are depositing, you see that the RHEED oscillation is now falling down and it is picking up here and it is going down, picking up here, going down.

So, it is showing some oscillation and this oscillation clearly shows, it is growing in a atomic layer by layer growth, otherwise you would not see this periodicity in the oscillation. But, you should also understand that, this is the RHEED oscillation for thermally grown film where, you can see in the first few monolayers, it is actually growing as stripes or as islands. As a result, you are not going to see any sort of oscillation here.

What does that mean, if you are planning to make 1 nanometer or 2 nanometer thin iron films, now thermally grown film is not the solution. You have to go for PLD grown film, because that is the one which is showing a very nice oscillation in the lower thickness level. Whereas, if you are going for 5 nanometer or 6 nanometer thick films, you can see here there is a nice two dimensional growth, that is why you see the oscillations in a regular fashion.

So, this is not bad, what happens is, first it grows using island mode but then, it recovers to a two dimensional mode. Whereas, in this case in PLD grown films, it starts with two dimensional growth and then, it becomes more rough to a three dimensional growth, that is why you see this oscillation is actually fading out. So, there is a compromise, if you want to grow higher thicknesses then, you can resort to this. So, plenty of changes happened with respect to thickness and with respect to the growth mode, which is important for nano structuring.

And this is the beautiful STM image of iron grown on copper 1 0 0 where, you can see that this iron islands are spreading on the copper 1 0 0 surface, this is for 0.18 monolayer, this is for 0.56 monolayer. Now, when you come to one layer, there is a absolute coverage of the first layer, now the second layers are already starting to grow, this white white islands are nothing but the second layer which is started growing. So, you can nearly enforce a two dimensional growth, if you are trying to grow iron and copper 1 0 0, which is not the case if you are going to grow on iron copper 1 1 1.

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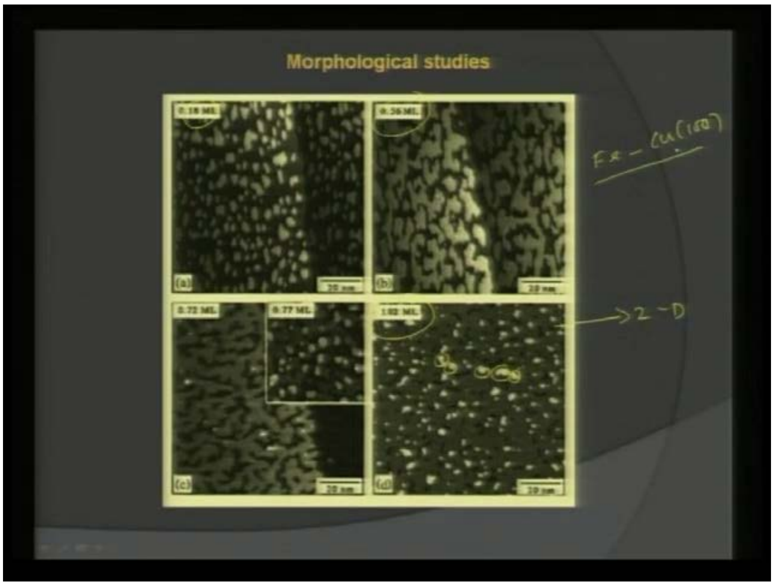

Morphological studies

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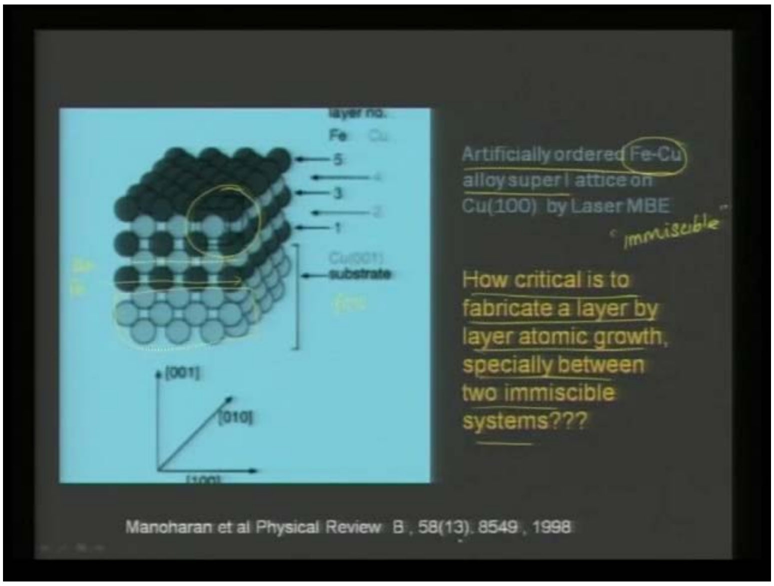

Artificially ordered Fe-Cu alloy superlattice on Cu(100) by Laser MBE

"immiscible"

How critical is to fabricate a layer by layer atomic growth, specially between two immiscible systems???

Manoharan et al Physical Review B, 58(13), 8549, 1998

Lastly, I would like to leave with another classic example of, how to use this approach to make artificial alloys, Artificially ordered alloys by the way, iron and copper cannot exists as alloy, because iron and copper are immiscible. They are immiscible, therefore this cannot form a alloy, in mother nature you would not see iron copper alloy. Therefore, is it possible for me to create a artificial alloy, because I have the capability of using molecular beam epitaxy to force growth.

So, in such case, if I want a iron copper artificial alloy, let me take a single crystal, copper 1 0 0 substrate, which is arranged in a cubic close packed way and this is a FCC lattice. Now, I can try to put one atomic plane of iron and I can put one atomic plane of copper and then, I can put one atomic plane of iron so on. Now, you can see, as I increase this periodicity, I can immediately come across a FCC lattice. So, this is the way to grow or to build the blocks by going for a two dimensional growth, so is it possible. How critical it is to fabricate a layer by layer atomic growth, especially between two immiscible systems and this has appeared in this journal, if one is interested we can read that.

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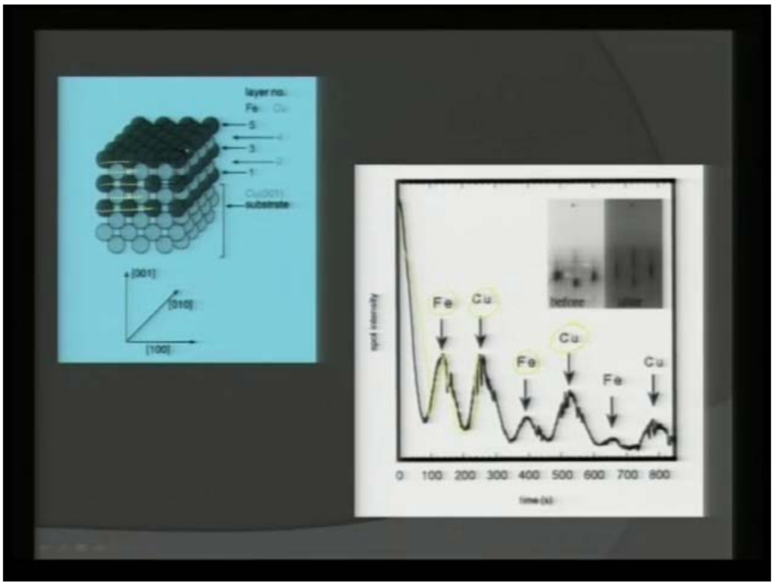

And I will again tell you to make this layers in alternate fashion, you need to first deposit iron and this is using RHEED oscillation, you can control the maxima. And then, you can stop there and go for the second layer, which is nothing but copper iron and then, iron copper and so on. As you can see the intensity, whenever you are depositing iron, it is growing rough, therefore the intensity is less. Whenever you are growing copper, the intensity is increasing, so copper is able to grow nicely on iron, but iron is not able to grow nicely on copper. This balance will be there, but nevertheless we can try to keep going for stackings of this order.

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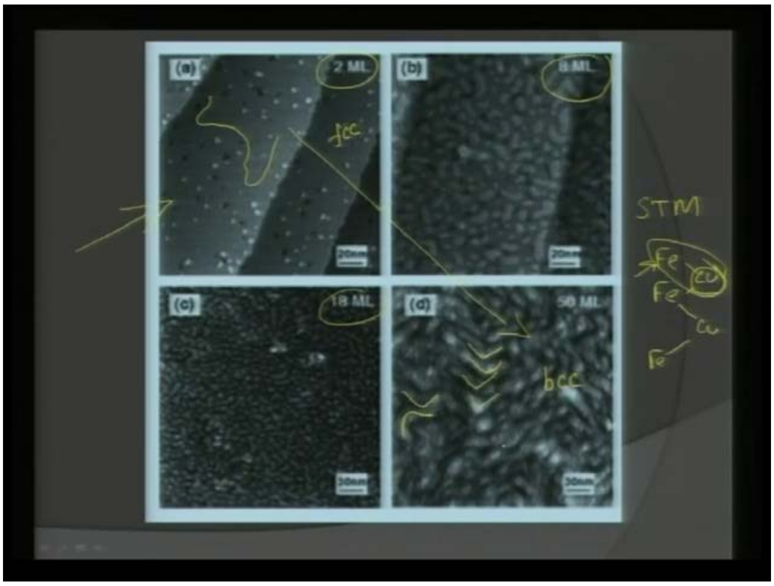

This is the STM image of this iron copper iron copper layers, so iron copper iron copper layers. So, you can see for two more layers, which is nothing but iron and copper, all this black holes are the first layer that is, iron and this grey region whatever you see here, this is nothing but copper and you can also see that, the third layer has just started falling on the top. So, you can clearly make such a iron copper interface at two monolayers then, at 8 monolayers and you can make upto 18 monolayers.

But, if you see, as you go from 2 to 50 monolayers, the surface has become rough and you can see this sort of stripes, this sort of 90 degree stripes are signature for a FCC iron copper to go to BCC iron copper. So, as you build these bilayers at a critical thickness, you can see there is a transformation from FCC to BCC. And you will also see the changes in the magnetic property for example, if you look at the roughness, if it is FCC, you see a roughness almost of this fashion. And once it transforms to BCC somewhere here, you see suddenly the roughness jumps somewhere here, indicating that there is a clear transformation between FCC and a BCC lattice.

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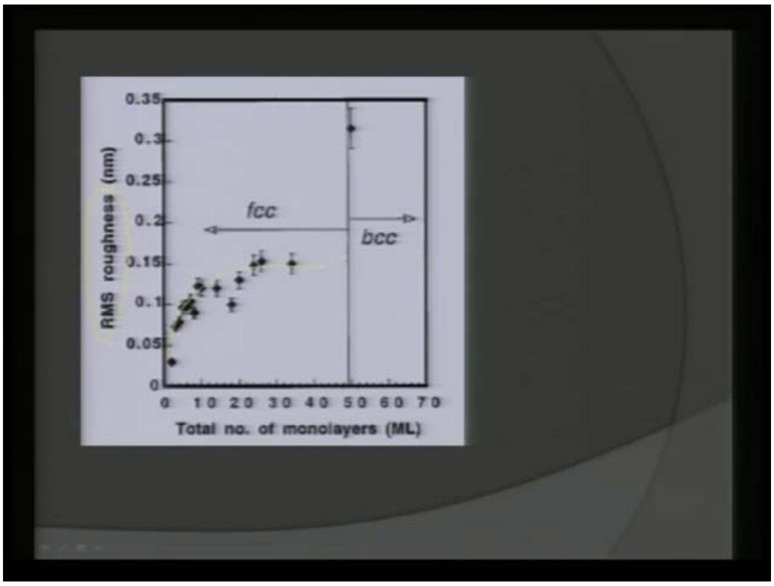

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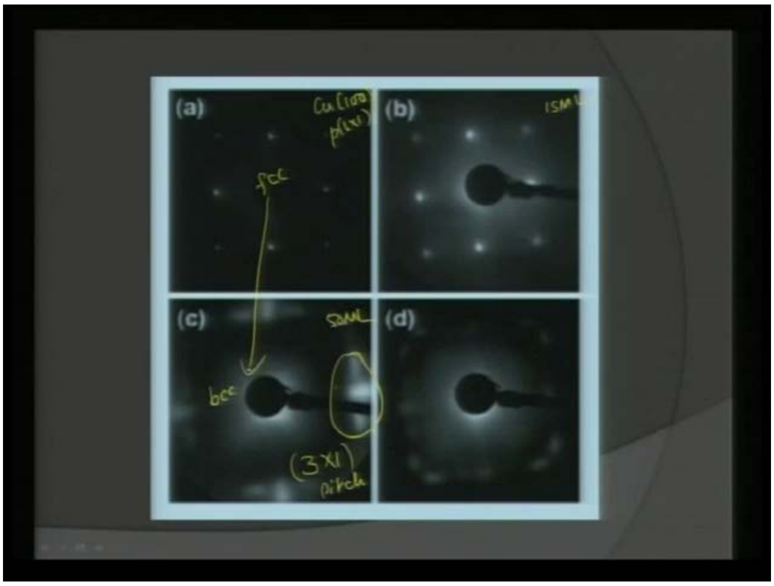

And you can also see that, from the RHEED pattern, this is copper 1 0 0, which is a clean FCC p 1 cross 1 pattern. And if you go to a 15 monolayers it is the same way, but if you go to 50 monolayers, as you see from these two, you can see this 3 cross 1 pattern, which is called a pitch pattern. And this is indicative that, from FCC, the iron copper multilayer has transformed to BCC. So, you can keep on monitoring both from STM, Scanning Tunneling Microscopic images as well as this one.

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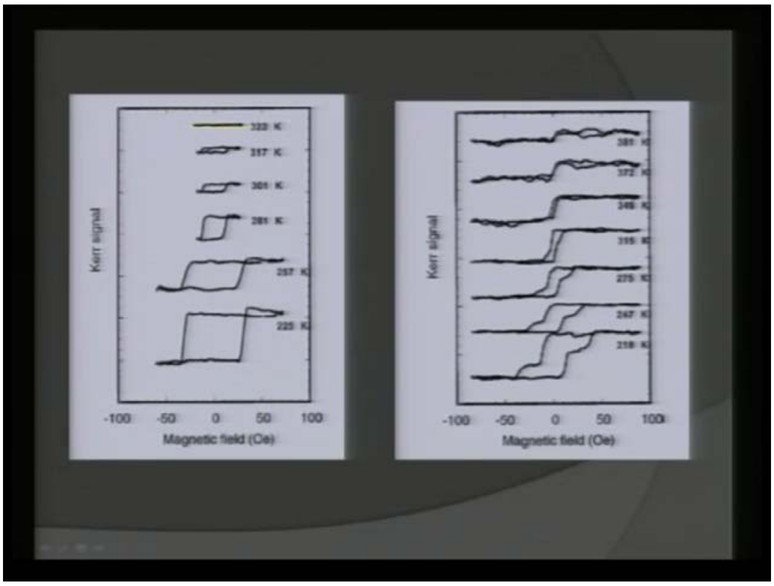

Typically this magnetic features can be recorded this way, the way we evaluate whether it is magnetic or not, you can go down and look at the loop and ask the saturation magnetization disappears, you decide that is the T c.

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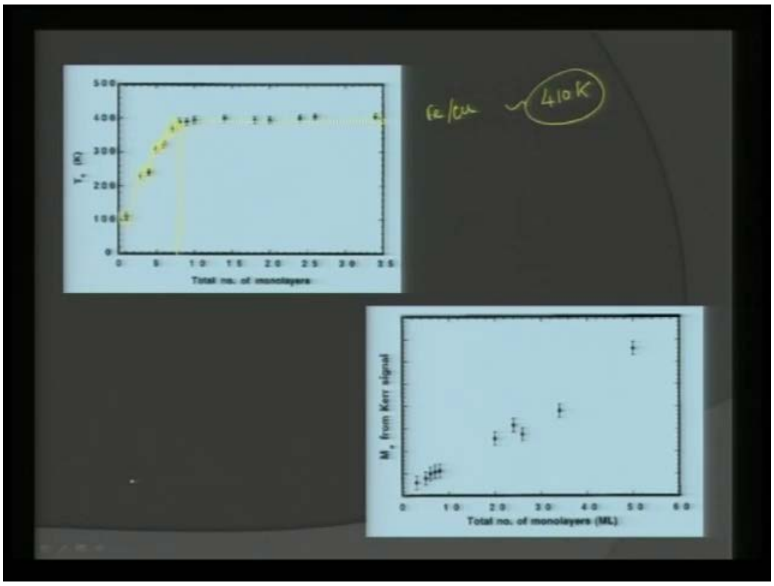

So, you can make a plot of T c versus this monolayers, so if you just put the first layer iron, it is like this then, the second layer copper then, the third layer iron then, fourth layer copper iron, copper iron. You can see that, the T c increases and then, it becomes almost steady, in other words even if you go for 100 repeats, the T c is going to remain the same. In other words, the iron copper 50 50 alloy will have a T c in bulk to be somewhere around approximately 410 Kelvin. So, what you are trying to say is, if this iron copper alloy, if it is artificially made which is 410 Kelvin, you do not need to go for a very thick film. You can achieve the same T c in a thickness of just 8 monolayers also, so this way you can control the nanostructuring.

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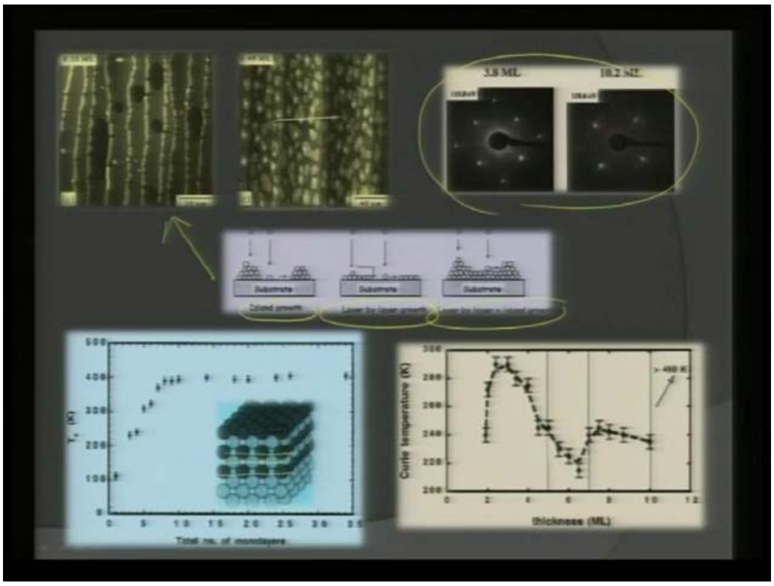

Therefore, I will wrap up here by saying that, we looked at the three growth modes, island growth, layer by layer growth and layer by layer and island growth where, I have shown you example. If you have thermally grown film it comes as a stripe, if you have pulsed laser deposition it comes out like this. You can easily map this transformation using LED and you can also indulge in making artificial alloys, because this is the nicest way to make artificial alloys. Because, you have control over atomic layer by layer growth and also, you are able to study the magnetic property of this individual layers and the bilayers, as you proceed with the layer thicknesses. So, with this I conclude and then we can take some examples in the next few lectures.