

**Surface Engineering of Nanomaterials**  
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**Lecture - 09**  
**Chemical Modifications**

Hello, in our next lecture we are going to discuss about the chemical modifications of the surface of that particular material. So, in our last lecture we have discussed about the physical modifications of our material surface. Now we are going to discuss on the chemical; that means, we are trying do certain kind of chemical reactions with the surface of that materials, so that we can make certain kind of changing into the surface chemistry or may be rather we can make certain kind of coatings or maybe some kind of layers onto the material surface.

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**Chemical modification:**

- ❖ Chemical modification techniques chemically alter the surface of a material without significantly affecting its bulk properties.
- ❖ For metals, many chemical modification techniques use acetylene, nitrogen or oxygen to reduce corrosion, wear as well as to increase hardness of the material.
- ❖ Some polymers are also modified chemically to enhance hydrophilicity or hydrophobicity of the base materials.
- ❖ Recent advances in polymer surface modifications have been promoted in the packaging industry and other applications.
- ❖ Recently, various chemical techniques are used to modify materials like metal, ceramic, polymers, alloys, composites etc.

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So, first initially you have to know, that what is the chemical modification means? Chemical modification techniques chemically alter the surface of a material without significantly affecting its bulk properties. So, that there should be any reactions on the surface of that particular material, but it will not change the bulk properties means overall properties of that particular material, but still there will be some kind of chemical reactions in between them. For metals many chemical modification techniques use acetylene, nitrogen or oxygen to reduce corrossions, wear as well as to increase the

hardness of the material. So, these all are the requirements why we are going to do the chemical modification. Some polymers are also modified chemically enhance the hydrophilicity or the hydrophobicity of the base materials. So, as I have already told in my last lecture or maybe in my previous lecture that we can change the material characteristics also, if some materials possesses hydrophilicity we can change into some hydrophobicity or maybe the vice versa.

Recent advances in polymer surface modifications have been promoted in the packing industry and other applications, maximum case we are using for the packing applications, barrier layer applications then your biotechnology and medical applications or maybe biomedical applications there are lots of work is going on.

Recently various chemical techniques are used to modify materials like metal, ceramic, polymers, alloys and composites. What are the importances of the chemical modifications? why we are going to do the chemical modifications then first is that chemical treatment has been used in industry to treat large objects that would be difficult to treat by other commonly used industrial techniques, simply may be I am dipping my material into some solvent maybe the size of that particular material will be bigger or maybe the (Refer Time: 02:52) but still it can be easily done, but if want to do it by the physical means, I covering of that whole area maybe will be difficult.

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**Importance of the chemical modifications:**

- ❖ Chemical treatment has been used in industry to treat large objects that would be difficult to treat by other commonly used industrial techniques.
- ❖ Chemical etchants are used to convert smooth hydrophobic polymer surfaces to rough hydrophilic surfaces by dissolution of amorphous regions and surface oxidation.
- ❖ Enhancement in electrical, optical, mechanical, and tribological properties of the solid material by chemical modification.
- ❖ Recently, Chemical modifications are the major key in the devolvement of microelectronics, biotechnology, automobile industries etc.

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Chemical etchants are used to convert smooth hydrophobic polymer surface to rough hydrophilic surface by dissolutions of amorphous regions and the surface oxidation. So, some kind of chemical reaction will be taking place by which some atoms or molecules can come out or maybe that surface can be works totally opposite, previously it was acting as a hydrophobic, now it is acting as a hydrophilic, so by using that etchants we can do it easily.

Enhancement in electrical, optical, mechanical and tribological properties of the solid materials by chemical modification and last one is that recently chemical modifications are the major key in the development of microelectronics, biotechnology, automobile industries. So, these all are the different zones where we are using these chemical modifications. What are those chemical modifications or maybe the types of chemical modification? Changing the surface chemistry;

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**Types of chemical modification:**

***Changing the Surface Chemistry:***

Surface chemistry improves the surface characteristic through:

- Chemical or electrochemical conversion
- Thermo-chemical diffusion
- Pack cementation diffusion
- Ion implantation
- Combination of laser beam melting and alloying
- Cluster beam deposition

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So, surface chemistry improves the surface characteristics through. So, there are several methods which we can adopt depending upon our requirement, suppose I need some materials maybe be which can react with these materials, which cannot be in maybe can be into this materials. So, depending upon the proper selections of the material, depending upon the proper choosing the methods of surface chemistry, you can do the several applications.


So, chemical or electrochemical conversions, thermo chemical diffusions, pack cementation diffusions, ion implantations, combination of laser beam melting and alloying and the cluster beam depositions. So, these all are the various types of methods by which we can do the surface chemistry.

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**Chemical or electrochemical conversion:**

**Chemical conversion:**

- A chemical manufacturing process in which chemical transformation takes place, i.e. the product differs chemically from the starting materials.
- In this process, a dilute solution of phosphoric acid and phosphate salts chemically reacts with the surface of the part being coated (iron, steel or aluminium) to form a layer of insoluble (crystalline phosphates)
- Example of chemical conversion:



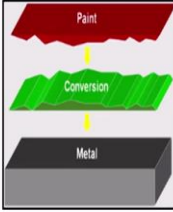
Chromate coating






Phosphate treatment

**Advantages:**

- Improves corrosion resistant
- Durability
- Electrical conductivity.



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So, what are those? First one is called the chemical or electrochemical conversions. So, a chemical manufacturing process in which chemical transformations take place; that means the product differs chemically from the starting materials. So, here you are having the best metals then you are putting certain kind of paint, when applying the paint maybe it is converting into some other materials which can react easily or maybe which can bond easily with your best metals, so that there will be some chemical modifications taking place.

In the process a dilute solution of phosphoric acid and phosphate salts chemically reacts with the surface of the part being coated iron, steel or aluminum to form a layer of insoluble crystalline phosphates. So, you are creating a layer in between your substrate and your coating. Example of chemical conversions: chromate coatings, phosphate treatments, what are the advantages improve corrosion resistant, durability and the electrical conductivity.

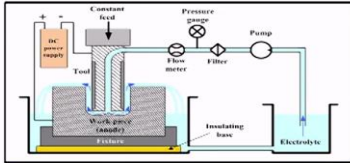
Then next slide we are going to discuss about the electrochemical conversions. So, from the name itself you can understand here we are adapting the same thing, we are putting

our materials into some common electrolyte then the chemical reactions will be taking place by which your material either maybe some ions or electrons can be taken out or maybe some ions or molecules can be deposited onto your material surface by the chemical reaction.

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**Electrochemical conversion:**

- It is based on the principle of electrolysis where tool act as cathode and work piece will act as anode.
- Low DC voltage enables the current to flow through the electrolyte with positively charged ions attracting the tool and the negatively charged ions attracting the work piece.
- Metal removal rate is faster at the area closer to the contact pieces due to high current.



**Properties of electrolyte:**

- It must possess high electrical conductivity.
- It should possess high Specific Heat.
- The viscosity must be as low as possible.
- It must be chemically stable and active.
- It should not be toxic and corrosive.

**Advantages:**

- Improvement in strength & temperature resistant.
- Produces complex shapes.

**Disadvantages:**

- Requires high power for proper working.
- Difficulty in designing & fabrication of tools.

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So, it is based on the principle of electrolysis, where tool act as cathode and work piece will act as anode. So, from this particular case you can understand that you are having that electrolyte, you are pumping that electrolyte then you are having some filter then directly it is going and it is making a certain kind of chemical reactions, generally we are calling it as a electrochemical machining process, by which your electrolyte in terms some, in presence of potential difference, it is creating certain kind of chemical reactions by which your material you are removing. So, generally in some cases we are calling it as a electrochemical machining also. Now we are having some nozzle, so just increasing or decreasing the nozzle you can increase or decrease the machining area, not only that you can do any kind of complex over there also.

What are the advantages? Improvement in strength and temperature resistant produces complex shapes. What are the properties of the electrolyte? It must possess high electrical conductivity, it should have that electrical conducting material properties, it should possess high specific heat the viscosity must be as low as possible, it must be chemically stable and active, it should not be toxic and the corrosive and the what are the

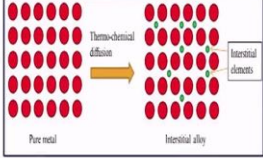
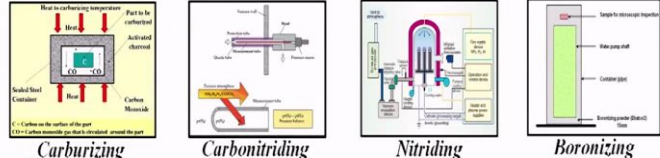
disadvantages; requires high power for proper working, difficulty in designing, and the fabrication of tools. So, there is certain kinds of little disadvantages are there.

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**Thermo-chemical diffusion:**

- In this processes, elements like carbon, nitrogen or boron are diffused into metal surfaces to enhance the surface properties and the strength of all-metal components.
- It is a pure thermal and chemical reaction as a consequence of the thermal dissociation of the gases.
- This process depends on:
  - ✓ Concentration gradient of diffusing species
  - ✓ Diffusivity of atomic species in host material
  - ✓ Time and temperature of the process.

*Types of thermochemical diffusion processes:*

**Carburizing**      **Carbonitriding**      **Nitriding**      **Boronizing**




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Next one is call the thermo chemical diffusions: in this process elements like carbon, nitrogen or boron are diffused into metal surface to enhance the surface properties and the strength of all components. In my previous slides also I have discuss that we are doing some kind of Carbonitriding or maybe the Nitriding or maybe the Boronizing or maybe some kind of carburizing.

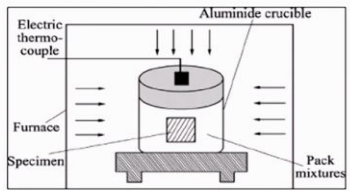
So, we are keeping that material into that particular environment and then that gas is coming, it is reacting with the metal surface and it is changing the material properties. So, this process depends on concentration gradient of diffusing species, diffusivity of atomic species in host materials, time and temperature of that particular process. So, here you are having that pure materials then when you are doing this thermo chemical diffusions in the presence of some gases or maybe some kind of bubbles. So, that gases it is going into the interstitial side of that particular base materials and it can change its properties. So, there are several methods one is call the carburizing, Carbonitriding, Nitriding, and the Boronizing these all are the different types of methods by which we can do the surface modifications.

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**Pack cementation diffusion:**

- ❖ It falls in the category of *in situ* chemical vapour deposition.
- ❖ It is a batch vapour-phase process that involves heating a closed pack to an elevated temperature for a given time during which a **diffusion coating** is produced.

$\text{Al} + \text{Al}_2\text{O}_3 + \text{NH}_4\text{Cl}$   
Substrate  $\xrightarrow[\text{Ar/H}_2 \text{ atmosphere}]{800-1100\text{ }^\circ\text{C} (4-12 \text{ hr.})}$  Aluminide coating on substrate



Aluminized Fasteners

Schematic diagram of pack cementation

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Next one is pack cementation diffusions. So, first let us know that what is called the pack cementation process. So, it is the process comes under the category of in situ chemical vapour depositions, then it is a batch vapour phase process that involves heating a closed pack to an elevated temperature for a given time during which diffusion coating is produced; that means, we are using several materials in a packing form; that means, we are mixing those materials then we are keeping those materials on to the substrate itself, then we are giving certain kind of temperature into some controlled atmospheres and by which we are doing the coating onto your base metal.

So, here we are using the aluminum, aluminum, alumina and the  $\text{NH}_4\text{Cl}$ . So, these all we are keeping on to the substrate then we are giving the temperature from 800 to 1100 degree centigrade, around 4 to 12 hour in the inert gas atmospheres or maybe sometimes we can use that organ and hydrogen atmosphere also then we are getting that alumite coating on substrates. So, this is the materials. So, previously it was made by some metals, now we are giving the coating on to these materials and this is known as the aluminized fasteners or maybe nut and bolt arrangements. So, these all are the schematic diagram of the pack cementation process. So, we are having that furnace, inside the furnace we can use some organ or hydrogen atmospheres or maybe the mixing of both atmospheres then we are maintaining this temperature and from this to this time and we are keeping those materials and it is generating certain kind of gases and that gas can do the coatings on to this material.

Next one is called the ion implantations. So, ion implantations means we are having some substrates then we are using certain kind of electron gun or maybe some kind of ion and then we are agitating those materials then from that targeted some ion is coming and it is directly falling on to your base metals then it is reacting or maybe it is going to the interstitial side and then by which you are going to do this modifications.

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**Ion implantation:**

- It is a process by which a gas is ionized and the ions are accelerated by a high electric field, and injected into the target wafer to hundreds of nm depth.
- It change the physical, chemical, or electrical properties of the solid by transferring their energy and momentum to the electrons and atomic nuclei of the target material.

**Advantages:**

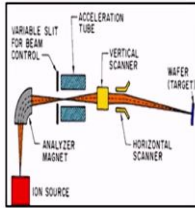
- Low temperature process.
- Wide selection of masking materials (photoresist, oxide, poly-Si and metal).
- Less sensitive to surface cleaning procedures.

**Disadvantages:**

- Very expensive equipment.
- Ions damage the semiconductor lattice.
- very deep doping are difficult or impossible.
- Crystallographic damage in the target crystal.

**Applications:**

- Semiconductor devices fabrication.
- Tool steel toughening.
- Surface finishing.



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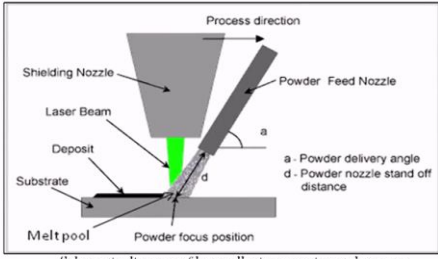
So, it is processes by which a gas is ionized and the ions are accelerated by a high electric field and injected into the target wafer to hundreds of nanometer depth in change the physical, chemical or electrical properties of the solid, by transferring their energy and momentum to the electrons and atomic nuclei of the target material. What are the advantages? Low temperature process, wide selection of masking materials like photoresist, oxide, poly-silicon and metal, less sensitive to surface cleaning process; disadvantages: very expensive equipment, ions damage semiconductor lattice, very deep doping are difficult or impossible, crystallographic damage in the target crystal. Applications: generally for thus electronic purpose, for the semiconductor purpose or maybe for the surface finishing we can use this kind of techniques.




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**Combination of laser beam melting and alloying:**

- A high power laser beam is used to modify not only the microstructure but also the chemical composition of a surface layer.
- This process involves the melting of a thin alloy layer into a substrate to yield an alloyed surface layer with desired composition by controlling the extent of mixing between the alloy layer and substrate.



The schematic diagram illustrates the laser alloying process. It shows a substrate with a melt pool on its surface. A laser beam is directed at the substrate, creating a melt pool. A powder feed nozzle is positioned above the substrate, delivering powder into the melt pool. A shielding nozzle is also present, providing protection for the laser beam. The process direction is indicated by an arrow. The powder focus position is marked. The powder delivery angle is labeled 'a' and the powder nozzle stand off distance is labeled 'd'. The diagram is captioned 'Schematic diagram of laser alloying experimental process'.



The image shows a laser beam melting and alloying process in progress. A laser beam is directed at a substrate, creating a melt pool. Powder is being delivered into the melt pool, and the laser beam is melting the powder and substrate together. The image is captioned 'Laser beam melting and alloying'.

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Next one is called the combinations of the laser beam melting and the alloying. So, in my last presentations also I have little bit discussed about this one, here also we are doing the same thing we are using certain kind of particles or maybe into the powder form and then that powder we are trying to put on to the metal surface and then by laser we are giving the heat on that particular surface, so that that powder is coming into the liquid form and it can deposit onto your metal surface. So, high power laser beam is used to modify not only the microstructure, but also the chemical composition of a surface layer. The process involves the melting of a thin alloy layer into a substrate to yield an alloyed surface layer with desired composition by controlling the extent of mixing between the alloy layer and substrate.

So, from that particular figure you can understand that we are putting the base materials on that top, by we are having some powder nozzle from which the powder is directly coming on to the base metals and this is the laser gun from that you are generating the laser and when it is generating certain heat, this powder materials is coming into a contact with its laser and then it is melting and it is making a layer onto that metal surface. So, this is called the laser beam melting and the alloying methods.

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**Different techniques involved in this treatment:**

- **One step alloying (known as Laser Gas Alloying)**
  - Delivering the alloy powder or wire to the molten zone simultaneously with irradiation.
  - Laser surface melting the substrate in a controlled atmosphere of gas (N<sub>2</sub>)
- **Two step alloying**
  - Preplacing a layer of the alloying elements by electroplating, vapor deposition, ion implantation, thermal spraying etc.
  - Preplacing a thin sheet, wire or powder with or without binding agent on the substrate

**Advantages:**

- Refinement of the grain size due to rapid quench rates and the generation of meta-stable structures.
- Modifies the surface morphology and near surface structure of components.
- Perfect adhesion of alloys to the interface of workpiece.

**Limitations:**

- A little imbalance in the process parameters can result a large variations in geometrical properties of the alloyed zone.

**Applications:**

- It is used in automotive industry for its high speed welding of body components.

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Then there are several different techniques also which we can adopt for the chemical modifications. So, in these slides actually we will briefly describe about the laser melting and the chemical reactions process. So, in this particular case we are first doing the melting then we are doing the alloying process. So, it is a two step process, why we are calling it as in the chemical modifications because first we are melting those materials, so that that powder and base material can be properly melted up then they can mix then they can do certain kind of chemical reactions in between them, so that the surface of that particular material can be changed.

So, first step what you are doing delivering the alloy powder or wire to the molten zone simultaneously with irradiation process, laser surface melting the substrate in a controlled atmosphere of gas in the nitrogen atmosphere; then in the second step preplacing a layer of the alloying elements by electroplating vapor deposition and ion implantations, thermal spraying etcetera. Preplacing a thin sheet, wire or powder with or without binding agent on the substrates; first initially we are mixing those then we are doing that chemical reactions by means any kind of electroplating or maybe vapor depositions or ion implantations, so that they are making a chemical reactions in between them.

What are the advantages? Refinement of the grain size due to rapid quenches rates and the generation of meta-stable structures modify the surface morphology and near surface

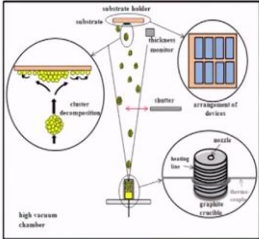
structure of the components perfect adhesions of alloys to the interface of the work piece, so that it can help the bonding of that particular material. There are certain limitations too a little imbalance in the process parameters can result a large variation in geometrical properties of the alloyed zone; what are the applications? It is used in automotive industry for its high speed welding of body components.

Next we will discuss about the cluster beam depositions. So, here we are using certain kind of Nano particles into the cluster form then we are alloying those Nano particles into the cluster form. So, directly it can deposit on to your material surface.

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**Cluster beam deposition:**

- Cluster beam deposition is one of the most recent emerging technologies for the deposition of nanoparticles as a type of cluster on substrate.
- It is one of several techniques classified as ion-assisted thin-film formation.
- The material to be deposited emerges and expands into a vacuum environment from a small nozzle of a heated confinement crucible.
- Homogeneous nucleation results in the generation of atomic aggregates or clusters by weak interatomic forces.
- **Advantages:**
  - ✓ Controllable growth of thin films with high degree of purity.
- **Disadvantages:**
  - ✓ Process is extremely complex.
- **Applications:**
  - ✓ Manufacturing of semiconductor devices and optical thin films



The diagram illustrates the cluster beam deposition process. It shows a high-vacuum chamber containing a heated crucible where material is evaporated. The resulting clusters travel through a substrate holder towards a substrate. A substrate heater and substrate monitor are also shown. The process results in the formation of a thin film on the substrate. The diagram also shows a stack of semiconductor devices and a wafer being processed.

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So, a cluster beam deposition is one of the most recent emerging technologies for the deposition of Nano particles as a type of cluster on substrate. It is one of the several techniques classified as ion assisted thin film formations. So, from this particular figure you can understand that we are making certain kind of cluster of that Nano particle and then directly it is going and it is depositing on to the material surface.

So, it should be the homogeneous nucleation result in the generation of atomic aggregates or clusters by weak interatomic forces. Advantages: controllable growth of thin films with high degree of purity depends upon how much time you are going to do these chemical reactions, if the chemical reaction will be more your thickness will be more or maybe it is a reaction will be less it should be less. There are certain disadvantages also, process is extremely complex applications, manufacturing of

semiconductor devices and optical thin films; in this cases we can use this kind of cluster beam depositions.

So, now we are going to summarize our study from the last two consecutive lecture. So, one is call the physical modifications.

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**Comparison between physical modifications and chemical modifications:**

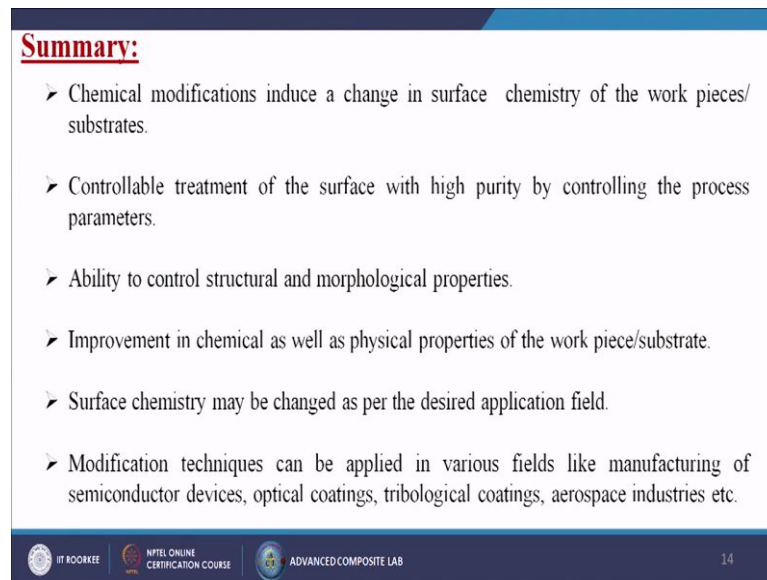
Physical modifications	Chemical modifications
1. It changes the surface metallurgy.	1. It changes the surface chemistry.
2. It does not uses any toxic chemicals.	2. It uses toxic chemicals.
3. Probability to form oxides during treatments.	3. Very less probability to form oxides during modifications.
4. It does not make any serious harmful.	4. It may be harmful if without proper precaution.
5. Most of the cases instrument are expensive.	5. It is less expensive except some modern instrument.
6. It is a non reactive process.	6. It is a reactive process.
7. Generally it is temperature dependent process .	7. Most of the cases it is room temperature process.

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Another is called the chemical modifications, what are the main differences? It changes the surface metallurgy; chemical differences change the surface chemistry. So, it is not going to change the chemical properties in terms of physical modifications, it does not use any toxic chemicals, but chemical modification use certain kind of toxic chemicals over there probability to form oxides during treatments, very less probability to form oxides during modifications because some kind of chemical reactions is going to take place. It does not make any serious harmful because it is not generating any kind of toxic gases, but while we are doing some kind of chemical modifications, there should be some kind of generation of the toxic gases which can be harmful to the environment.

Most of the cases instrument are expensive, this are the less expensive except some modern instrument you need; it is a non reactive process. It is a reactive process because reaction is taking place. Generally it is temperature dependent process most of the process it is room temperature process or maybe sometimes you need some kind of controlled temperature and maybe the atmosphere too for the some special cases.

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**Summary:**

- Chemical modifications induce a change in surface chemistry of the work pieces/ substrates.
- Controllable treatment of the surface with high purity by controlling the process parameters.
- Ability to control structural and morphological properties.
- Improvement in chemical as well as physical properties of the work piece/substrate.
- Surface chemistry may be changed as per the desired application field.
- Modification techniques can be applied in various fields like manufacturing of semiconductor devices, optical coatings, tribological coatings, aerospace industries etc.

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Next come to the summary or maybe now we are into the last part of this particular lecture where we have to summarize whole study. So, chemical modification induces a change in surface chemistry of the work piece or substrates, controllable treatment of the surface with high purity by controlling the process parameters, ability to control structural and morphological properties. So, it is a one kind of chemical process where we can do the chemical reactions of that particular material with the substrate and the target materials, so that it can be easily modified your material surface.

Improvement in chemical as well as physical properties of the work piece or substrate, surface chemistry maybe changed as per the desired application field, modification techniques can be applied in various fields like manufacturing of semiconductor device, optical coatings, tribological coatings, aerospace industries etcetera. So, several applications are there for the chemical modifications.

Thank you.