

Examples of CVD processes

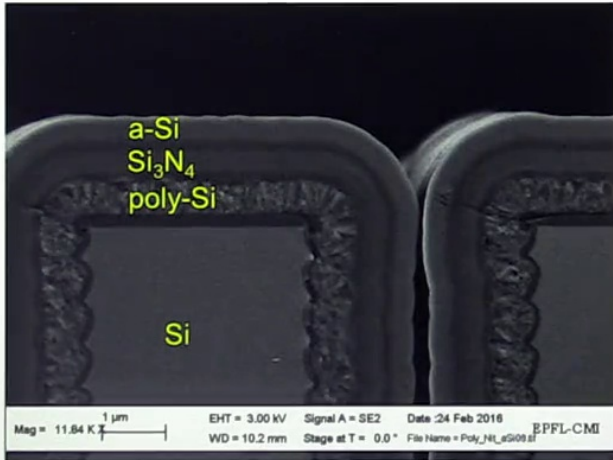


- LPCVD of polycrystalline and amorphous Si
- LPCVD of Si_3N_4 and $\text{Si}_x\text{N}_y\text{H}_z$
- LPCVD low-temperature oxide
- PECVD of diamond

Micro and Nanofabrication (MEMS)

In this lesson we will give a few examples of CVD processes for depositing specific materials. We will start by discussing the low-pressure chemical vapor deposition of polycrystalline and amorphous silicon. Then, we will discuss the LPCVD of silicon nitride and hydrogenated silicon nitride. The latter material has interest because of its lower intrinsic mechanical stress with respect to the pure silicon nitride. Next, we will discuss the LPCVD of so-called low-temperature oxide, or LTO. Finally, we will discuss the plasma-enhanced chemical vapor deposition of diamond films.

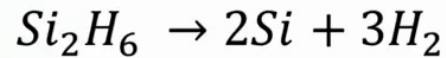
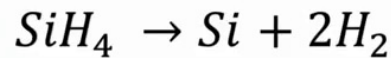
LPCVD of polycrystalline and amorphous Si



- Poly-Si is used in microelectronics as material for the gate of the transistors (MOSFETs)
- It can be used as electrical interconnection material when strongly doped with impurities
- It can be used as electrical resistor material when weakly doped with impurities
- It can be used as structural material in mechanical microsystems
- Amorphous Si (a-Si) is used in solar cells

Micro and Nanofabrication (MEMS)

Polycrystalline silicon, or polysilicon, is a very important material that is used in microelectronics for fabrication of the gate of transistors, the so-called MOSFETs, or metal-oxide semiconductor field-effect transistors. When the polysilicon is doped with impurities, it is a conducting material that can be used for realization of electrical interconnects. For microsystems applications it is used as a structural material, for example, for realization of mechanical inertial sensors. In the picture we see an etched silicon microstructure that was later covered by a polysilicon layer using LPCVD. We can recognize the crystalline structure of the individual grains. Crystalline formation is induced by underlying single-crystalline silicon. After the deposition of a silicon nitride layer, also by LPCVD, one has deposited, again, silicon by LPCVD- there's this layer. This is now amorphous as the nitride does not provide nucleation sites for crystalline generation. Amorphous silicon is used in solar cell applications.

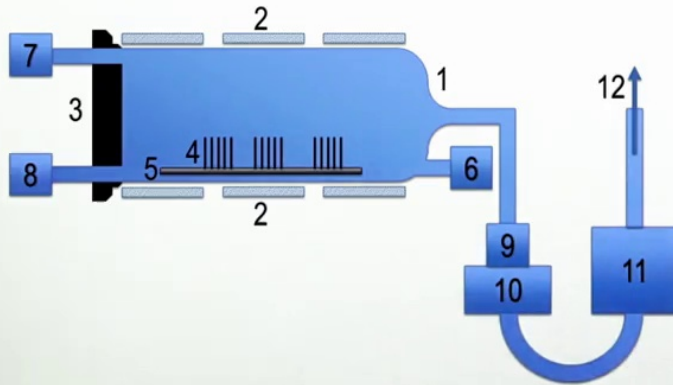


- Poly-Si is deposited from silane (SiH_4) or disilane (Si_2H_6) in a pressure range of 150-350 mbar and in a temperature window of 590-650 °C
- Amorphous Si is deposited in a temperature window of 525-585 °C
- Either Si or fused silica (SiO_2) substrates can be coated
- No float glass or Pyrex wafers are allowed, neither presence of metal or organic films
- Up to a few μm poly-Si can be deposited per run

Micro and Nanofabrication (MEMS)

Here we show chemical reactions involved in the deposition of polysilicon. One uses either silane gas or disilane gas in the pressure range of 150 to 350 millibar and in the temperature window around 590 to 650 degrees Celsius. Amorphous silicon is deposited at lower temperatures at which the mobility of deposited atoms on a substrate is lower. In the LPCVD reactor, one deposits the polysilicon on either silicon or fused silica substrates. Pyrex or float glass wafers are not allowed due to their low melting temperature. And also, the presence of metals or organic materials in the reactor is not tolerated. During a typical deposition run, a few micrometers of polysilicon can be deposited.

LPCVD of polycrystalline and amorphous Si



1. Fused silica tube
2. Heating elements (3 zones)
3. Entrance lock
4. Three fused silica boats, each for 25 wafers of 100 mm or 150 mm Ø
5. Temperature sensor
6. Reactive gas (SiH_4 or Si_2H_6) or nitrogen (N_2)
purge gas back entrance
7. Gases front entrance
8. Pressure sensor
9. Pressure regulation valve
10. Pump
11. Gas scrubber
12. Evacuation

Micro and Nanofabrication (MEMS)

This slide shows an LPCVD reactor, as we have seen before. Also, a schematic diagram is presented showing a fused silica boat filled with wafers. A boat can contain up to 25 wafers so that high throughput deposition is possible. The reactor is configured with a pressure sensor, with a pressure regulation valve, and with a pumping unit, so that one can well-control the pressure. A gas scrubber avoids that toxic byproducts of the chemical reaction are released into the environment.



- Si_3N_4 is used in microelectronic processes as passivation layer, mechanical protection or electrical insulation coating material
- It is used as chemically protective masking layer in HF or KOH etching
- Thin membranes can be made for microsystems applications

Micro and Nanofabrication (MEMS)

Another important material that is widely used in microfabrication is silicon nitride. It is used in microelectronic processes as passivation layer as it is a very inert and chemically-resistant material. It has also interesting mechanical properties and it can be used for realization of thin membranes, for example, or as an electrical insulating coating material. It is a material that is used in etching processes to resist to aggressive chemicals, for example, processes that use HF or KOH to locally protect the material underneath. In this picture we see again our etched silicon structure which has been covered with a polysilicon layer by LPCVD, followed by deposition of a silicon nitride layer by LPCVD.



- Stoichiometric Si_3N_4 is deposited by thermal decomposition of dichlorosilane (SiH_2Cl_2) and reaction with ammonia (NH_3) in a pressure range of 150-250 mbar and in a temperature window of 700-840 °C
- Up to 0.8 μm Si_3N_4 can be deposited per run (residual stress ~ 1300 MPa)

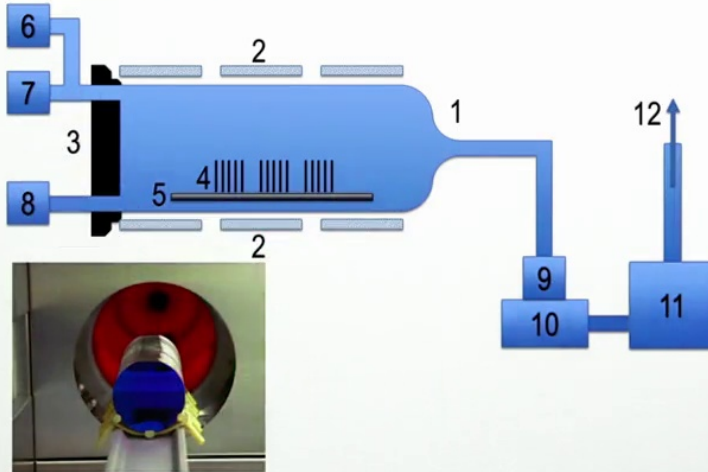
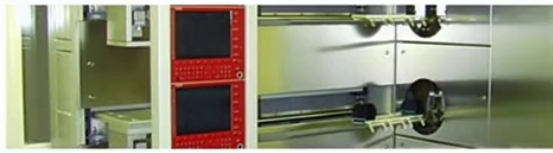


- Low-stress $\text{Si}_x\text{N}_y\text{H}_z$ can be deposited by tuning reaction gas concentrations
- Up to 2 μm of low-stress $\text{Si}_x\text{N}_y\text{H}_z$ can be deposited (residual stress ~ 200 MPa)
- Either Si or fused silica (SiO_2) substrates can be coated; no float glass or Pyrex wafers are allowed, neither presence of metal or organic films

Micro and Nanofabrication (MEMS)

We see here the chemical reaction by which silicon nitride is deposited in an LPCVD process. One uses two gases- dichlorosilane and ammonia- to deposit the silicon nitride layer, and the release of hydrogen chloride and hydrogen. Somewhat less than one micrometer is typically deposited per run. This stoichiometric silicon nitride- which is deposited at temperatures in between of 700 to 840 degrees Celsius upon cooling down on a silicon wafer- is characterized by a relatively large residual stress. This may be unwanted for certain applications as it can lead to mechanical failure of devices. Therefore, it's also possible to deposit non-stoichiometric silicon nitride by adjusting the ratio of the two precursor gases, so one varies x and y . In this way we get hydrogenated silicon nitride which is characterized by a much smaller residual stress. Therefore, it is possible to deposit thicker layers. As a substrate that can be used in this type of process, we have to use either silicon or fused silica, like before.

LPCVD of Si_3N_4

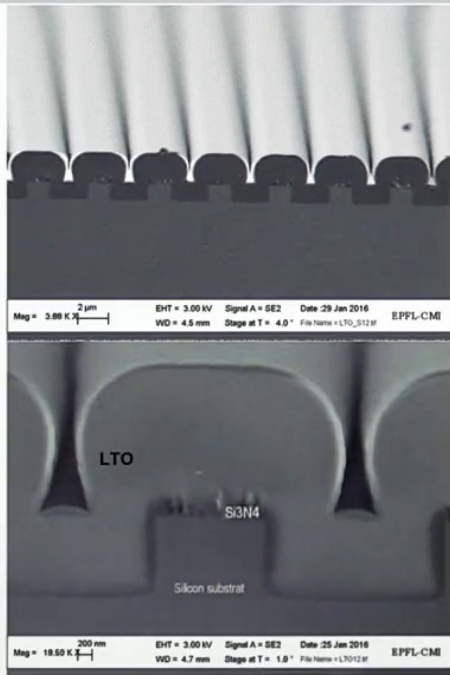


1. Fused silica tube
2. Heating elements (3 zones)
3. Entrance lock
4. Three fused silica boats, each for 25 wafers of 100 mm or 150 mm Ø
5. Temperature sensor
6. Ammonia reactive gas (NH_3) or nitrogen (N_2) purge gas entrance
7. Dichlorosilane reactive gas (SiH_2Cl_2) or nitrogen (N_2) purge gas entrance
8. Pressure sensor
9. Pressure regulation valve
10. Pump
11. Gas scrubber
12. Evacuation

Micro and Nanofabrication (MEMS)

Here we show the reactor and schematic diagram that is used in an LPCVD process for silicon nitride. It is very similar to the reactor that is used for the deposition of polycrystalline and amorphous silicon, except that there are now two entrances for two simultaneously-used precursor gases.

LPCVD of SiO_2 at low temperature (400-450°C)



- Known as LTO (Low Temperature Oxide), it is used as isolation layer in between metal layers or poly-Si in microelectronics
- It is used as a mask against diffusion or implantation
- It is used as final passivation layer on Si chips
- It is used as sacrificial layer in microsystems

Micro and Nanofabrication (MEMS)

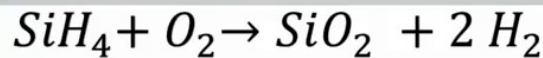
Another widely-used material in microfabrication is silicon dioxide or silica. We have already seen that silicon dioxide can be realized by thermal oxidation of the surface of a silicon wafer at high temperatures of about a thousand degrees Celsius. LPCVD enables to deposit silicon dioxide at much lower temperature that is at 400 to 450 degrees Celsius. That is why this oxide is known as Low-Temperature Oxide, or LTO. It is used as isolation layer in between metal layers or in between conducting polysilicon layers in microelectronics. It can be used as a protective mask and as a final passivation layer on silicon chips, too. In microsystems applications, it can be used as a sacrificial layer, that is, a layer on which a functional material like polysilicon is deposited, after which the silicon dioxide is chemically etched away so that one gets a freestanding polysilicon mechanical microstructure. The picture shows an LTO layer which is deposited on a silicon wafer that was microstructured using a silicon nitride mask.



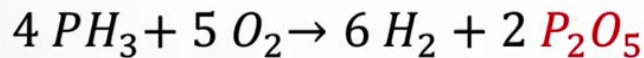
- Strongly phosphor-doped LTO (**PSG: Phospho-Silicate Glass**) or phosphor & boron-doped LTO (**BPSG: Boro-Phospho-Silicate Glass**) is used as diffusion source, smoothing layer due to its creeping behavior at high temperature, or passivation layer with barrier function against Na^+ ions and H_2O
- PSG shows creep at 1000-1050 °C for P mass concentrations > 6%
- BPSG shows creep at 700 °C ; the B mass concentration should be < 5% for stability

Micro and Nanofabrication (MEMS)

It is also possible to dope the silicon dioxide with phosphorus atoms. Strongly phosphorous-doped LTO is known as phosphosilicate glass, or PSG. This material can be used as a diffusion source, that is, it is deposited on a silicon wafer after which, during heating, it releases its phosphorus by diffusion into the silicon. It can also be used as a smoothing layer- as during heating, it shows creeping behavior- or it can be used as a passivation layer. It is also possible to dope the LTO with both boron and phosphorus. And in this case, this material is known as Borophosphosilicate glass, or BPSG. It has similar properties as the PSG.



- LTO is deposited by the reaction of silane (SiH_4) with oxygen (O_2) in a pressure range of 90-250 mbar and in a temperature window of 400-450 °C
- Up to 3 μm LTO can be deposited per run

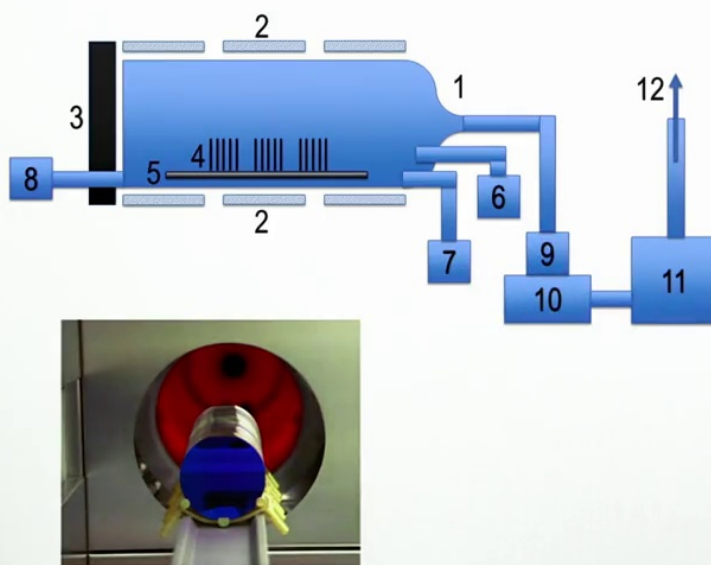


- Trimethylborate ($\text{B}(\text{OCH}_3)_3$) and phosphine (PH_3), in combination with silane (SiH_4), are used for deposition of PSG ($\text{P}_2\text{O}_5\text{-SiO}_2$) and BPSG ($\text{B}_2\text{O}_3\text{-P}_2\text{O}_5\text{-SiO}_2$)

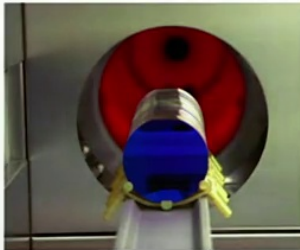
Micro and Nanofabrication (MEMS)

This is the chemical reaction for the deposition of the silicon dioxide. One uses silane and oxygen gas as precursor gases at pressures of about 90 to 250 millibar in a temperature window of 400 to 450 degrees Celsius. Up to a few microns of LTO can be deposited per run. For realization of the PSG or BPSG, additional precursor gases are needed, namely, trimethylborate and phosphene. This leads to incorporation of these oxides in the silica film.

LPCVD of SiO_2 at low temperature



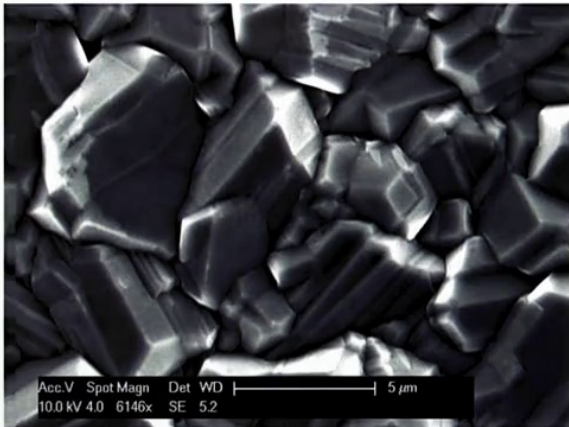
1. Fused silica tube
2. Heating elements (3 zones)
3. Entrance lock
4. One fused silica boats for 25 wafers of 100 mm or 150 mm Ø
5. Temperature sensor
6. Entrance for reactive gases (SiH_4 , PH_3 / SiH_4 , $\text{B}(\text{OCH}_3)_3$) or nitrogen (N_2) purge gas
7. Entrance for oxygen gas (O_2)
8. Pressure sensor
9. Pressure regulation valve
10. Pump
11. Gas scrubber
12. Evacuation



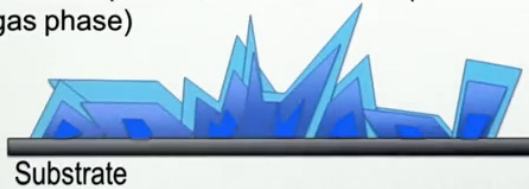
Micro and Nanofabrication (MEMS)

Here we see a schematic diagram of an LPCVD deposition system for silicon dioxide, which has also the option to realize Phosphosilicate glass and borophosphosilicate glass by switching on the supply of the appropriate precursor gases.

Diamond



Boron-doped diamond electrode (0.1 % B in gas phase)

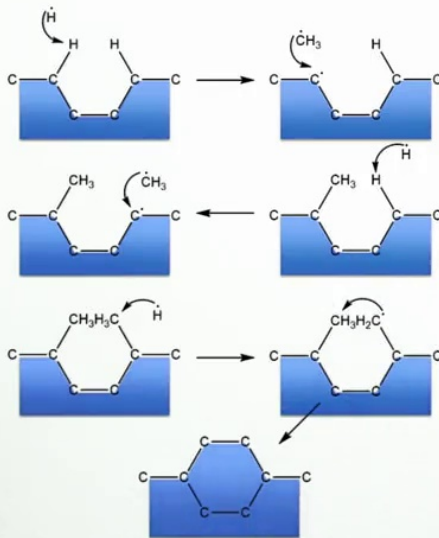


- Diamond has a high thermal conductivity, but negligible electrical conductivity; it can therefore be used as heat sink for high-power laser diodes and transistors
- Diamond is hard, chemically inert and has a low coefficient of thermal expansion
- Synthetic diamond can be used as a wide band gap (5.5 eV) semiconductor and can be doped with P or B
- B-doped diamond can be used as electrodes in electrochemical applications

Micro and Nanofabrication (MEMS)

The last application we want to show is the plasma-enhanced chemical vapor deposition process of diamonds. Diamond has a very high thermal conductivity and can be used as heat sink in high-powered diode and transistor applications, for example. It is also chemically inert and can be used as electrode material in electrochemical applications. When doped with boron, the thus-obtained conducting material can be used in harsh chemical environments to probe the properties of the chemical liquid of interest without having substantial and unwanted chemical interaction with the electrode itself. The picture shows such boron-doped diamond electrode. In particular we see here, the crystalline structure which is sketched here again, in cross-section, and which originates by the preferred growth of the diamond along certain crystal facets.

PECVD of diamond

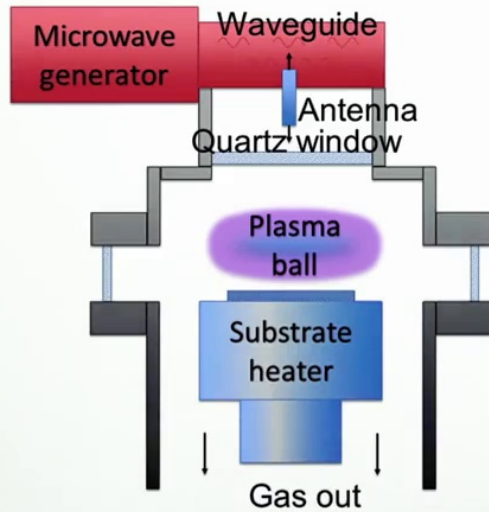


- Growth requires activation of the gaseous reactants, usually H_2 and methane (CH_4) at 50-200 mbar pressure
- The growing diamond lattice is prevented from rearrangement to graphitic carbon by termination with hydrogen atoms at $700\text{ }^{\circ}\text{C} < T < 900\text{ }^{\circ}\text{C}$
- In the plasma, H_2 dissociates into H atoms, which react with the source hydrocarbon and create a complex mixture of hydrocarbon species, including reactive C-containing radicals
- The H atoms also remove hydrogen from the surface CH bonds, creating surface radical sites that will react with new hydrocarbon species to form a diamond lattice

Micro and Nanofabrication (MEMS)

This diagram illustrates the growth of the diamond layer, starting from the gaseous reactants, hydrogen and methane. The deposition temperature is in between 700 and 900 degrees Celsius. In the plasma, the hydrogen gas is dissociated in individual hydrogen atoms which react with hydrocarbons to create a complex mixture of hydrocarbon species. The individual hydrogen atoms can remove hydrogen from the surface by recombination into molecular hydrogen. Thereby, they create radical sites that can react now with hydrocarbon species to form the diamond lattice. This process is repeated continuously. And finally, one gets here the diamond structure.

Diamond PECVD equipment



- Microwave plasma can be generated above a substrate, minimising the effect of plasma heating on the sample, allowing almost independent control of plasma and substrate parameters
- Substrate temperature is typically in the 750 °C – 900 °C range
- Microwave plasma CVD growth rates are in the 0.1-10 $\mu\text{m h}^{-1}$ range

Micro and Nanofabrication (MEMS)

Here we show a schematic illustration of a diamond plasma-enhanced chemical vapor deposition reactor. A microwave generator creates the energy for generation of the plasma in the reactor. A typical microwave plasma CVD growth rate for diamond is in between 0.1 and 10 micrometer per hour.

Summary



- Several illustrative examples of CVD processes given
- LPCVD of Si, Si_3N_4 , $\text{Si}_x\text{N}_y\text{H}_z$, and SiO_2
- PECVD of diamond

Micro and Nanofabrication (MEMS)

In this lesson we have given several experimental examples of CVD processes. We discussed the low-pressure chemical vapor deposition of some of the most important materials in microelectronics and microfabrication, like polycrystalline and amorphous silicon, silicon nitride, hydrogenated silicon nitride, and silicon dioxide. Finally, we have discussed a plasma-enhanced chemical vapor deposition process for deposition of diamond films.
