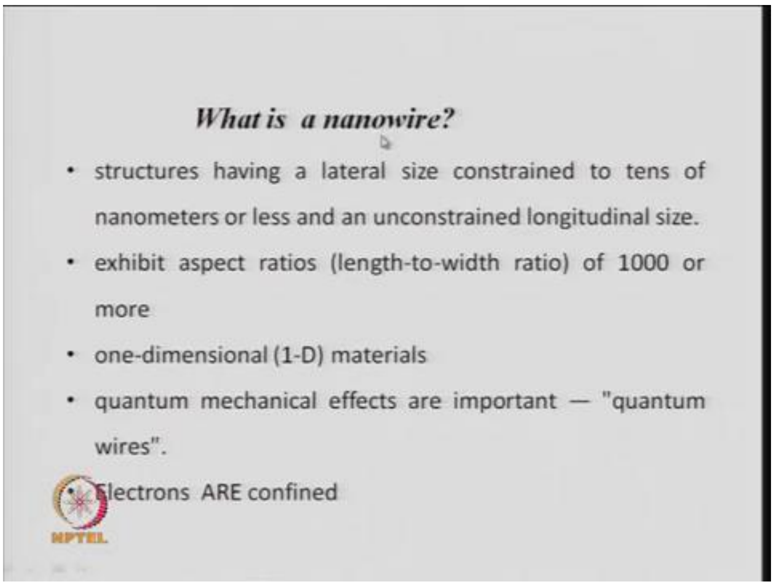
Nano Structured Materials-Synthesis, Properties, Self Assembly and Applications
Prof. Ashok K Ganguli
Department of Chemistry
Indian Institute of Technology, Delhi

Module - 3
Lecture - 18
Metal and Metal Oxide Nanowires – I

Welcome back to this course on nanostructured we are in module three and today we will be doing the lecture number four. Previously, in the first second third lectures of this module we discussed a class of and isotopic nanostructures. Basically the carbon nanotubes, their synthesis their properties based on chirality and the thickness and what are the different applications of carbon nanotubes. So, that is what we covered in the previous three lectures of this model, so today the we would be going into and other class of and isotropic structures and a class of nanowires which are one dimensional wires.

These are not based on carbon, but these are based on any metal and metal oxide are sulfide and other doped nanowires. The thing in common is with carbon nanotubes that these are also and isotropic structures with a one of the axis very long and the other axis the other two axis very short. So, it can be a tube are a rectangular nanowire depending on the cross section of the nanowire.

(Refer Slide Time: 01:51)



So, what is a nanowire? These are structures having lateral size constraints to few nanometers an unconstrained longitudinal size that is unconstrained length which can be and in terms of microns say 100 microns 200 microns or maybe 500 nanometers which will be a small wire, but what is important is the lateral size that is can be the diameter of the nanowire. If the cross section is circular, then that diameter is few nanometers can be 10 nanometers, 15 nanometers 20 nanometers etcetera. So, the cross section if it is circle, then you have a diameter or if the cross section is a square, then the side of the square will be few nanometers and this kind of a structure which is very long, but having small lateral size is a nanowire.

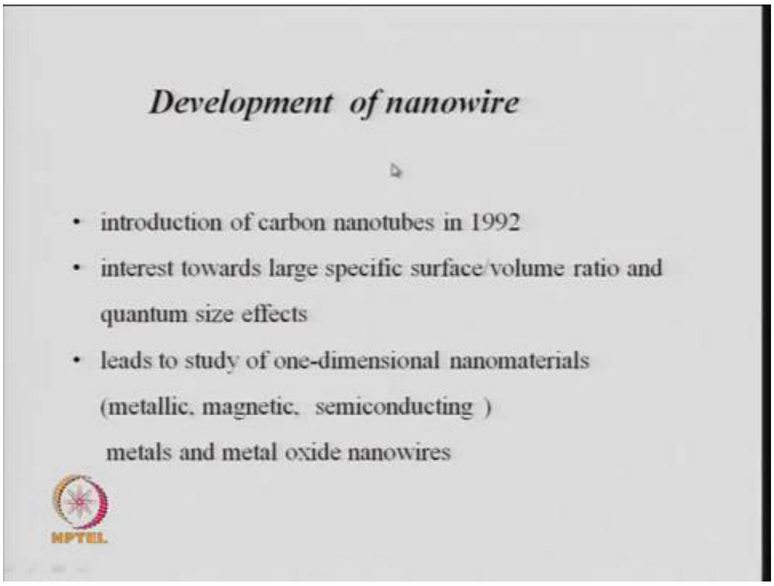
Now, these nano wires can be hollow if it is hollow then there is only a surface, but most the time we are discussing of a wire, which is filled that is it is complete. It has a atoms in all places from the center of the circle a cross section circle do the outer periphery. Now, this kind of nanowires exhibit aspect ratio, which is the ratio of the length to width of thousand or more for example, if you have a wire of around one micron, which is like 1000 nanometers. You have a diameter, which is like you know 1 nanometer, then the racial aspect ratio will be 1000, so you have say few microns 5 micron or 10 microns that is 5000 nanometers 10,000 nanometers.

If the diameter is ten then 10,000 divided by 10 will give you a ratio aspect ratio of 1000, so typically the length to width ratio is of the order of 1000 or more, but it can also be small fought a small nano wires. These are classified as one dimensional materials because of this a constraint allow two dimensions only in one dimension, it has a large size and hence these are called one dimensional materials. Now, such materials where there is a constrained along certain axis in this case two axis there is a constraint that means the size is restricted.

Then, you will have quantum mechanical effects and hence many times the nanowires are also called quantum wires if the dimensions are so small that it exhibits quantum properties. So, typically most of the nanowires which have diameters of 10 nanometers or less will show quantum effects and then these nanowires will be called quantum nano wires. So, most important thing is what is being constrained due to the size are electrons and these electrons will be confined and you know if you can find electrons the property of that material is very different from a material where electrons are not confined. So, in a nano wire because of the size restriction along two axis, the electrons are confined in those two axis.

That means they cannot move beyond a certain distance in those two directions they are only allowed to move along the longitudinal side. So, such in such a case in a typical nanowire electrons are allowed to move along the longitudinal length which is the length and constrained in the other two dimensions. This brings about certain quantum mechanical effects in these quantum nano wires, now what is the history behind the development of the nano wire.

(Refer Slide Time: 06:33)

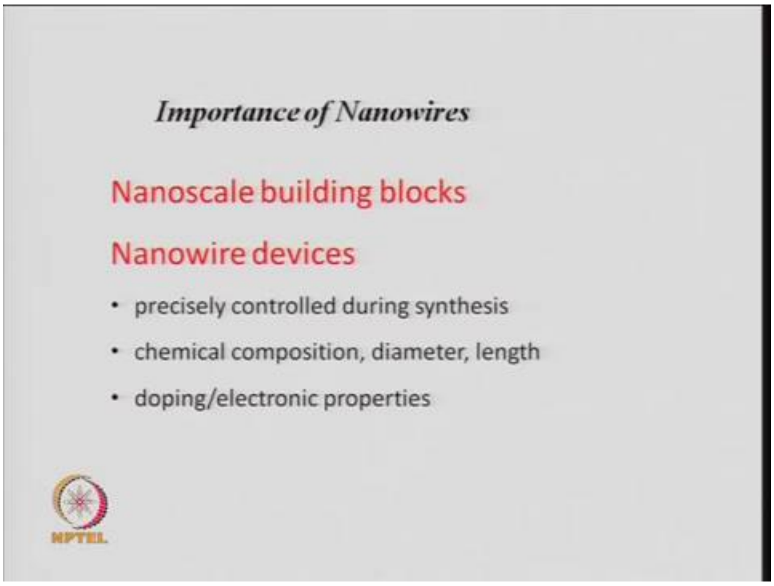


Actually, the history begins with the carbon nano tubes the carbon nano tubes were discovered in 1992. Other nano wires of non carbon materials like silicon or germanium or tin dioxide oxide sulfide you have sulfide nanowires like tungsten disulphide niobium disulphide etcetera those were synthesized much later the first a nanotubes or nanowires where found in 1992. The carbon nano tubes as we discussed in our previous lectures are generated mechanistically, you can think about it by rolling graphene sheet you get a carbon nano tube. So there it is hollow that is the first time that you have this kind of a object where a there are nano dimensions along a two axis and that is large dimension along the third axis.

That is a carbon nanotube and that is the beginning of the development of other nanowires important thing is any such and isotropic structure like nanotubes and nanowires will have a very large surface to volume ratio. That is one thing that it will have, a very large surface to volume ratio and second thing is it will show quantum effects because of the confinement of electrons. So, these nano wires were developed with these properties in mind specifically the surface to volume ratio will be very high and other effects from this will be following typically in catalysis and functionalization etcetera.

Here, surfaces are important, so all those properties where surfaces are important will be exhibited in these kind of nanowires and quantum effects will be exhibited. Now, this development of nanowires lead to several important one dimensional nano materials. Some, of them were metallic some are magnetic you can make semiconducting nanowires and you can make nanowires with unusual optical properties. Many of them were made of metals some of metal oxide and also you can make metal phosphides metal sulphides and many other materials can now be made in the form of nano wires.

(Refer Slide Time: 09:15)

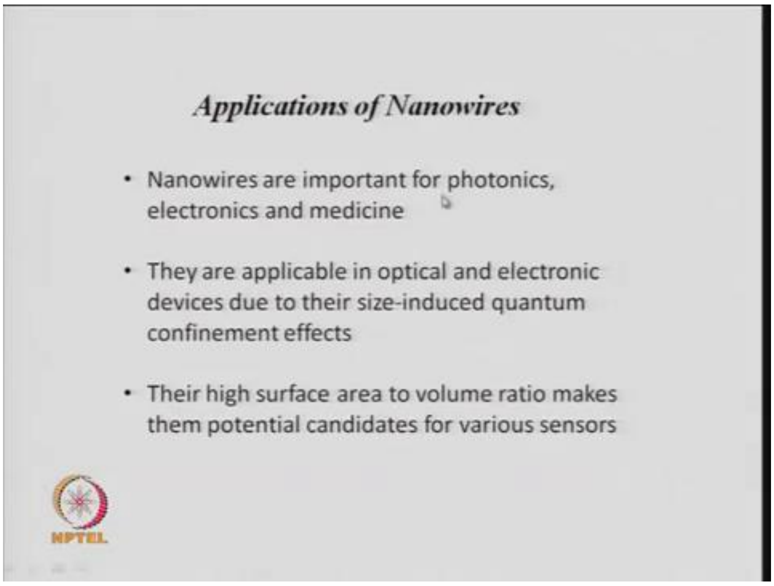


Now, what is the importance of the nanowires the importance comes from the two points that we discussed one is very high surface to volume ratio and the other is the quantum effects. So, these two points are key in any future device building, so these nano wires can act as nano scale building blocks. So, if you want to make a complicated circuit based on nanostructured objects then these nanowires will be some components of that overall circuit which is based on nanostructured materials.

So, you can ultimately make nanowire based devices using these nanowires as building blocks and you can precisely control these diameter and length during the synthesis. You can control their chemical composition and the diameter and length as I said and you can also add electrons or wholes.

You can dope some other elements and change the electronic properties, so the nano wires can be tuned based on certain doping or by change in chemical composition. Their electronic properties can also be modified by changing the diameter are the length of the nano tube the of the nano wire. So, you can think of the future devices will be based on nanowires because they will be acting as the interconnect between compliments. So, you have like a standard electronic device has not capacitors resistors all connected with some copper wiring on PCB boards that is the old electronics. The model of the future electronics will have component, which are connected through nano wires, so that is the future of devices based on nanowires.

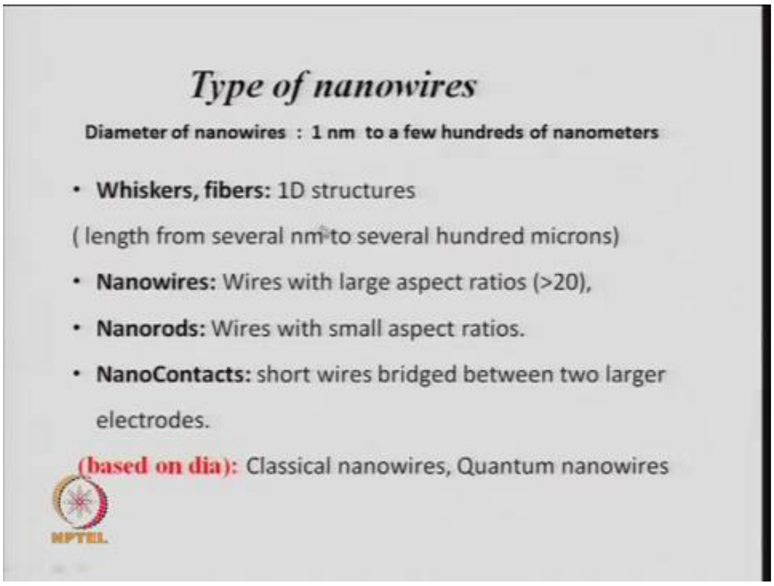
(Refer Slide Time: 11:28)



The applications of such devices and such nano wire are important in the field of photonics electronics and medicine they are also applicable in a wherever you have sized induced quantum confinement effect. Wherever such effects play a role, you can use nano wires because in nano wires, you will observe such size induced quantum confinement effects. Now, the high surface area to volume, which is the other property makes them potential candidates for various sensors because for sensors the wire or the surface of the wire has two sense the environment around it.

So, there are some molecules around say a particular wire which is going to sense it, so higher the surface area better it is for the incoming molecules to be sensed by the nano wire. So, a large surface area to volume will make them very important candidates for sensing applications.

(Refer Slide Time: 12:37)



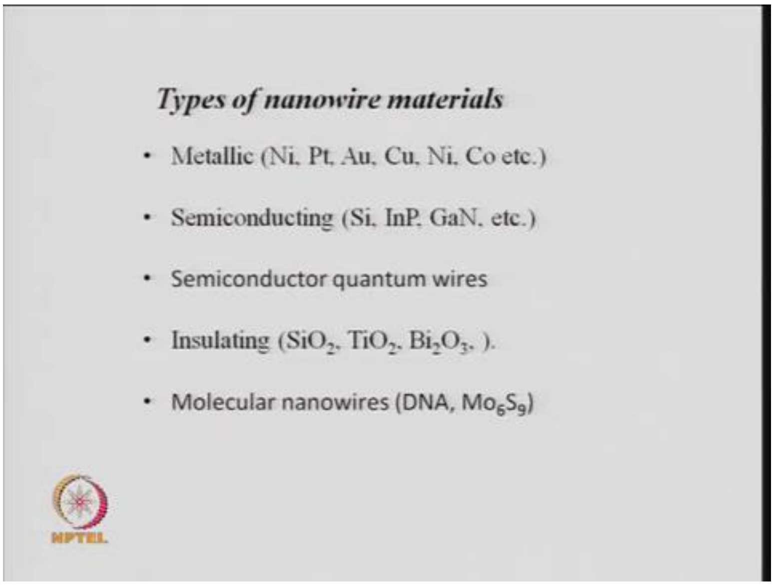
Now, you can have various names different names or classifications of nanowires by changing that thinking about various thicknesses of the nano wires. For example, you can have and nanowire of few nanometers 2 to 5 nano meters very thin nano wires or you can have very thick nano made wires with a diameter of 100 nanometers. So, depending on the thickness sometimes we call them whiskers are fibers which have several nanometer length to several 100 microns if you have a very high aspect ratio say greater than 20, then typically we call them as nano wires.

So, in the general nomenclature of nano wires, we can have several sub classification by various names we call them whiskers or fibers or nano rods or nano contacts typically nanowires is a term where you have very large aspect ratio. Then, the aspect ratio is very small then we call them nano rods, so in nano rod the thickness that is the diameter of the nanostructured and a one d nanostructured material.

The diameter will be high and the length will be small, so the length divided by the width or the diameter will be a small number whereas, for a nanowire the aspect ratio will be a very large. If you have short wires bridged between two larger wires or two larger electrode then we call them nano contacts. So, you can have several terms like this like nano wires nano rods and nano contacts and with meanings which are slightly varying depending mainly on the diameter or the aspect ratio of these nanostructured materials which are one dimensional in nature. Now, if the diameter is very large, then you move away from the quantum mechanics effects

Hence, if the diameter is very small we call them quantum nanowires because they will show quantum effects if the diameter is very large, then they will be classical nanowires because they will not be showing quantum effects. So, based on diameter alone you can make this classification between classical nano wires and quantum nano wires.

(Refer Slide Time: 15:18)



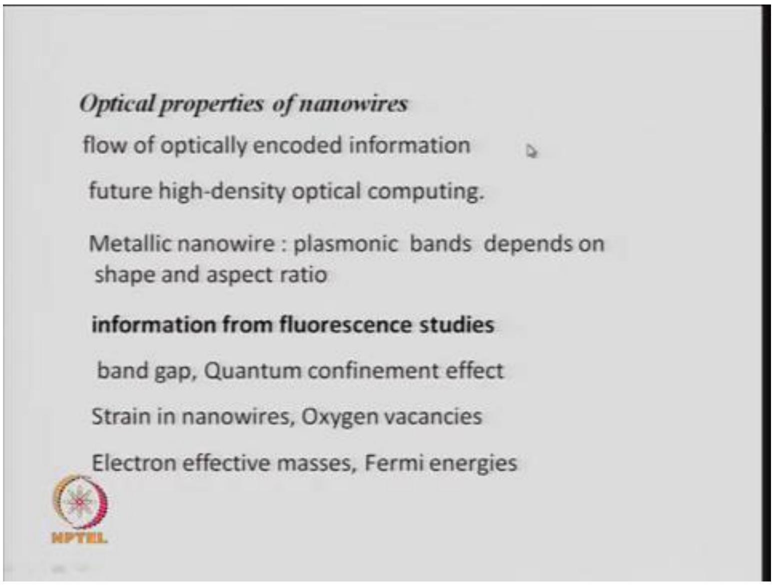
Now, based on materials what is the a type of material of this one dimensional nanostructure based on that you can have different names or this a different classifications based on type of material you have. So, you can have a nanowire of metals so pure nickel metal nanowire or pure platinum metal nanowire like that you can have metallic nanowires you can also have metallic alloy nanowires.

That means you have two metals mixed or alloyed together forming a one dimensional nanostructure that will be a alloy nanostructure a alloy nano wire. So, you can have different terms based on the material you can make semiconductor nano wires. For example, if you make a nanowire of silicon are gallium nitride or indium phosphide whichever has a band gap which is of the order of a few electron volts say 1, 2, 3, 4 electron volts 0.1, 2, 3 electron volts. Then, you call them semiconducting and nanowires typically silicon indium prostrate gallium nitride zinc oxide think sulfide there are many semiconducting materials and if you can draw them into wires you call them semiconducting nanowires.

Then, you can have semiconductor quantum wires if these wires have a dimension such that you see a quantum confinement effects. Then, you can make semiconductor quantum wires you can make insulating nanowires if you take materials whose band gap is very high say 4 electron volts, 5 electron volts, 6 electoral volts. If the band gap is very high of those semiconducting materials, then we call them insulators and if you make a wires of such materials, then those are called insulating wires. These are typically of silicon dioxide titanium dioxide bismuth oxide, these are some examples, but you can have many more oxides which have band gap very high beyond the range of semiconductors especially higher than 4, 5, 6 electron volts.

You can make nano wires of molecules, so molecular nano wires here these are all of solids which have extended structures their atomic structure extends in three dimensions. If you have molecules like d n a is a molecule or you have a cluster or molybdenum and sulfur at then these clusters join in one dimension, then you can have molecular wires. So, the difference between molecular wires and the metallic nanowires on semiconducting nanowires is that the metallic and semiconducting nanowires have an extended atomic structure. You know they extend in three dimensions that structure, whereas these molecules have small sizes and you link these molecules to make a one dimensional structure then you get and molecular nanowire.

(Refer Slide Time: 18:57)

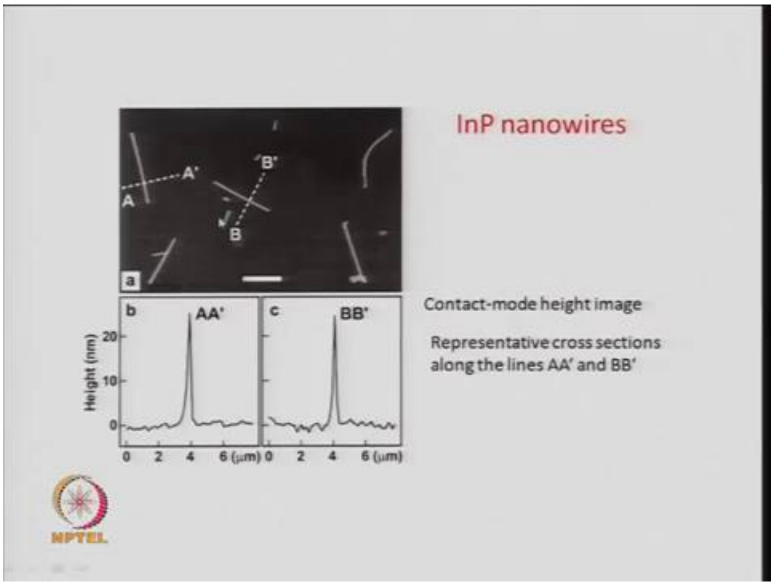


Now, what are the properties which are of a importance you can study electronic properties magnetic properties or optical properties. For example you can flow optically encoded information, so since this is like a nanowire if you have one end you receive information from the other end you can decode the information. If this is possible, then you can use it for the flow of optically encoded information you can use them in high density optical computing. The principal is same you have optical information coming in on one side of this nanowire and the optical information is decoded at the other end of the nanowire.

You can use metallic nanowires because metals nanostructures or metal show plasmonic ranks plasmonic bands are basically due to oscillations of a conduction electrons and these are quantized. So, this quantized oscillations or the conduction electrons is considered as a plasmon. These plasmonic bands are present in metallic nanowires and these plasmonic bands can be changed or modulated based on the shape and aspect ratio are these metallic nano wires. So, this is a very important application because by modulating the size and shape and the aspect ratio of the metallic nanowire you can modulate the plasmonic bands.

Hence, it can participate in passing information or many other applications, now you can do a lot of fluorescence studies by which you can get information about the optical characteristics of the nano wire. For example, you can if you do fluorescence or photoluminescence measurements on these nanowires you can find out that band gap, you can find out about the quantum confinement effect about the strain in the nano wires about oxygen vacancies. You can also get information on the effective masses of the electron and the Fermi energies, so many such characterization is possible by the optical characterization of nano wires.

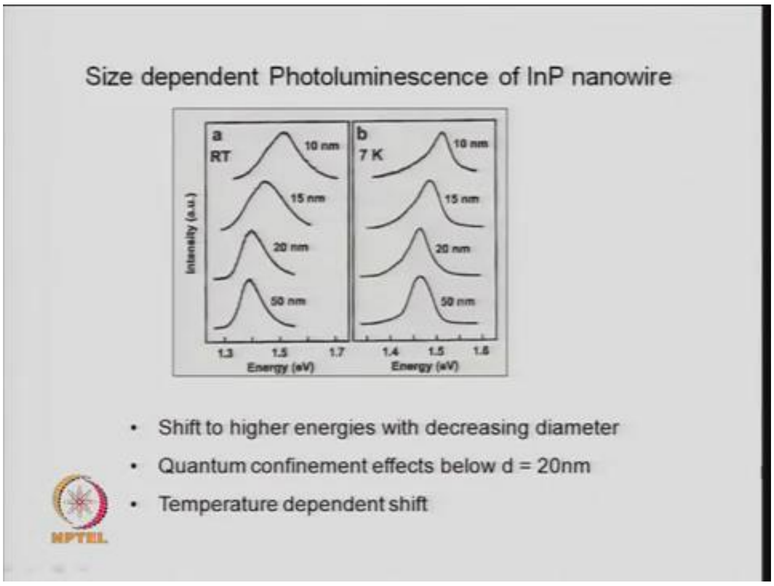
(Refer Slide Time: 21:34)



Now, this is an example of an indium phosphide, which is a semiconductor nanowire and indium these are the nanowires this is an electron micrograph of nano wires. Now, if you measure across this diameter, so if you move from point a to point a prime along the diameter since there is no material here the nano wire is only here. So, initially you do not see anything and then because the nanowire will have some height, so your what your measuring is using an AFM and this is called the contact mode AFM and in the contact mode AFM as you move from the point a to point a prime. Then initially you do not see anything because there is no nano wire there, then when you hit this part of the nano wire, then you start measuring the height of the nano wire.

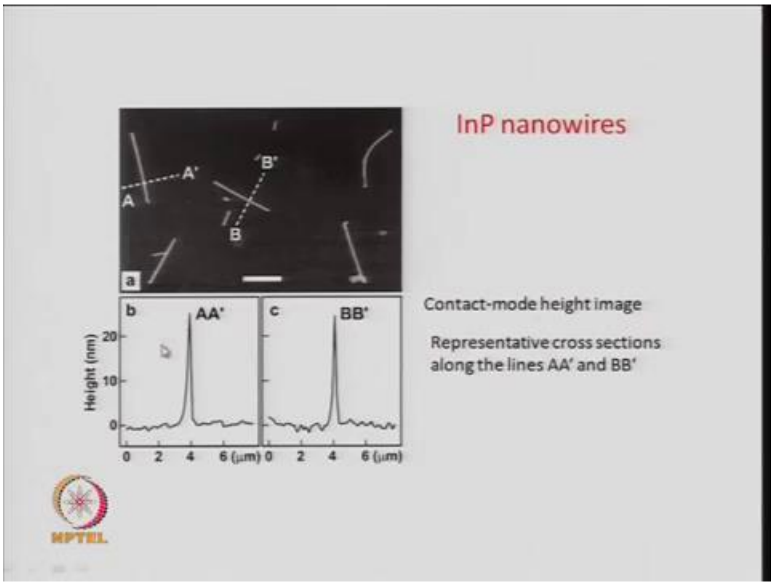
Then, again you cross the nano wire then the in the height goes down, so by this contact mode AFM, you can measure the height of this nanowire which gives you an idea of the thickness of the nano wire. Similarly, if you go across B to B prime, you see the similar plot, so you can see that the height of the nano the nano wire is around 20 to 25 nanometers in thickness.

(Refer Slide Time: 23:12)



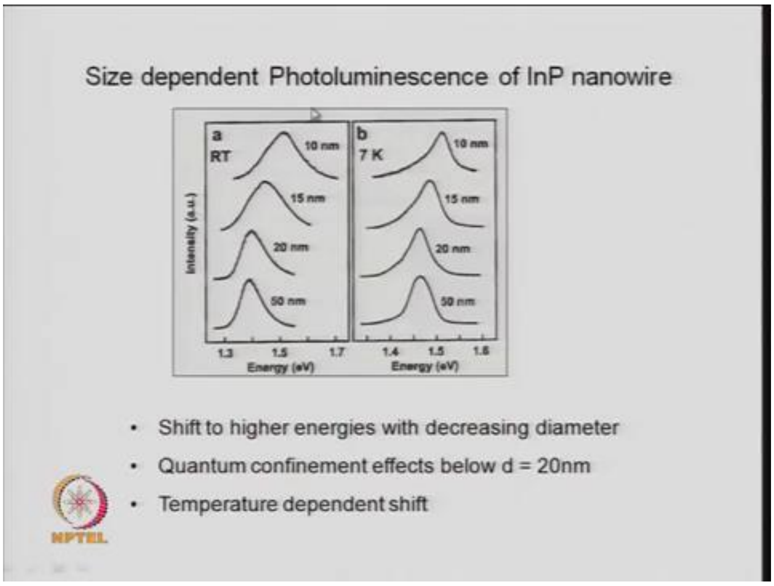
So, similarly you can study optical properties which are dependent on size.

(Refer Slide Time: 23:22)



So, either you directly you can measure the size using what is called the z movement of the AFM or your measuring basically the z the direction which is also the height using a AFM.

(Refer Slide Time: 23:37)

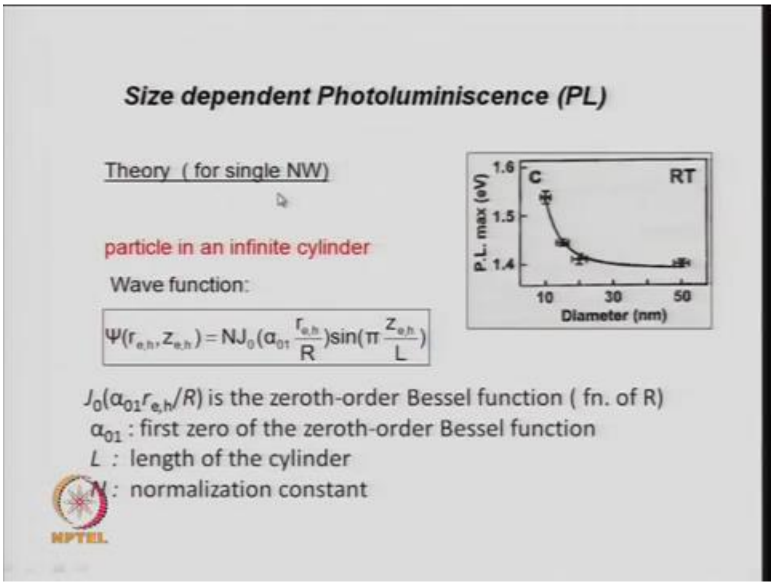


You can study optical properties also to know the size because the size depends on at the photoluminescence depends on this size. It is shown here that if you take a nano wire which is 50 nanometers thick or 20 nanometers thick and you decrease the diameter of the wire from 50, 20, 15 to 10 nanometers. You can see that initially there is no shift of the position of this peak, so this is coming around 1.4 electron volts slightly less than 1.4 electron volts. If you go below a certain diameter say you go to 15 nanometer, 10 nanometer you are reaching a region where you now start seeing quantum confinement effects and because of that when the diameters is very small, you see a shift of the peak position.

Now, the peak has shifted from this position to now it is come to more than 1.4, it is now 1.45 or something. You decrease the diameter to ten nanometers and the peak has further shifted to more than 1.5 electron volts. Now, this is at room temperature you can see the shift act small size, similarly if you go at low temperatures this is at 7 Kelvin, you again see this shift in the size and this is at a different energy. So, both the temperature at room temperature the maxima the PL maximum is somewhere and it shifts with decrease in the diameter at low temperature at 7 Kelvin the maximum comes at some other energy.

So, there is a shift in the maximum with temperature and there is a shift because of the size also. So, the shift to higher energies with decreasing diameter and these shifts are seeing a due to quantum confinement effects and it can been seen in nanowires with diameter which is below 20 nanometers. The temperature dependent shift also you can measure if you do a study at various temperatures you will see the PL maximum for the 50 nanometer wire was around 1.4 electron volt. If you do the same measurement at 7 Kelvin for the 50 nanometer wire, the energy of the of the PL maximum is around 1.46 electron volts. So, it shifts just because you have changed the temperature from room temperature to much low temperature at 7 Kelvin. Now why does this size dependent photoluminescence occur, what is the relationship between this energy and the size.

(Refer Slide Time: 26:46)

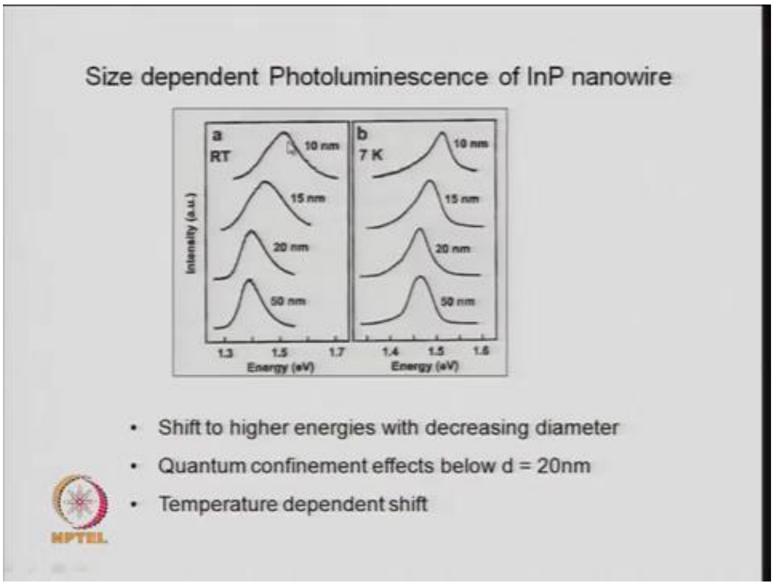


So, for that there is theory for single nano wires which has been developed, now it has been developed on the ideas of what we know as a particle in a box problem. That means in quantum mechanics you have must have studied basic quantum chemistry or quantum mechanics that when you have an electron, which is not allowed to move beyond a certain distance, it is confined within certain region.

That means it has a very high potential energy outside that region, so the electron will never go there, it will always be staying where the potential is much lower. So, you confine it now if you confine it in a box means along x y z along all three directions, you can only move to a certain distance. So, that is a particle in a box and for that what is a wave function of the electron is known and has been solved. Now, in this case this is not a particle in the box, but it is slightly modified problem it is particle in a cylinder. This cylinder one of the length is infinite, you consider a very long length for the cylinder infinite may be a long length, so here that length we keep as l.

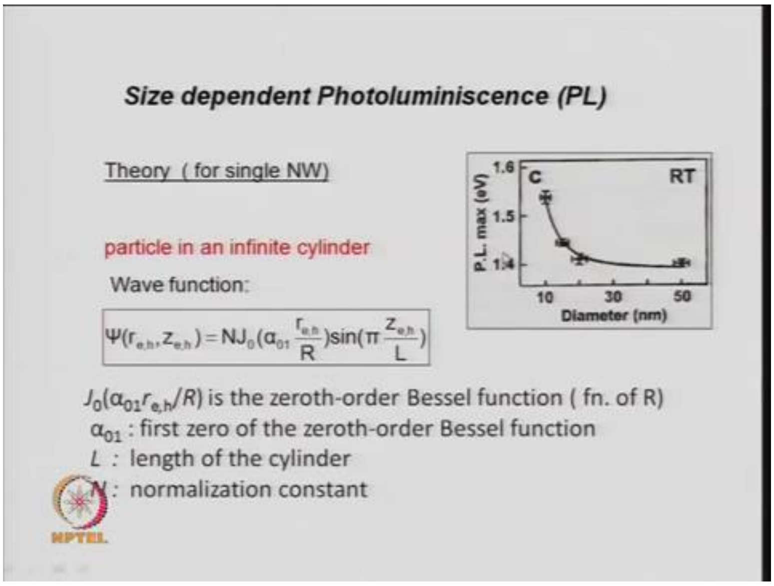
So, capital l is a very long length for the cylinder in which the electron is confined it is confined basically in two dimensions in the third dimension which is the longer direction it is considered to be in finite. Now, for such a particle in a infinite cylinder, the function is comes out like this where it is given as basal function where j is a basal function. It is a function of these parameters a and what is important to note is that this basal function is depending on r which is like the radius of your it is a function of the radius or the size. Now, you can see that the pl maximum will depend on this wave function and here what is shown is what we saw in a previous slide given in a different manner that the PL maximum, which comes at certain electron volts decreases as the diameter increases.

(Refer Slide Time: 29:17)



So, if you go back that PL maximum comes at some electron volts it decreases when you increase the size.

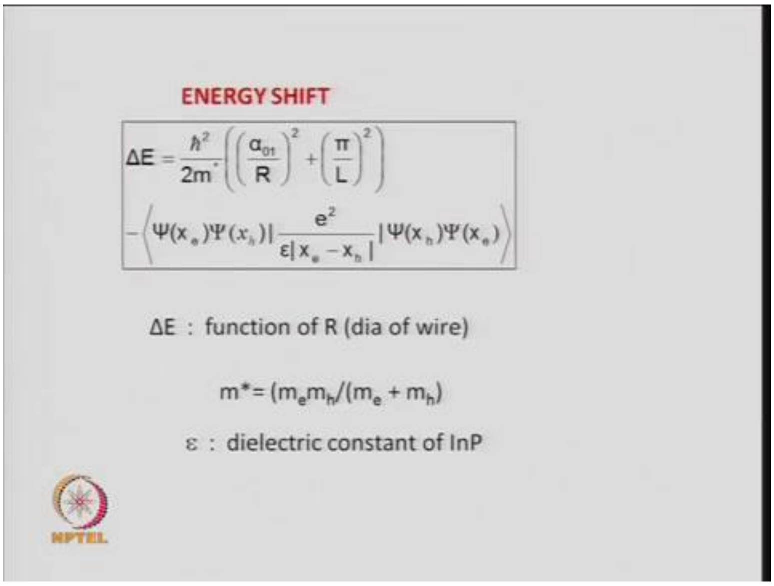
(Refer Slide Time: 29:30)



The same thing is plotted here instead of showing the maxima there you plot the energy on the y axis and you can see that the value of the energy decreases as the size of the diameter increases. Now, this same thing is being obtained actually from understanding of this wave function where the size is very important. So, these wave function of whether you can do it for an electron or you can do it for a hole either of that the equation is same and where l is the length of the cylinder.

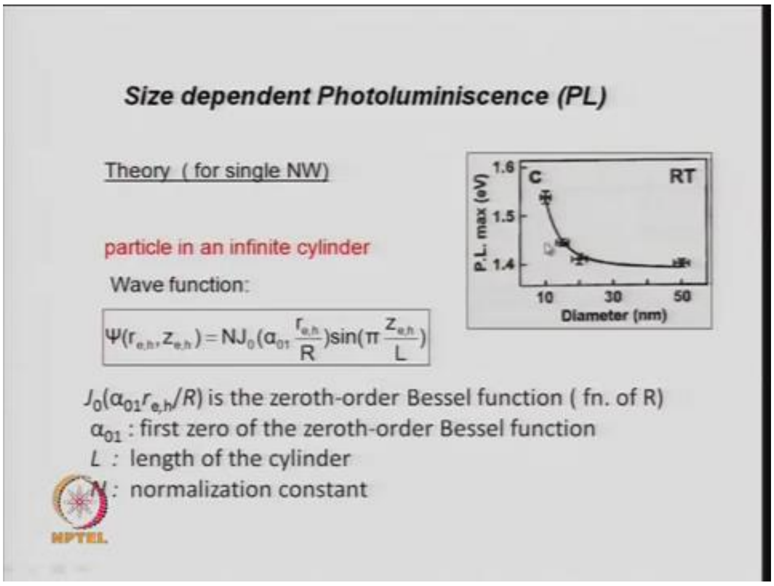
You assume it a wave much larger then been other two axis and n is a normalization constant and j is your basal function which is a function of r which is a inverse function of r. So, this is the function, but what is more important for us is to explain the energy shift, why is the maximum in the energy the PL maximum shifting as a function of size.

(Refer Slide Time: 30:43)



So, for that you can derive from the equation of the wave function you can derive this equation where delta e is the change in energy is the energy shift and that comes out like this term. There are these integrals and this is the Dirac notation for the wave function the epsilon is the dielectric constant of the material, which is indium phosphide and m star is called the effective mass or the reduced mass, which is given by this equation. What you ultimately find is that the shift is energy is a function of the diameter of the wire.

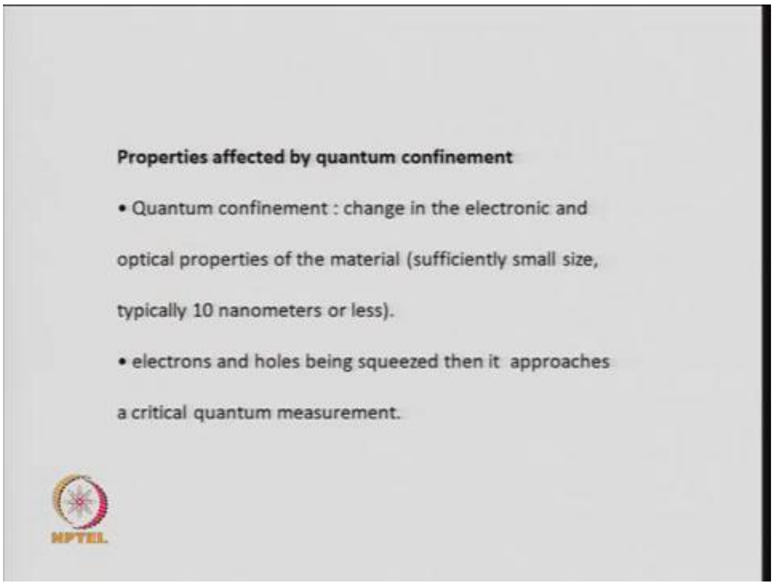
(Refer Slide Time: 31:29)



So, from that you can explain this it this block that how the energy shifts as a function of the diameter theoretically you can solve this equation and get the parallel what you see experimentally by doing aphotoluminescence experiment.

Either way photoluminescence or fluorescence is the same thing some people especially in physics use that term photoluminescence, whereas in chemistry we use that term as fluorescence.

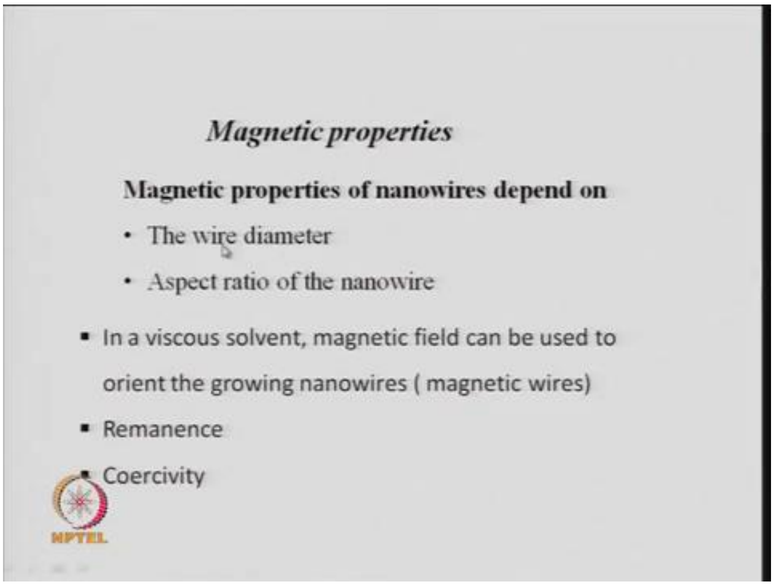
(Refer Slide Time: 32:08)



Now, the properties affected by quantum confinement like we saw already the optical property is affected by quantum confinement, the a maximum of the a absorption in the PL is a the maximum of the PL. I beg your pardon, it is the PL max maximum is shifting with size that is by quantum confinement. Now, you can also see a shift in the electronic properties apart from the optical properties. Typically, where the dimension is 10 nanometers or less that means the diameter is typically 10 nanometers or less there you will start seeing such quantum effects. Now, what is happening is because the size is small the electrons and holes are being squeezed and when it is being squeezed then all these effects will start showing up.

Then, you will see these critical quantum effects or measurements in experiments because the electrons and holes are being squeezed in a very small region of space or we are saying that they are being confined. Now, other than electronic the optical properties electronic properties and we will discuss some more electronic properties soon. If you want to make a wire obviously its properties will be different than normal Fe 3 O 4 which you know.

(Refer Slide Time: 33:32)



The magnetic properties of such materials are also affected, now if you take a material which is magnetic in nature and then you make and nanowire obviously it will have different magnetic properties. So, what does the magnetic properties depend on if you make wire or a nanowire of a magnetic material like iron oxide Fe 3 O 4 is the magnetic material. Properties of the nano wires depend on the wire diameter and the aspect ratio of the wire, so how small is the diameter of the wire and what is the aspect ratio the ratio between the length and diameter is the aspect ratio. So, these two things will control the magnetic properties of the nanowires now magnetic nanowires can be made by a simple technique.

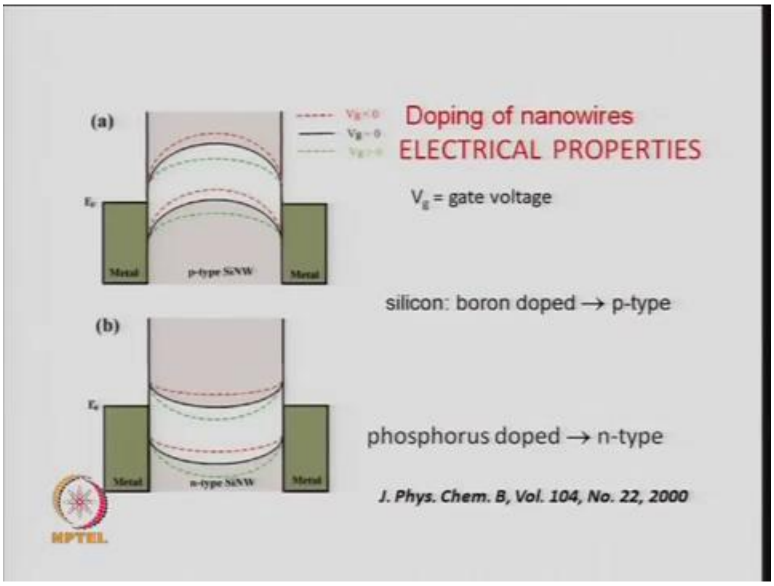
Then, the nano wires are growing in a viscous solvent if you apply a nano magnetic field then you can orient the growing nano wires. So, it is possible to orient nano wires in one direction if you apply a magnetic field a suitably in a viscous solvent. So, this is an interesting way of getting aligned nano wires, so you will get say thousands of nanowires all aligned in one direction because you are applying a magnetic field when the nano wire is growing.

So, you will you can get very nice aligned magnetic nanowires and the properties which you will see the properties where you will see this effect of the wire diameter or the aspect ratio are what has called the reminisce. If you measure the magnetization as a function of magnetic field, then when you bring the field back to 0 in a magnetic material you will still have some magnetization that is called the remanence and this remanence will depend on the wire diameter and aspect ratio. That is one thing the remanence will change with this size of the diameter of the wire, the other thing which will change is what is called the coercivity.

So, what is coercivity when you apply a magnetic field and start measuring the magnetization the magnetization first increases and then goes to a saturation value you keep increasing the field the magnetization keeps increasing. Then, once you start decreasing the magnetic field and you bring the magnetic field to 0. Then, the magnetization starts decreasing, but it does not go to 0, it will have some finite magnetization then you have to apply a magnetic field in the opposite direction to bring the magnetization to 0.

Finally, when the magnetization becomes 0 at a very large negative field, then that field is called the coercive field or the coercivity of that material and this coercive field will change as you change the diameter or the aspect ratio of the nanowires. Now, that is what we discussed about magnetic properties, how these two important properties the remanence and the coercive field with change on the diameter of the magnetic nano wires.

(Refer Slide Time: 37:21)



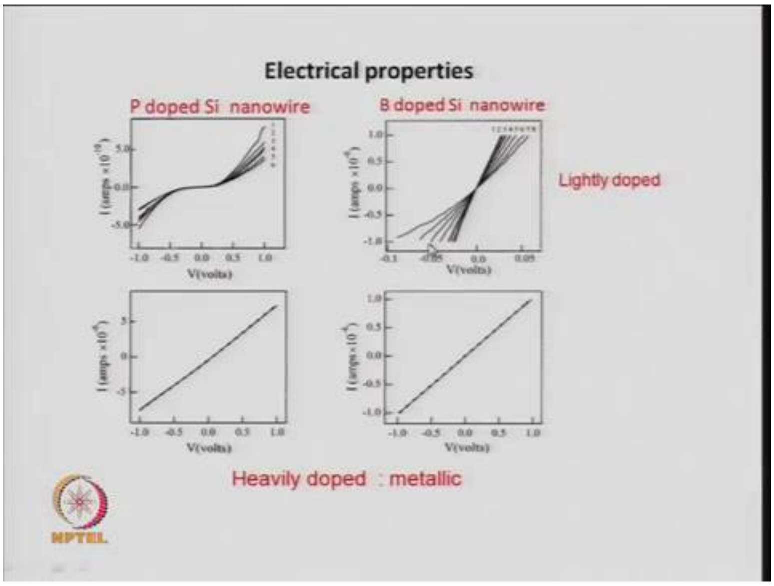
Coming to electrical properties, these are example of a nanowire which is a doped nanowire so this is a silicon in which boron is doped. So, you know in any semiconductor if you dope boron and silicon, then you get a p type semiconductor, but this is not an ordinary semiconductor it is a nano wire. So, it is a y type silicon nanowire and it is attached to two metals on either side, so you have a p type nanowire silicon nanowire between two metal electrodes and the Fermi level is shown here for the metal.

If in the nano wire the Fermi level is like this now what happens when you apply a gate voltage when you apply when the gate voltage is 0, the Fermi level is a here you know somewhere there when the gate voltage is 0. If you look at the red curve that is when the gate voltage is less, then you will get a maximum which is much higher, so this maximum in the Fermi level means that you will have higher electrical conductivity. So, by doping the nanowire you can get much higher conductivity in the p type doped nanowires the connectivity can be increased by having a negative gate voltage.

However, if you have a n type nanowire between the two metals, then by applying a high gate voltage that is a positive gate voltage. You will have the minimum in conductivity because as you see the Fermi level is bending and you have the minimum in the Fermi level is somewhere here.

So, by having a positive gate voltage in a n type semiconductor you can have the minimum in the Fermi level. So, you have a minimum conductivity at for a n type semiconductor, so you can control the electrical properties of nanowires by doping the nanowires like in silicon where boron is doped or phosphorous is doped. So, you get p type and n type semiconducting nanowires and you can control the connectivity by applying a suitable gate voltage.

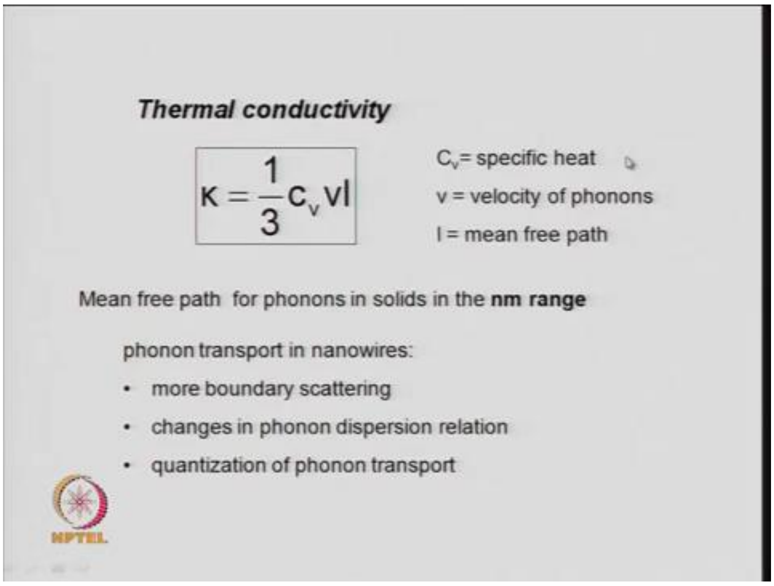
(Refer Slide Time: 40:06)



Now, further if you look at the amount of doping if you have lightly doped samples for example, in the top two I guess you have small amount of boron doped silicon are phosphorus doped silicon a very lightly doped. That means the concentration of the dopant is not very high, in that case you see a particular behavior of the current versus voltage so the current increases as you increase the voltage the current decreases as you decrease the word age this is understandable. This is not linear, you see this plot is not linear and this linearity is found in these doped a semiconducting wires only when it is heavily doped and then it gives you this linear characteristic which is typical of a metallic property.

So, heavily doped nano wires can give rise to metallic properties and so you can vary the nature of the property from semiconducting to metallic by suitable amount of doping a in these a silicon nano wires. Now, coming to that was electrical conductivity, so these electrical properties, which we discussed.

(Refer Slide Time: 41:40)



Now, if we compare the thermal conductivity where basically it is a flow of heat, now thermal conductivity is given by this equation it is related to specific heat it is related to velocity of phonons. So, what are phonons phonon are quantized lattice vibrations and if the velocity of those phonons v, then the thermal conductivity is directly proportional to the velocity of the phonons. Now the l is the mean free path the which is the a average a distance that a phone on travels before it collides. So, this is the average the mean free path for phonons in solids is typically few nanometers, this is important.

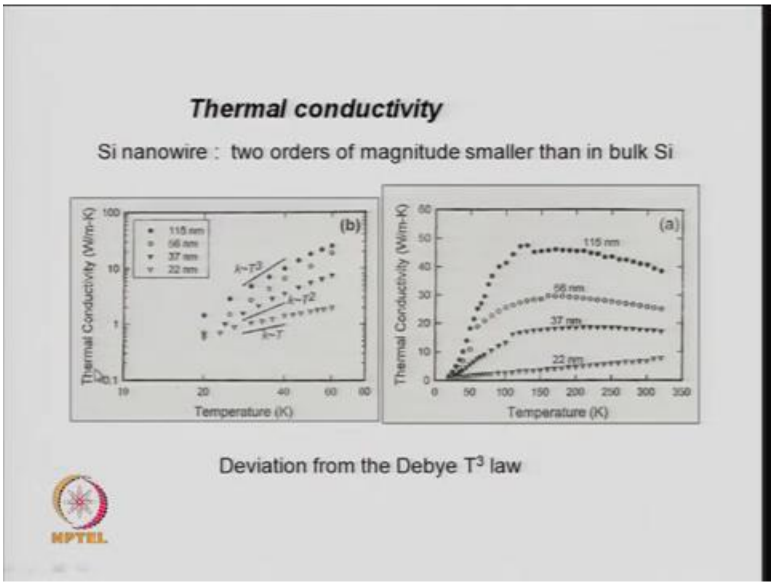
Now, then you have phonon transport that means the movement of phonons is basically the flow of heat. So, the if the phonons move very fast if v is high, then the flow of heat is very high that means thermal conductivity is very high. So, phonon transport in nanowires results because of the small dimension of the nanowires because the cross sectional area is small in these nanowires.

So, certain things will happen which are not happening in normal materials, so since we have reduced the dimension along two axis certain changes will occur in the thermal conductivity in the movement of the phonons. So, what are these changes the phonon transport in nanowires leads to more boundary scattering, because the nano wire is very narrow. So, there is more scattering on the phonons with the boundaries, then this is result in the variation of what we call as the phonon dispersion curve. Now, the phonon dispersion is basically explained as a function of energy of the phonon as a function of wave vector.

So, wave vector is defined as inverse of the wave length, now there are diagrams or figures which you can study where phonon dispersion curves are given phonon dispersion relations are given which is basically e versus k plot. Here, small k is the wave vector not this k this is this should be thermal conductivity this is kapa in most books you will read this as kapa. Here, what we are talking about in phonon dispersion is the relation between energy versus small k, which is given by inverse of the wavelength. The magnitude of the wave vector is given by 2 pi by lambda and these changes in the phonon dispersion relation for a bulk material and the nanowire is important.

That will control the thermal conductivity, then the quantization of the phonon transport will be affected. So, the phonon transport ultimately will be different in nanowires compared to bulk material you have the same say. So, you your studying any glass and your studying the thermal conductivity of glass, now if you make a glass fiber of cross section which is of say 10 nanometers. Then, there will be a certain difference in the thermal conductivity of the glass wire compared to a glass sheet.

(Refer Slide Time: 45:46)



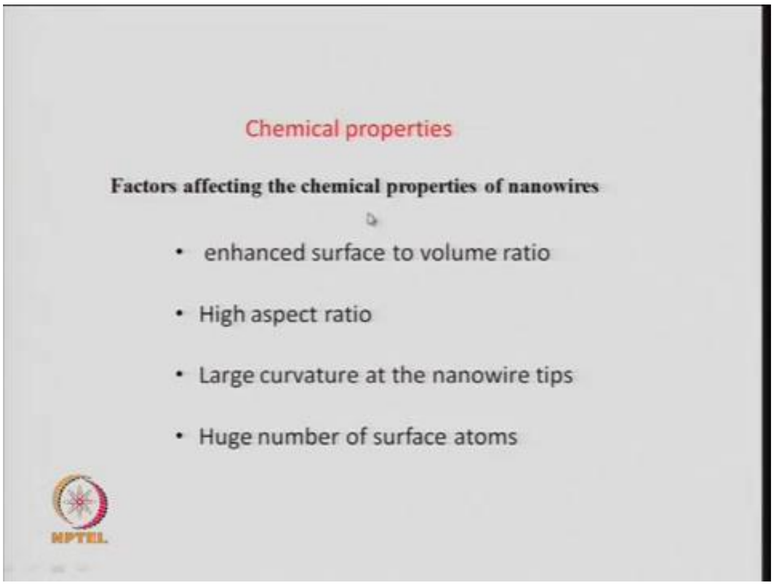
Now, that can be seen here for example, this is a plot of the thermal conductivity, which is given by watts per meter Kelvin and it is plotted with temperature. So, the thermal conductivity for different nano wires the nano wires have different diameters. So, you have 22 nanometer diameter 37 nanometer diameter up to 115 nanometer diameter and you have got various four plots for these four cases you see that the nanowire which has high diameters say 115 nanometers. These are these closed circles which you see and the one which has 20 nanometer is this a triangle upside down triangle which is open and that has a plot like this.

Now, if you look at it carefully this plot the thermal conductivity is kind proportional to the temperature it is quite linear which can be seen even clearer. Here, you are plotting from 10 Kelvin to 80 Kelvin this temperature scale is from 10 Kelvin to 80 Kelvin which is a very small region of temperature 10, 80 Kelvin is somewhere here. So, only this part ten to eighty is this whole figure, whereas if you show the entire plot up till say 350 Kelvin. Then, the whole curve looks like this and in this you see the 22 nanometer is nearly linear with temperature and that is what is written that is the thermal conductivity is proportional to t.

However, as you increase the diameter of the nanowires the shape changes drastically and at some sizes say around 37 or something k proportional to t square, but if it goes very high like the bulk diameter of around 100, 115, then k is proportional to t cube. So, from t to t cube is two orders of magnitude higher, so silicon nano wire, which is the diameter is in nanometer sized is two orders of magnitude smaller than the thermal conductivity of bulk silicon. The bulk silicon means that the diameter is of the order of maybe 500 nanometers 600 nanometers or even microns.

So, that will be always the like behave like the 115 nanometers because this is where you have now lost those quantum effects and you are behaving the material is behaving like a classical are a normal material. So, thermal conductivity is much smaller in nanowires compared to bulk material now, so we discussed electronic properties optical properties magnetic properties the thermal conductivity.

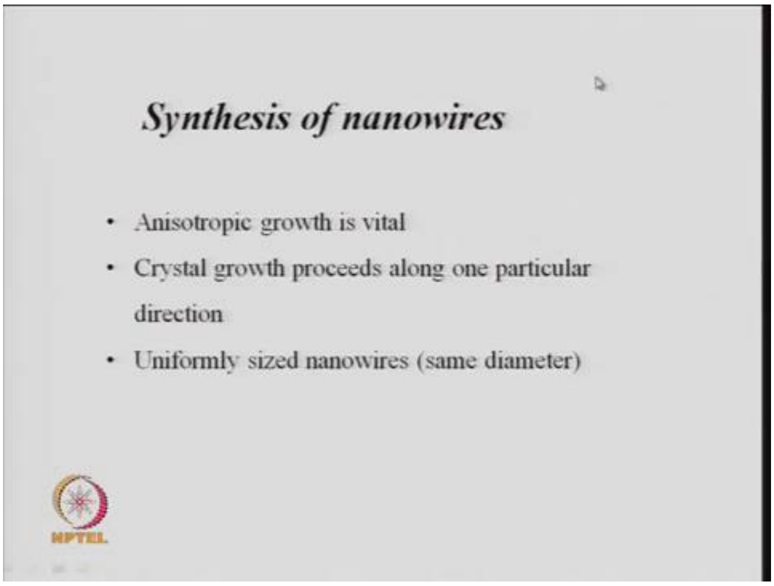
(Refer Slide Time: 49:16)



So, let us come to chemical properties, which are the properties which are affected and why are they affected. Now, because the surface to volume ratio in nanowires is very high the surface will be very reactive in these materials, which have high aspect ratio. Apart from that, when there is a large curvature at the nano wire tips, the nano wire at the end of the wire it will be having the courage it at the tip.

The reactivity again will be very high, this was this is similar to what we discussed in carbon nanotubes where at the end of the carbon nano tube wires, the reactivity is much higher. So, in the chemically the nanowires will be highly reactive because they are very high surface area and if it has a high surface area there will be large number of atoms on the surface. If there are a large number atoms, on the more the atoms on the surface more will be the reactivity and so chemically such nano wires will be very reactive.

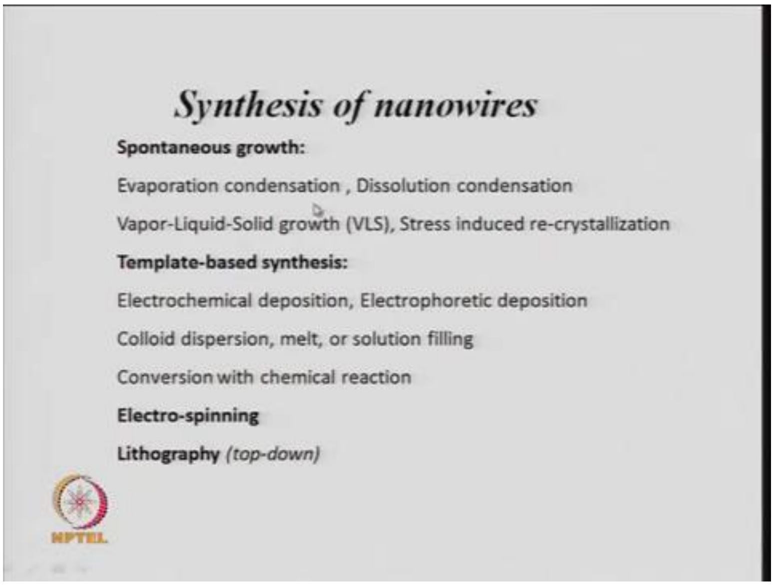
(Refer Slide Time: 50:23)



Now, let us come to synthesis of nanowires the most important thing in nanowires is to maintain anisotropic group you do not want growth in all directions to be happening at the same rate the nanowire should grow fast in one direction. It a should grow in one direction and it should have very small size in the other two direction, so such a unequal growth is what is called anisotropic growth is important for the generation for nano wires. Now, crystal growth when crystallization takes place you have to control the crystallization such that ultimately it proceeds only along one particular direction.

Then, you have to control the uniformity of the size of the nanometer because you may be growing thousands of millions of nano wires, now how to maintain that one nanowire and the second nano wire. The third nano wire has the same a nearly same diameter, then only you will get uniform diameter or homogeneous nanowires and that is important for applications.

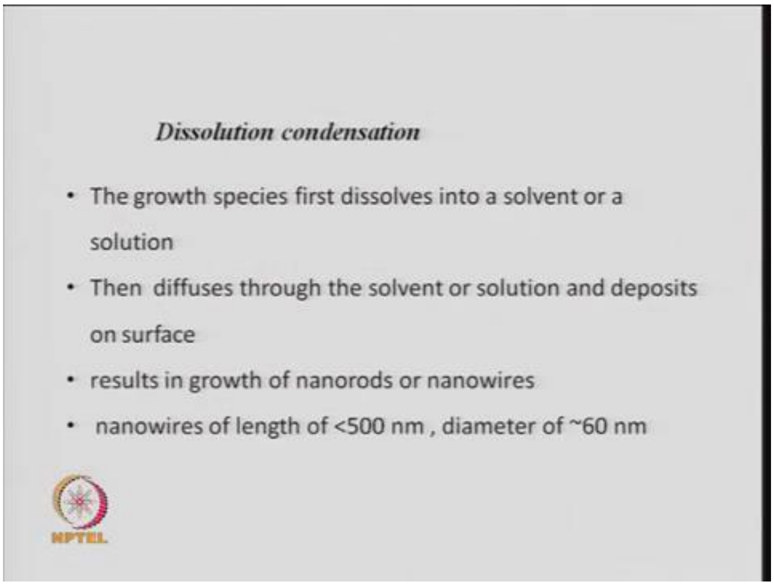
(Refer Slide Time: 51:46)



So, you evaporate and then condense to make nanowires then dissolution and condensation so one is from the vapor state you condense another is from solution you condense. The third is what is the vapor liquid solid growth, which we discussed a lot when we discussed carbon nanotubes and other general methods of synthesis of anisotropic nanostructures it was discussed in some earlier module. Now, you can also have template based synthesis and several methods are there electrochemical deposition colloidal dispersions melt growth etcetera.

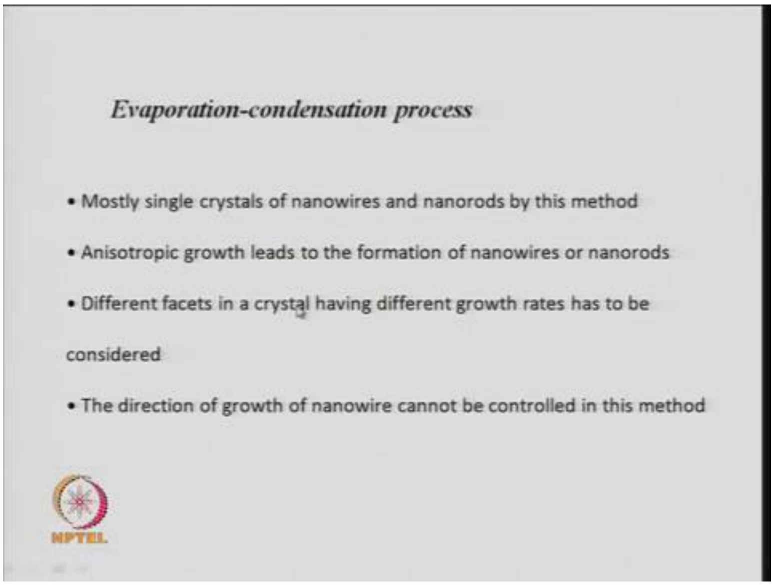
Then, there is lot of electro spinning of fiber lot of textile people work on electron spinning when they make fibers for textiles and of course you can make fibers a nanowires using lithography which is the top down approach. So, using lithography you can get very precise nano wires, but of course the technique is very technologically advanced. So, it is an expensive technique to make nanowires using lithographic techniques what we will discusses the growth using this chemical processes which are much cheaper and so we will just discuss these three processes.

(Refer Slide Time: 53:17)



In the dissolution condensation process, the growth species say you want to grow some silicon nanowire then that is the growth species that you have to dissolve in a solvent or a solution. So, once you dissolve it then that diffuses through the solvent and deposits on a surface so first it has to dissolve and then it has to there may be a gradient a gradient of a temperature or a gradient of a chemical potential or something. So, when it diffuses due to the gradient through the solvent and it deposit on a particular surface. Now, this is the dissolution condensation method it can give rise to nano rods or nano wires and typically you get small nano wires out of them like 500 nanometers or less and the diameter.

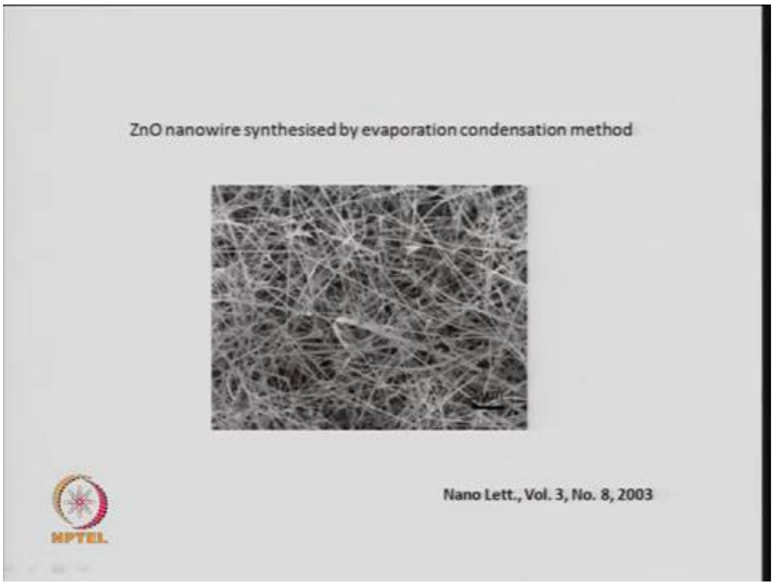
(Refer Slide Time: 54:26)



When you do evaporation condensation process mostly single crystals of nano wires and nano rods are synthesized by this matter. So, from the term evaporation and condensation you can understand that you have to first evaporate suppose you're not going to make silicon nano wires Then, you take silicon either powder on bit any in that or something and then you evaporate that silicon and then slowly condense it on a substrate. So, that is the procedure and that leads to anisotropic growth to from nano wires or nano rods and you have to kind of control the different facets of the growing nano crystalline phase.

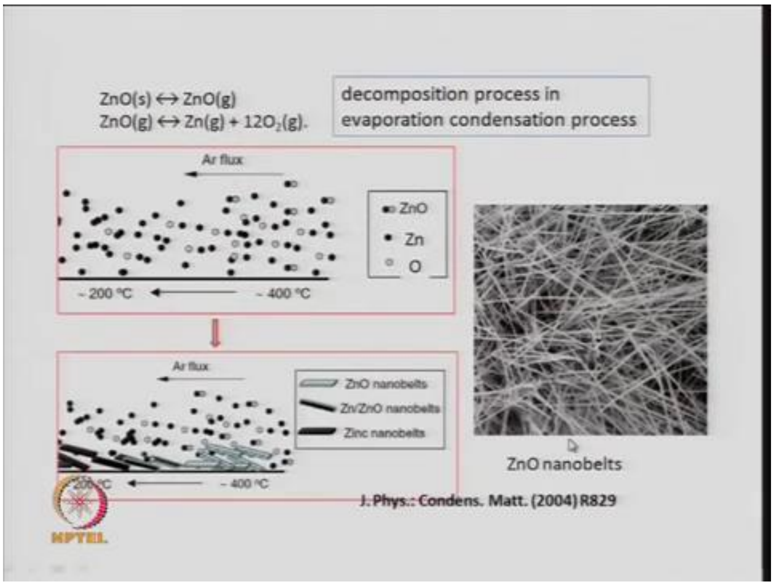
If you want a particular facet to be facing the end so depending on if you want a very particular plane of the crystalline lattice to be exposed. Then, the growth conditions have to be controlled in a certain manner such that you get single crystalline nanowires with one particular specific plane h k l plane exposed. Now, the direction of a growth of nanowire is normally not easy to control in this method because they are evaporating and condensing, so that is a drawback of this method where you cannot control the direction of growth of the nanowire.

(Refer Slide Time: 55:57)



Now, this is a TEM picture to show you the growth of zinc oxide nano wire zinc oxide is a semiconductor. You see you have large bunch of nano wires, but they are not aligned along around one direction which we were we just mentioned that the direction of growth of nano wire cannot be controlled. You make a large is like a forest of nanowires made by evaporation condensation method by which has been published in a journal which is called nano letters in 2003.

(Refer Slide Time: 56:34)



Now, this is another example of the decomposition process in evaporation condensation, so you this is zinc oxide, so zinc oxide takes solid zinc oxide and you make it into gas, so you evaporate.