PH3EC2 Vapour Growth and Epitaxial Growth

Lecture 2: Hydrothermal growth

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2.1 Hydrothermal Growth

Hydrothermal synthesis includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures. The principle of hydrothermal method is that an insoluble material at ambient temperatures could be made soluble using high temperatures and pressures. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called an **autoclave**, in which a nutrient is supplied along with water. A temperature gradient is maintained between the opposite ends of the growth chamber. At the hotter end the nutrient solute dissolves, while at the cooler end it is deposited on a seed crystal, growing the desired crystal.

2.1.1 Procedure

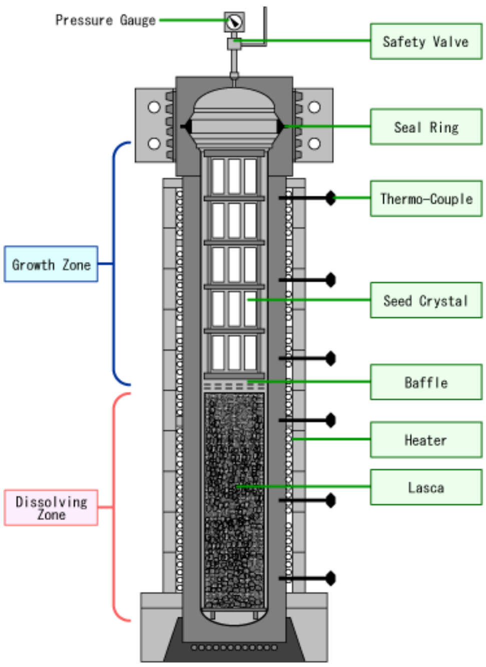

Figure 2.1: *Schematic of an autoclave*

The schematic of autoclave is shown in figure 2.1. The finely divided particles of material to be grown are taken in the bottom of vessel and suitably oriented single crystal seed plates are suspended in the upper growth region. A dilute alkaline solution is then poured into the remaining 60 to 80% of free space of vessel. The vessel is then placed inside a furnace that has been designed to heat the lower dissolving section isothermally hotter than the upper growth region which is also maintained isothermal. Under these condition the alkaline solution expands and is compressed; the pressure inside reaches very high. Under these high temperatures and pressures the materials in the lower compartment of the autoclave dissolve in the alkaline solution to become saturated solution. This saturated solution rises due to the convection caused by the temperature difference between the upper and lower compartments of the autoclave. When the solution reaches the upper compartment of the autoclave, it becomes supersaturated because of the lower temperature of the compartment, and according to the degree of the temperature difference it is crystallized on the seed crystal.

2.1.2 Advantages of the hydrothermal method

- With this method it is possible to grow crystals of compounds with high melting points at lower temperatures.
- Materials which have a high vapour pressure near their melting points can be grown by the hydrothermal method.
- The method is also particularly suitable for the growth of large good-quality crystals while maintaining control over their composition.

2.1.3 Disadvantages of the method

- The need of expensive autoclaves
- The impossibility of observing the crystal as it grows.

2.1.4 Design aspects of autoclave

Since the experiment is carried out relatively above atmospheric temperature, high pressure autoclave are necessary. The autoclave is steel or a special high temperature alloy vessel whose strength is great enough to sustain pressure-temperature conditions expected in the experiment. The material should posses high strength characteristics and corrosion resistance against alkaline and acidic solution. The vessel should be easily assembled and dissembled. Depending on the pressure conditions there are following classes of autoclaves:

2.1.4.1 Low pressure autoclaves

- Made out of glass (pyrex glass vessels or quartz tubes)
- For temperature to about 300^0C and pressure limited to 10 atmosphere.

Advantages

- Good visibility of growth process
- resistance to acid solutions

Disadvantages

- Low pressure and temperature capability
- Ease of attack by basic solutions

2.1.4.2 Medium pressure autoclaves

- For pressure upto 500 atmospheres and temperature near 400^0C
- Steel (ordinary low carbon) vessels with flat plate enclosures
- Provided with safety pressure seals
- Easily assembled and requires minimum mechanical precision

2.1.4.3 High pressure autoclaves

- For pressure upto 3000 atmospheres and temperature upto 450^0C
- Robust steel enclosure
- Removable liner permits no corrosions as in complex vessels

2.1.4.4 High pressure-modified Bridgman autoclaves

- For pressure upto 3700 atmospheres and temperature upto 500^0C
- The initial seal that closes the vessel is made by mechanical tightening
- The unsupported area closure makes it seal when the force of generated pressure acts upon the piston

To overcome safety hazards, the high pressure equipment is placed below ground or thick walled barricade is made out of sandbags.

2.1.5 Growth of Quartz

Schematic diagram of autoclave is shown in figure 2.2. Nutrient quartz is placed in the hotter bottom zone (dissolving zone) and frame holding the seed crystals are placed in the upper part (crystallizing zone) of the vessel. A dilute alkaline solution (1.0 M NaOH) is then poured into the remaining 80% of free space. The vessel is then closed and placed inside a furnace that gives desired temperature and temperature gradients. As the temperature of the vessel reaches operating conditions (400^0C at dissolving zone and 360^0C at crystallizing zone), the nutrient quartz begins to dissolve and saturate the solution. The top portion of the autoclave is cooler which causes the supersaturation of the solution. The seed crystal plates begins to grow as the supersaturated solution deposits solid phase. Convection currents caused by temperature gradient accomplish the continuous growth. The baffle arrangement (5% opened) allows transport of newly saturated solution to the growth zone and the depleted solution away. This continuous cycle of solution and deposition permits growth of larger crystals.

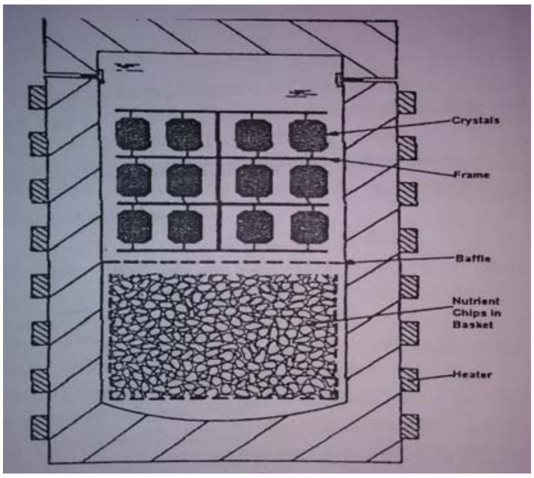

Figure 2.2: *Schematic diagram of an autoclave*

2.1.6 Growth of Quartz

The typical growth conditions are:

Crystallizing temperature	490^0C
Temperature gradient ΔT	50^0C
Degrees of fill	80%
Solution	1.0 M K_2CO_3
Growth rate	0.25 mm per day.

2.1.7 Growth of garnet

The typical growth conditions are:

Crystallizing temperature	350^0C
Temperature gradient ΔT	10^0C
Degrees of fill	88%
Solution	20 M KOH
Growth rate	0.1-0.2 mm per day.