Surface Engineering of Nanomaterials
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Lecture - 25
Size Effect in Physical and Other Properties of Nanostructured Coatings

Hello, in our this particular lecture actually we are also going to discuss the size effect, but size effect on different parameters or maybe different properties that physical and other properties, means some optical properties will come, some magnetic properties we are going to discuss, some sensor properties we are going to discuss and some melting may be the thermal properties we are going to discuss. So, this lecture actually depends on the size effects on various properties which we have not discussed in our past some previous slides.

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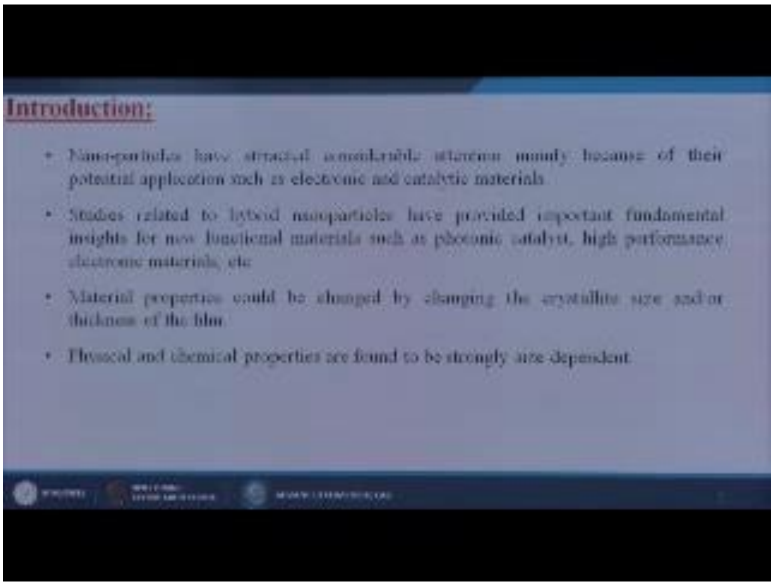

So, first is that introductions where we are going to discuss about the Nano-particles which have attracted considerable attention, mainly because of their potential applications such as electronic and catalytic materials yes of course. This is the well known fact that when we are going to use the Nanomaterials, it is having the versatile applications, it is having the versatile properties which it is showing so that we can use that Nano-particles for several applications, it can increases so many properties at a time and also it is easy to use, is it sometimes it is easy to synthesize and sometimes it is easy to hazard free or maybe the environmental friendly materials.

Studies related to hybrid nanoparticles have provided important fundamental insights for new functional materials such as photonic catalysts, high performance electronic materials etcetera. So, as I told already in my several lectures that application of the nanocomposites or maybe that nanomaterials are numerous; we can use this kind of materials for several applications we can make these materials more tiny, so that it can show the some other material properties together or maybe several material properties can be obtained from this particular technology. Material properties could be changed by changing the crystallized size and or the thickness of the film, you know last 2 or 3 lectures I have discussed about that how the material properties is changing when we are trying to reduce the particle size of that particular nanofiller, when we are reducing the thickness of that particular nanocomposites. So, we are trying to change the material properties.

Physical and chemical properties are found to be strongly size dependent. So, here the same thing when we are talking about the physical properties of these nanocomposites or maybe that chemical properties of these nanocomposites, we are getting that the size dependency of that particular nanofiller is when we are reducing that size, these properties are enhancing, these properties is giving very good results.

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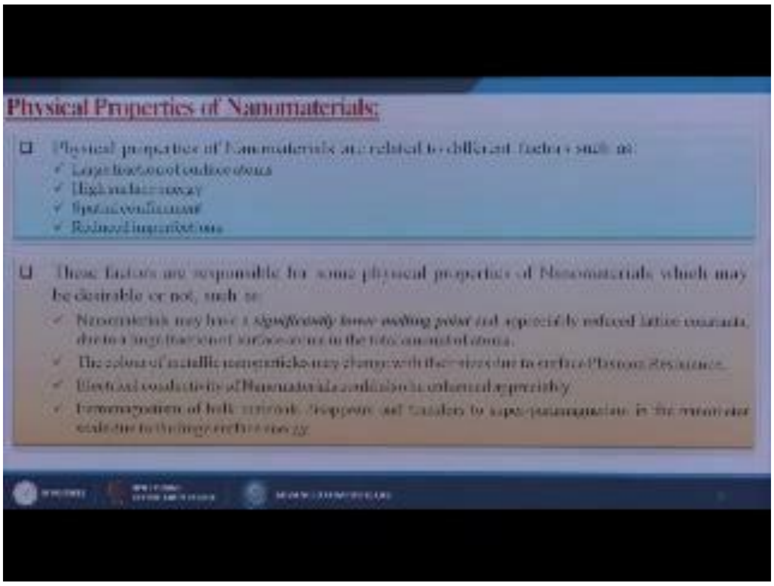

So, first is that physical properties of Nanomaterials; physical properties of Nanomaterials are related to different factors such as: large fraction of surface atoms, high surface energy, special confinement, reduced imperfections. So, when we are talking about these Nanomaterials, these nanomaterials are related to the different factors such as large fraction of surface atoms, high surface energy special confinement and reduced imperfections. These factors are responsible for some physical properties of Nanomaterials which may be desirable or not such as Nanomaterials may have a significantly lower melting point and appreciably reduced lattice constants due to a huge fraction of surface atoms in that total amount of atoms. That means, if we are going to use certain kind of nanoparticles or maybe the nanofillers, inside our systems or maybe the inside our coatings that may reduce the melting point of that particular material.

The color of the metallic nanoparticles may change with the size due to surface plasmon resonance. So, that is the optical properties of these particular Nanoparticles, is going to be changed when we are doing, when we are decreasing the crystal structure or maybe that crystal size of that particular Nanoparticles. Electrical conductivity of Nanomaterials could also be enhanced appreciably. Ferromagnetism or maybe the properties of bulk materials disappears and transfers to super-paramagnetism in the nanometer scale due to the huge surface energy. So, all these things are the beauty of that particular material when we are changing its shapes, size from micrometer level to nanometer level. So, this is the main vital parameter, why we are doing the size dependency, why we are reducing the size for getting some better properties, which we are going to see in details in our next subsequent slides.

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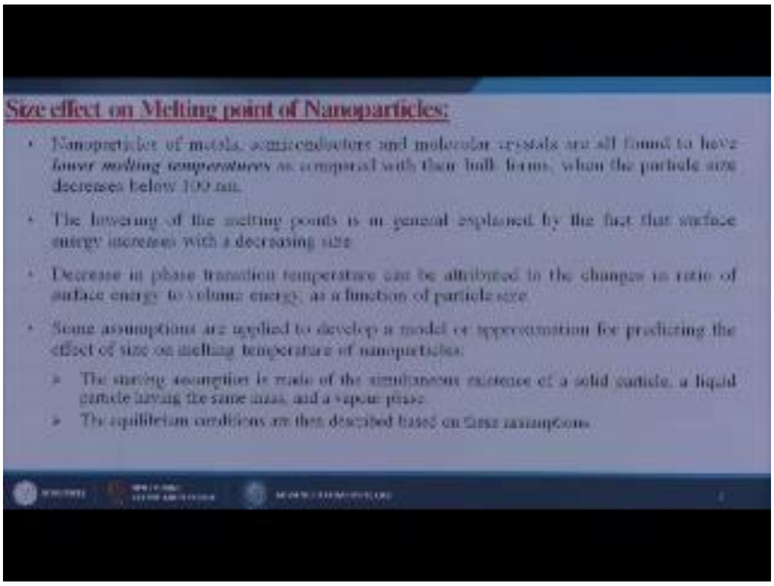

So, first is that size effect on melting point of Nanoparticles. Nanoparticles are metals semiconductors and molecular crystals are all found to have lower melting temperatures as compared with their bulk forms when the particle size decreases below 100 nanometer. So, Nanoparticles are metals, semiconductors and molecular crystals are all found to have lower melting temperatures. So, when I am using this kind of particle size well below in under 100 nanometer, we have seen that the melting temperature of these materials is also reducing. The lowering of the melting points is in general explained by the fact that the surface energy increases with a decreasing size. So, when the surface energy increases, automatically the melting point is decreasing. Decrease in phase transition temperature can be attributed to the change in ratio of surface energy to volume energy as a function of particle size.

Some assumptions are applied to develop a model or approximation for predicting the effect of size on melting temperature of Nanoparticles; the starting assumptions is made of the simultaneous existence of a solid particle, a liquid particle having the same mass and a vapor phase, the equilibrium conditions are then described based on these assumptions.

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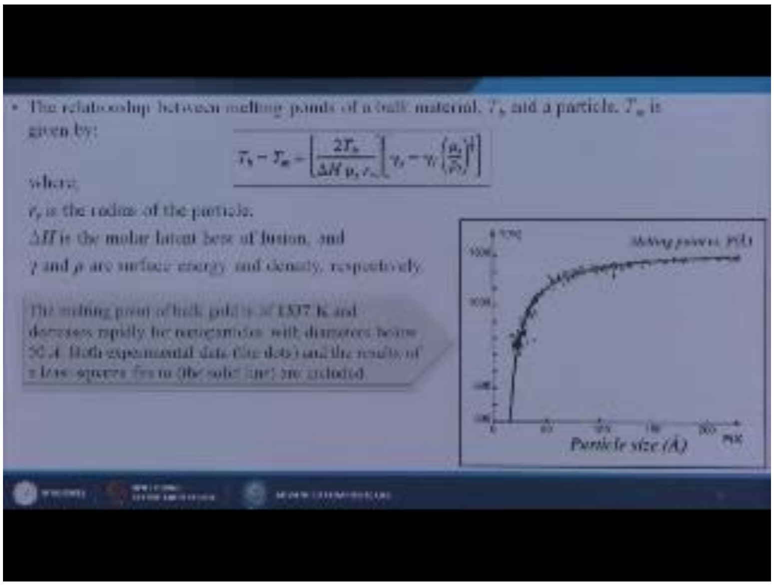

So, the relationship between melting point of a bulk material T b is nothing but the melting point of that bulk material and the particle melting point is T m is given by T b minus T m is equal to 2 T b by delta H rho s r s into gamma s minus gamma L by into rho s by rho L to the power two-third; where r s is the radius of the particle, del H is the molar latent heat of fusion, and gamma and rho are surface energy and density respectively.

So, in this particular graph we are going to show that how we are trying to change the practical size from micro to nano so that our melting temperature is changing. The melting point of bulk gold is of 1337 Kelvin and decreases rapidly for Nano particles with diameters below 50 angstrom. Both experimental data the dots and the results of a least-square fits to the solid line are included like this. So, when the particle size is decreasing automatically the melting point is coming down.

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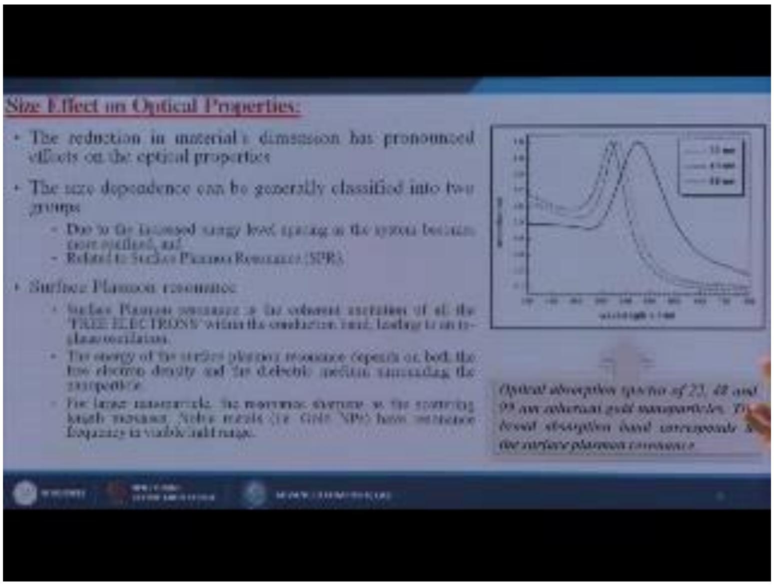

Then the side effect on optical properties; the reduction in material dimension has pronounced effects on the optical properties. So, the size dependence can be generally classified into 2 groups: first groups is that due to the increased energy level spacing other systems become more confined and second is that related to surface Plasmon resonance. So, what is the surface Plasmon resonance? It is nothing, but the coherent excitations of all the free electrons within the conduction band leading to an in phase of oscillation. The energy of the surface Plasmon resonance depends on both the free electron density and the dielectric medium surrounding the nanoparticle for larger nanoparticle the resonance sharpens as the scattering length increases, noble metals like gold Nanoparticles have resonance frequency in visible light range. So, this is known as the surface Plasmon resonance.

So, in this particular case we are showing that how the particle size is changing in then how is absorption properties in terms of wavelength is also changing. So, when you are talking about that 22 nanometers, the graphs is looking like this; when you are changing it up to 14 nanometers and then when we are changing to 99 nanometers, the wave length is totally sitting to the right hand side; that means, that wavelength of that particular material is increasing. So, optical absorption spectra of 22, 48 and 99 nanometer spherical gold Nanoparticles, the broad absorption band correspondence to the surface Plasmon resonance.

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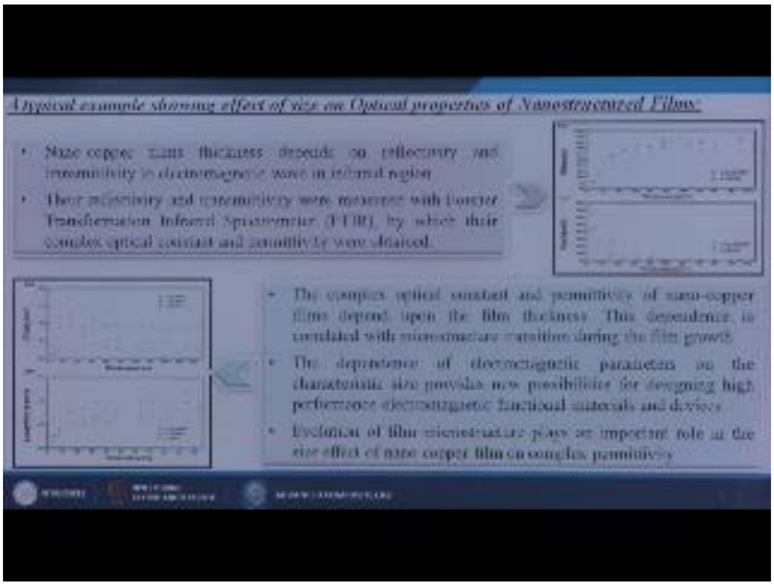

A typical example showing effect of size on optical properties of nanostructure films; Nano-copper film thickness depends on reflectivity and transmittivity of electromagnetic wave in the infrared regions, their reflectivity and transmittivity were measured with fourier transformation infrared spectrometer; that means, we have done the FTIR by which their complex optical constant and permittivity were obtained which has been shown in this particular case. The complex optical constant and permittivity of Nano-copper films depend upon the film thickness; this dependence is correlated with microstructure transition during the film growth. So, here we are showing the thickness into the x axis and real part and imaginary part into the y axis. So, which is giving you that how the thickness is changing and how its electrical impedance properties are going to be changed?

The dependence of electromagnetic parameters and the characteristic size provides new possibilities for designing high performance electromagnetic functional materials and devices. Evaluation of flame microstructure plays an important role in the size effect of Nano-copper film on complex permittivity that means, when we are trying to incorporate the small, small Nanoparticles inside the system, the permittivity of that particular nanocomposite is going to be reduced. So, due to that the material electrical properties is totally changing, the dielectric properties of that material is totally changing, the impedance parameter of that material is totally changing, if we go for the micro size

Nanoparticles it is showing the different properties, but when we are reducing that particle size to the nanometer range the properties is totally changing.

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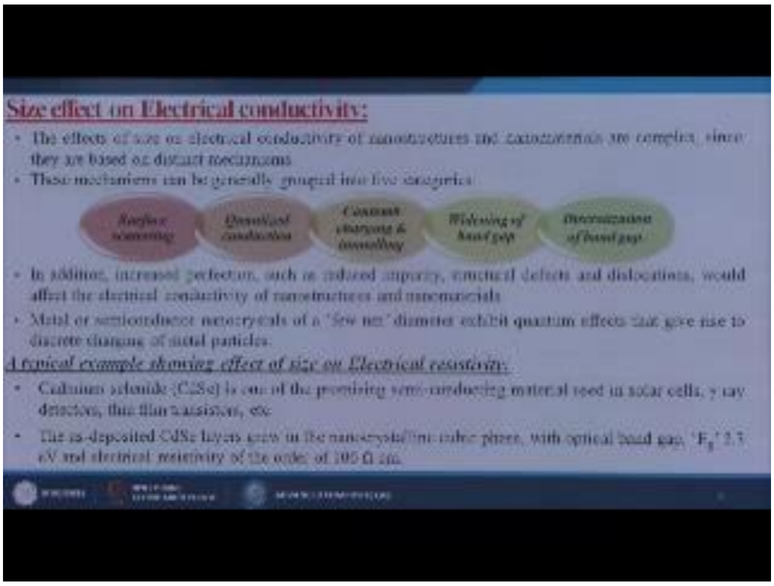

Size effect on electrical conductivity; the effects of size on electrical conductivity of nanostructures and Nanomaterials are complex, since they are best on this distinct mechanisms, these mechanisms can be generally grouped into 5 categories, surface scattering; quantized conduction; column charging and tunneling; widening of band gaps discretization of band gap. In addition increased perfection such as reduced impurity structural defects and dislocations would affect the electrical conductivity of nanostructures and Nanomaterials, metal or semiconductor nanocrystals of a few nanometer diameter exhibit quantum effects that give rise to discrete charging of metal particles.

A typical example showing effect of size on electrical resistivity: cadmium selenide is one of the promising semiconducting material used in solar cells, that gamma ray detectors, thin flint transistors it etcetera. The as-deposited cadmium selenide layers grew in the nanocrystalline cubic phase, with optical band gap, that is 2.3 electron volt and electrical resistivity of the order of 106 of ohm centimeter. So, this is all are the value. So, when we are reducing the size of these Nanoparticles, the total electrical properties of these particular materials is changing.

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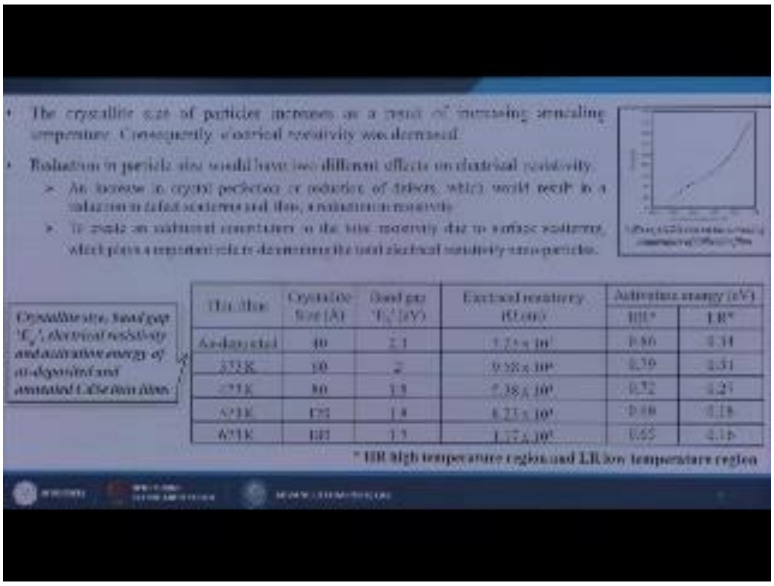

The crystallite size of particles increases as a result of increasing annealing temperature, consequently electrical resistivity was decreased. Reduction in particle size would have two different effects on electrical resistivity and increase in crystal perfections or reduction of defects which would result in a reduction in defect scattering and does a reduction in resistivity. To create an additional contribution to the total resistivity due to the surface scattering which plays a important role in determining the total electrical resistivity nano-particles.

So, here the crystallite size band gap and electrical resistivity and activation energy of as deposited and anneal CdSe thin films. So, here this is the thin films as deposited 373 Kelvin, 473 Kelvin, 573 Kelvin 673 Kelvin. Crystallized height is totally change increasing it I s from 40 angstrom to 60 angstrom to 80 to 120 to 180. Band gap is also decreasing its starting from 2.3 to 2 then 1.8, 1.8 then 1.7 electrical resistivity is also changing and activation energy is also decreasing. So, here higher temperature region and LR is the low temperature region. So, these all are the properties where when we are decreasing the crystallized site, the material property, electrical resistivity the band gap and activation energy of that particular material is totally changing.

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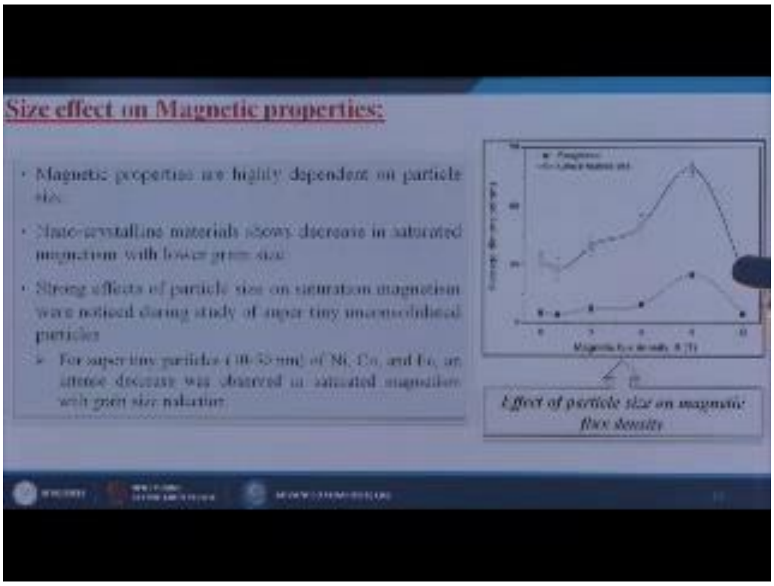

Then size effect of magnetic properties: here the magnetic properties are highly dependent on particle size, nanocrystalline material shows decrease in saturated magnetism with lower grain such strong effects of particle size on saturation magnetism where noticed during study of super tiny unconsolidated particles. For super tiny particles 10 to 50 nanometer of nickel, cobalt and iron and intense decrease was absorbed in saturated magnetism with grain size reduction. So, here is the magnetic flux density and here is the average dimension. So, one is called the roughness another one is called a lateral feature size. Effective particle size on the magnetic flux density; you can see that when the particles average dimensions is going increase, the magnetic flux density is also increasing, but when the particle size is also decreasing the magnetic flux density is also decreasing. So, in that particular case the size effect of my magnetic properties is totally depend upon the particular size of that particular material.

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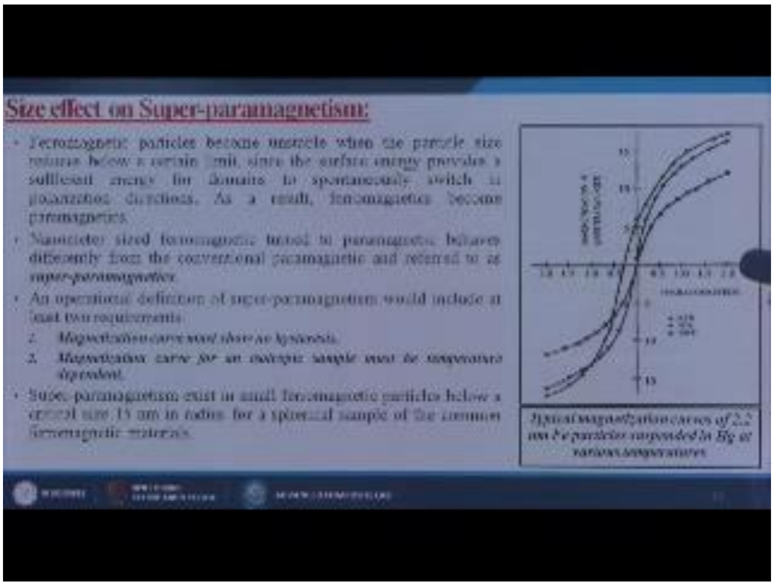

Next is the size effect on super paramagnetism: ferromagnetic particles become unstable when the particle size reduces below a certain limit, since the surface energy provides a sufficient energy for domains to spontaneously switch in polarization directions, as a result ferromagnetics become paramagnetic, nanometer sized ferromagnetic turn to paramagnetic behaves differently from the conventional paramagnetic and referred to as super paramagnetic.

An operational definition of super paramagnetism would include at least two requirements, magnetization curve must show no hysteresis, magnetization curve for an isotropic sample must be temperature dependent; super-paramagnetism existence in all ferromagnetic particles below a critical size 15 nanometer in radius for a spherical sample of the common ferromagnetic materials. So, same thing we are telling over here also that if we change the particle size from micro to nano, the magnetic properties is also changing the material is showing the superparamagnetic. So, here the typical paramagnetization curves of 2.2 nanometer iron particles suspended in mercury at various temperatures. So, it has been shown in this particular case.

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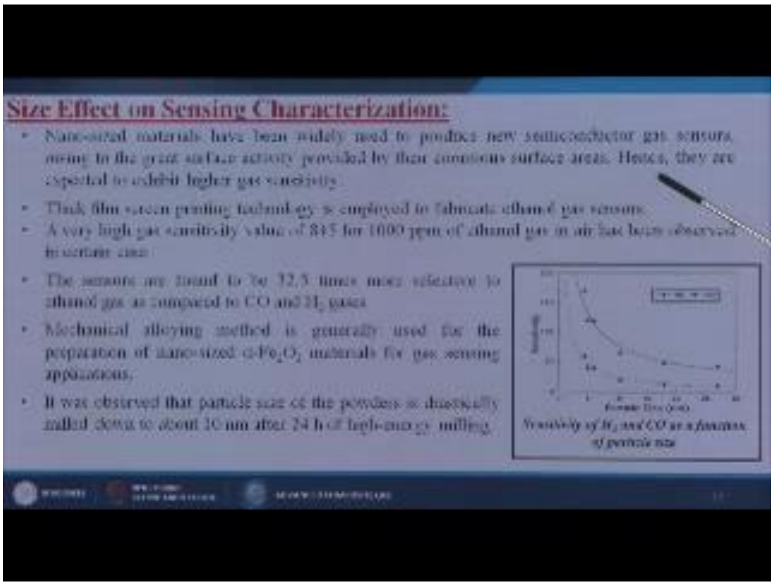

Next size effect on sensing characterizations; as I told already nowadays we are working on the sensor which is a very useful instrument that which can save our life. So, when we are talking about these kind of sensors, the main vital parameters of these sensors is called the sensitivity; that how fast the sensor is sensing the material. So, when you are talking about the sensitivity, we have shown that into the different zone means different medium one is the hydrogen medium another one is the carbon monoxide medium, how our sensor is showing the sensitivity. So, Nano-sized materials have been widely used to produce new semiconductor gas sensors, going to the great surface activity provided by their enormous surface areas hence they are expected to exhibit higher gas sensitivity.

Thick film screen printing technology is employed to fabricate eternal gas sensors. A very high gas sensitivity value of 845 for 1000 ppm of ethanol gas in air has been observed in certain case. The sensors are found to be 32.5 times more selective to eternal gas as compared to carbon monoxide and hydrogen gases. Mechanical alloying method is generally used for propulsion of nano-sized alpha iron oxide materials for gas sensing applications. It was observed that particle size of the powder is drastically milled down to about 10 nanometer after 24 hours of high-energy milling.

So, when we are reducing the particle size by the milling operations and we are using that small particle size for the sensing applications, we can show the sensitivity of that particular material is tremendously enhancing it is almost 32.5 times better than the micro site. So, here also we are getting the same thing when we are using the smallest particle size, we are getting the maximum sensitivity, but when slowly slowly we are increasing the particle size the sensitivity of that particular material is getting decreased.

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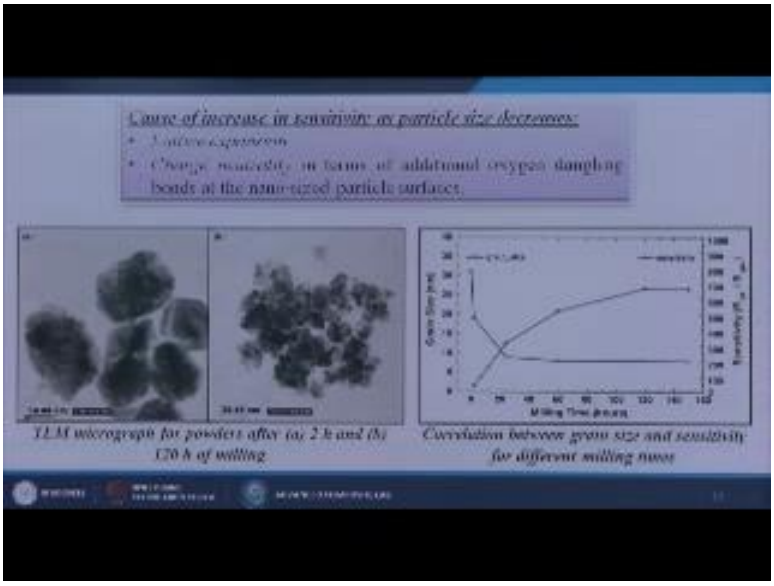

Cause of increase in sensitivity at particle size decreases, first one is called the lattice expansions; second one is called the charge neutrality in terms of additional oxygen dangling bonds at the Nano-sized particle surfaces. So, here is the transmission electron micrograph for powders after 2 hours and after 120 hours of milling. Just we are going to show you that when we are doing the 2 hours milling, probably there is a chance of large particles present inside the systems, but when we are going for a long hours; that means, 120 hours means almost 5 days continuous rigorous milling we are doing, the particle is coming into the small size; in small size means the surface area of that particle is increasing not only that the crystallized size is also decreasing and thus it is showing the better properties in terms of sensing applications.

Right hand side is the correlation between grain size and sensitivity for different milling times. So, when we are talking about the grain size, when the grain size is reducing the sensitivity of that particular material, when the grain size is around 30 then the sensitivity is also showing around 800, but the problem is that that time sensitivity is too low. So, when the grain size we are decreasing, the sensitivity of that particular material is increasing drastically. So, that is the beauty of this kind of nanoparticle.

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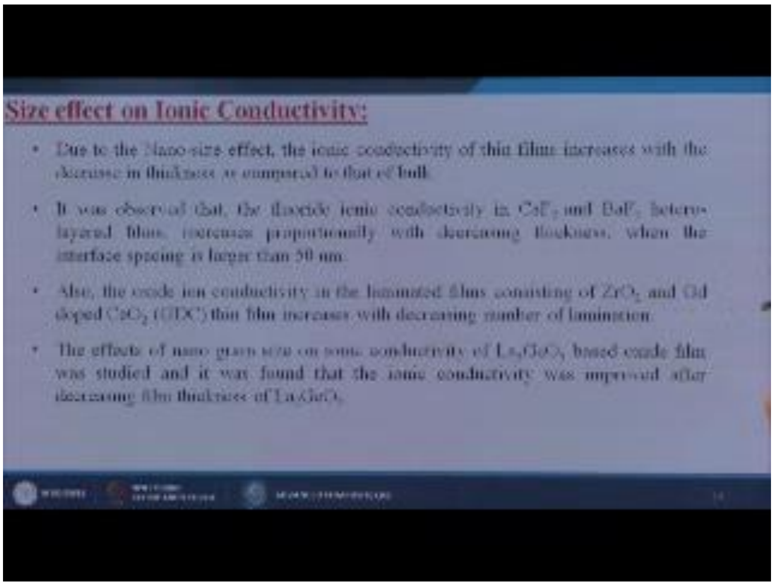

Then side effect on ionic conductivity; due to the nano-size effect the ionic conductivity of thin flings increasing with the decrease in thickness as compared to that of bulk. So, it was observed that the fluoride ionic conductivity in calcium fluoride and the barium fluoride hetero layered films increased proportionally with decreasing thickness when the intercept spacing is larger than 50 nanometer, also the oxide ion conductivity in the laminated film consisting of zirconia oxide and galadiam doped C o 2 selenium oxide thin film increases with decreasing number of laminations. The effect of nanograin size on ionic conductivity, that is the main vital point over here nanograin size of ionic conductivity of lanthanum, gallium, penta oxide, based oxide film was studied and it was found that the ionic conductivity was improved after decreasing the film thickness of lanthanum, germanium, penta oxide.

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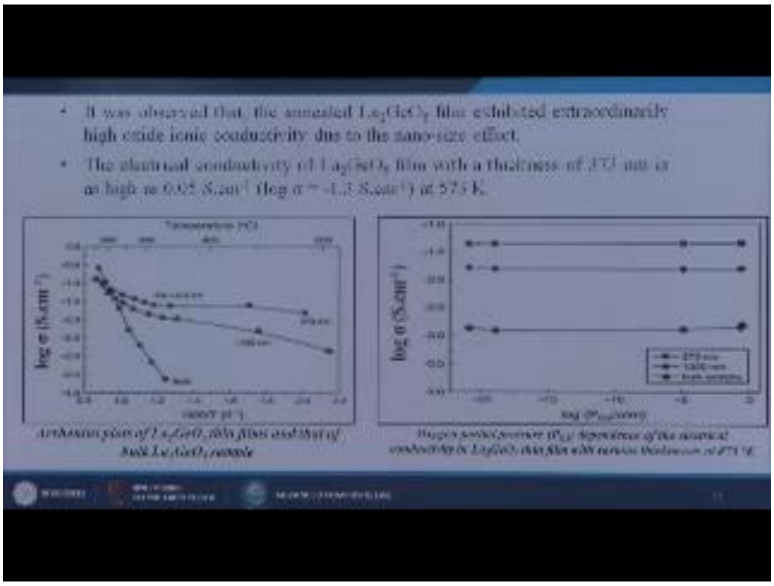

So, it was observed that the hanging lanthanum, germanium, pentoxide flames exhibited extraordinarily high oxide ionic conductivity due to the nano-size effect. The electrical conductivity of lanthanum, germanium pentoxide film with a thickness of 373 nanometers he is as high as 0.05 Siemens per centimeter. So, log sigma is equal to minus 1.3 Siemens per centimeter at 573 degree Kelvin. So, here this is the Arrhenius plot of these thin films and that of bulk thin film over. So, here from the bulk we can see that how the drastically the value is changing, but when you are using that 100 nanometer or maybe 300 nanometer size particle size, the how is showing the electrical conductivity almost constant at that particular temperature.

Here also we are showing that different oxygen partial pressure dependence of the electrical conductivity in lanthanum, germanium pentoxide thin film with various thicknesses at 873 Kelvin. So, here this is the pressure versus the electrical conductivity and here we are getting with pressure keeping a changing the different nanoparticle size also, but still the electrical conductivity is remain same. So, these all are the techniques by which we can change the material properties from micro to nano so, that we can get the better properties in terms of optical, in terms of magnetic, in terms of electrical conductivity or maybe any other physical and thermal properties.

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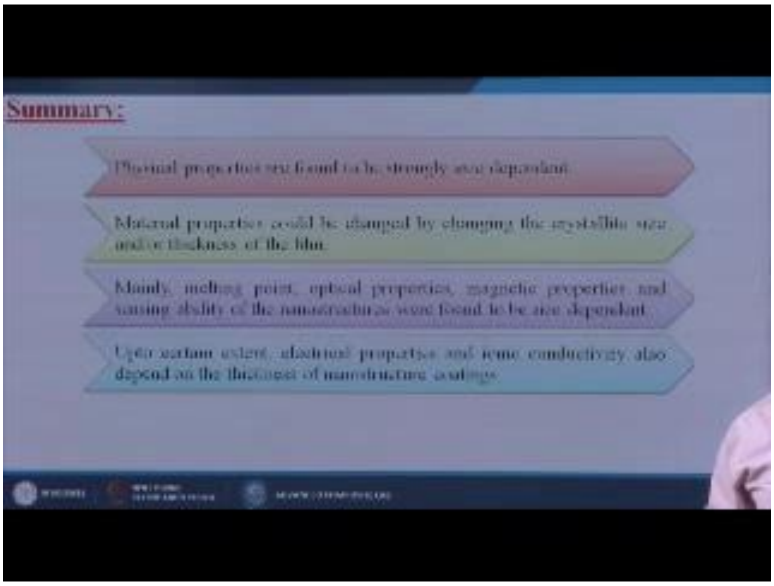

So, now we have come to the summary of this particular lecture that physical properties are found to be strongly size dependent, material properties could be changed by changing the crystallized size and thickness of the film. In our last consecutive 5 lectures we are still every time we are discussing about the crystallized size, about the thickness of film how they are affecting the material properties, in terms of mechanical properties, optical properties, magnetic properties then thermal properties then some kind of sensing properties and so on.

Next mainly melting point, optical properties, magnetic properties and sensing ability of the nanostructures were found to be size dependent, in this particular lecture up to certain extent electrical properties and ionic conductivity also depend on the thickness of nanostructure coatings. So, this is the main motto of this particular lecture that overall we are trying to show that only two properties which can be the vital parameters by which we can get the enhance properties of any nanocomposites that is one is the called the particle size or maybe the grain size or maybe the crystallite size of that particular nanoparticle, what we are using for making these nanocomposites and second is called the what is the thickness of that particular nanocomposites because if the thickness will be more, the consumption of that nanoparticle or maybe the loading will be the more thus it will be resulting some kind of good properties.

So, we have seen that when we are changing from micro to nano, that total properties is drastically changing from lower value to the higher value, not only that previously it was showing only a single good properties or maybe too good properties, now it is showing n number of good properties. So, simultaneously we are getting so many good properties together.

Thank you.