Chapter 3

Bulk Materials

3.1 Properties of Gallium Arsenide[1]

3.1.1 Gallium: the element

The element gallium was predicted, as eka-aluminum, by Mendeleev in 1870, and subsequently discovered by Lecoq de Boisbaudran in 1875; in fact de Boisbaudran had been searching for the missing element for some years, based on his own independent theory. The first experimental indication of gallium came with the observation of two new violet lines in the spark spectrum of a sample deposited on zinc. Within a month of these initial results de Boisbaudran had isolated 1 g of the metal starting from several hundred kilograms of crude zinc blende ore. The new element was named in honor of France (Latin *Gallia*), and the striking similarity of its physical and chemical properties to those predicted by Mendeleev (Table 3.1) did much to establish the general acceptance of the periodic Law; indeed, when de Boisbaudran first stated that the density of Ga was 4.7 g/cm^3 rather than the predicted 5.9 g/cm^3, Mendeleev wrote to him suggesting that he redetermine the value (the correct value is 5.904 g/cm^3).

Property	**Mendeleev's prediction (1871) for eka-aluminum, M**	**Observed properties of gallium (discovered 1875)**
Atomic weight	ca. 68	69.72
Density, g.cm^{-3}	5.9	5.904
Melting point	Low	29.78
Vapor pressure	Non-volatile	10^{-3} mmHg, 1000 °C
Valence	3	3
Oxide	M_2O_3	Ga_2O_3
Density of oxide (g/cm^3)	5.5	5.88

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[1] This content is available online at <http://cnx.org/content/m22970/1.7/>.

Properties of metal	M should dissolve slowly in acids and alkalis and be stable in air	Ga metal dissolves slowly in acids and alkalis and is stable in air
Properties of hydroxide	$M(OH)_3$ should dissolve in both acids and alkalis	$Ga(OH)_3$ dissolves in both acids and alkalis
Properties of salts	M salts will tend to form basic salts; the sulfate should form alums; M_2S_3 should be precipitated by H_2S or $(NH_4)_2S$; anhydrous MCl_3 should be more volatile than $ZnCl_2$	Ga salts readily hydrolyze and form basic salts; alums are known; Ga_2S_3 can be precipitated under special conditions by H_2S or $(NH_4)_2S$, anhydrous $GaCl_3$ is more volatile than $ZnCl_2$.

Table 3.1: Comparison of predicted and observed properties of gallium.

Gallium has a beautiful silvery blue appearance; it wets glass, porcelain, and most other surfaces (except quartz, graphite, and Teflon®) and forms a brilliant mirror when painted on to glass. The atomic radius and first ionization potential of gallium are almost identical with those of aluminum and the two elements frequently resemble each other in chemical properties. Both are amphoteric, but gallium is less electropositive as indicated by its lower electrode potential. Differences in the chemistry of the two elements can be related to the presence of a filled set of 3d orbitals in gallium.

Gallium is very much less abundant than aluminum and tends to occur at low concentrations in sulfide minerals rather than as oxides, although gallium is also found associated with aluminum in bauxite. The main source of gallium is as a by-product of aluminum refining. At 19 ppm of the earth's crust, gallium is about as abundant as nitrogen, lithium and lead; it is twice as abundant as boron (9 ppm), but is more difficult to extract due to the lack of any major gallium-containing ore. Gallium always occurs in association either with zinc or germanium, its neighbors in the periodic table, or with aluminum in the same group. Thus, the highest concentrations (0.1 - 1%) are in the rare mineral germanite (a complex sulfide of Zn, Cu, Ge, and As); concentrations in sphalerite (ZnS), bauxite, or coal, are a hundred-fold less.

3.1.2 Gallium pnictides

Gallium's main use is in semiconductor technology. For example, GaAs and related compounds can convert electricity directly into coherent light (laser diodes) and is employed in electroluminescent light-emitting diodes (LED's); it is also used for doping other semiconductors and in solid-state devices such as heterojunction bipolar transistors (HBTs) and high power high speed metal semiconductor field effect transistors (MESFETs). The compound $MgGa_2O_4$ is used in ultraviolet-activated powders as a brilliant green phosphor used in Xerox copying machines. Minor uses are as high-temperature liquid seals, manometric fluids and heat-transfer media, and for low-temperature solders.

Undoubtedly the binary compounds of gallium with the most industrial interest are those of the Group 15 (V) elements, GaE (E = N, P, As, Sb). The compounds which gallium forms with nitrogen, phosphorus, arsenic, and antimony are isoelectronic with the Group 14 elements. There has been considerable interest, particularly in the physical properties of these compounds, since 1952 when Welker first showed that they had semiconducting properties analogous to those of silicon and germanium.

Gallium phosphide, arsenide, and antimonide can all be prepared by direct reaction of the elements; this is normally done in sealed silica tubes or in a graphite crucible under hydrogen. Phase diagram data is hard to obtain in the gallium-phosphorus system because of loss of phosphorus from the bulk material at elevated temperatures. Thus, GaP has a vapor pressure of more than 13.5 atm at its melting point; as compared to 0.89 atm for GaAs. The physical properties of these three compounds are compared with those of the nitride in Table 3.2. All three adopt the zinc blende crystal structure and are more highly conducting than gallium nitride.

Property	**GaN**	**GaP**	**GaAs**	**GaSb**
Melting point (°C)	> 1250 (dec)	1350	1240	712
Density (g/cm^3)	ca. 6.1	4.138	5.3176	5.6137
Crystal structure	Würtzite	zinc blende	zinc blende	zinc blende
Cell dimen. (Å)^a	$a = 3.187$, $c = 5.186$	$a = 5.4505$	$a = 5.6532$	$a = 6.0959$
Refractive index^b	2.35	3.178	3.666	4.388
k (ohm^{-1}cm^{-1})	10^{-9} - 10^{-7}	10^{-2} - 10^{2}	10^{-6} - 10^{3}	6 - 13
Band gap (eV)^c	3.44	2.24	1.424	0.71

Table 3.2: Physical properties of 13-15 compound semiconductors. ^{a} Values given for 300 K. ^{b} Dependent on photon energy; values given for 1.5 eV incident photons. ^{c} Dependent on temperature; values given for 300 K.

3.1.3 Gallium arsenide versus silicon

Gallium arsenide is a compound semiconductor with a combination of physical properties that has made it an attractive candidate for many electronic applications. From a comparison of various physical and electronic properties of GaAs with those of Si (Table 3.3) the advantages of GaAs over Si can be readily ascertained. Unfortunately, the many desirable properties of gallium arsenide are offset to a great extent by a number of undesirable properties, which have limited the applications of GaAs based devices to date.

Properties	**GaAs**	**Si**
Formula weight	144.63	28.09
Crystal structure	zinc blende	diamond
Lattice constant	5.6532	5.43095
Melting point (°C)	1238	1415
Density (g/cm^3)	5.32	2.328
Thermal conductivity (W/cm.K)	0.46	1.5
Band gap (eV) at 300 K	1.424	1.12
Intrinsic carrier conc. (cm^{-3})	1.79×10^{6}	1.45×10^{10}
Intrinsic resistivity (ohm.cm)	10^{8}	2.3×10^{5}
Breakdown field (V/cm)	4×10^{5}	3×10^{5}
Minority carrier lifetime (s)	10^{-8}	2.5×10^{-3}
Mobility (cm^2/V.s)	8500	1500

Table 3.3: Comparison of physical and semiconductor properties of GaAs and Si.

3.1.3.1 Band gap

The band gap of GaAs is 1.42 eV; resulting in photon emission in the infra-red range. Alloying GaAs with Al to give $Al_xGa_{1-x}As$ can extend the band gap into the visible red range. Unlike Si, the band gap of GaAs is direct, i.e., the transition between the valence band maximum and conduction band minimum involves no momentum change and hence does not require a collaborative particle interaction to occur. Photon generation by inter-band radiative recombination is therefore possible in GaAs. Whereas in Si, with an indirect band-gap, this process is too inefficient to be of use. The ability to convert electrical energy into light forms the basis of the use of GaAs, and its alloys, in optoelectronics; for example in light emitting diodes (LEDs), solid state lasers (light amplification by the stimulated emission of radiation).

A significant drawback of small band gap semiconductors, such as Si, is that electrons may be thermally promoted from the valence band to the conduction band. Thus, with increasing temperature the thermal generation of carriers eventually becomes dominant over the intentionally doped level of carriers. The wider band gap of GaAs gives it the ability to remain 'intentionally' semiconducting at higher temperatures; GaAs devices are generally more stable to high temperatures than a similar Si devices.

3.1.3.2 Carrier density

The low intrinsic carrier density of GaAs in a pure (undoped) form indicates that GaAs is intrinsically a very poor conductor and is commonly referred to as being semi-insulating. This property is usually altered by adding dopants of either the p- (positive) or n- (negative) type. This semi-insulating property allows many active devices to be grown on a single substrate, where the semi-insulating GaAs provides the electrical isolation of each device; an important feature in the miniaturization of electronic circuitry, i.e., VLSI (very-large-scale-integration) involving over 100,000 components per chip (one chip is typically between 1 and 10 mm square).

3.1.3.3 Electron mobility

The higher electron mobility in GaAs than in Si potentially means that in devices where electron transit time is the critical performance parameter, GaAs devices will operate with higher response times than equivalent Si devices. However, the fact that hole mobility is similar for both GaAs and Si means that devices relying on cooperative electron and hole movement, or hole movement alone, show no improvement in response time when GaAs based.

3.1.3.4 Crystal growth

The bulk crystal growth of GaAs presents a problem of stoichiometric control due the loss, by evaporation, of arsenic both in the melt and the growing crystal (> *ca.* 600 °C). Melt growth techniques are, therefore, designed to enable an overpressure of arsenic above the melt to be maintained, thus preventing evaporative losses. The loss of arsenic also negates diffusion techniques commonly used for wafer doping in Si technology; since the diffusion temperatures required exceed that of arsenic loss.

3.1.3.5 Crystal Stress

The thermal gradient and, hence, stress generated in melt grown crystals have limited the maximum diameter of GaAs wafers (currently 6" diameter compared to over 12" for Si), because with increased wafer diameters the thermal stress generated dislocation (crystal imperfections) densities eventually becomes unacceptable for device applications.

3.1.3.6 Physical strength

Gallium arsenide single crystals are very brittle, requiring that considerably thicker substrates than those employed for Si devices.

3.1.3.7 Native oxide

Gallium arsenide's native oxide is found to be a mixture of non-stoichiometric gallium and arsenic oxides and elemental arsenic. Thus, the electronic band structure is found to be severely disrupted causing a breakdown in 'normal' semiconductor behavior on the GaAs surface. As a consequence, the GaAs MISFET (metal-insulator-semiconductor-field-effect-transistor) equivalent to the technologically important Si based MOSFET (metal-oxide-semiconductor-field-effect-transistor) is, therefore, presently unavailable.

The passivation of the surface of GaAs is therefore a key issue when endeavoring to utilize the FET technology using GaAs. Passivation in this discussion means the reduction in mid-gap band states which destroy the semiconducting properties of the material. Additionally, this also means the production of a chemically inert coating which prevents the formation of additional reactive states, which can effect the properties of the device.

3.1.4 Bibliography

- S. K. Ghandhi, *VLSI Fabrication Principles: Silicon and Gallium Arsenide.* Wiley-Interscience, New York, (1994).
- *Properties of Gallium Arsenide.* Ed. M. R. Brozel and G. E. Stillman. 3rd Ed. Institution of Electrical Engineers, London (1996).

3.2 Synthesis and Purification of Bulk Semiconductors[2]

3.2.1 Introduction

The synthesis and purification of bulk polycrystalline semiconductor material represents the first step towards the commercial fabrication of an electronic device. This polycrystalline material is then used as the raw material for the formation of single crystal material that is processed to semiconductor wafers. The strong influence on the electric characteristics of a semiconductors exhibited by small amounts of some impurities requires that the bulk raw material be of very high purity ($>$ 99.9999%). Although some level of purification is possible during the crystallization process it is important to use as high a purity starting material as possible. While a wide range of substrate materials are available from commercial vendors, silicon and GaAs represent the only large-scale commercial semiconductor substrates, and thus the discussion will be limited to the synthesis and purification of these materials.

3.2.2 Silicon

Following oxygen (46%), silicon (L. silicis flint) is the most abundant element in the earth's crust (28%). However, silicon does not occur in its elemental form, but as its oxide (SiO_2) or as silicates. Sand, quartz, amethyst, agate, flint, and opal are some of the forms in which the oxide appears. Granite, hornblende, asbestos, feldspar, clay and mica, etc. are a few of the numerous silicate minerals. With such boundless supplies of the raw material, the costs associated with the production of bulk silicon is not one of abstraction and conversion of the oxide(s), but of purification of the crude elemental silicon. While 98% elemental silicon, known as metallurgical-grade silicon (MGS), is readily produced on a large scale, the requirements of extreme purity for electronic device fabrication require additional purification steps in order to produce electronic-grade silicon (EGS). Electronic-grade silicon is also known as semiconductor-grade silicon (SGS). In order for the purity levels to be acceptable for subsequent crystal growth and device fabrication, EGS must have carbon and oxygen impurity levels less than a few parts per million (ppm), and metal impurities at the parts per billion (ppb) range or lower. Table 3.4 and Table 3.5 give typical impurity concentrations in MGS and EGS, respectively. Besides the purity, the production cost and the specifications must meet the industry desires.

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[2] This content is available online at <http://cnx.org/content/m23936/1.7/>.

Element	Concentration (ppm)	Element	Concentration (ppm)
aluminum	1000-4350	manganese	50-120
boron	40-60	molybdenum	< 20
calcium	245-500	nickel	10-105
chromium	50-200	phosphorus	20-50
copper	15-45	titanium	140-300
iron	1550-6500	vanadium	50-250
magnesium	10-50	zirconium	20

Table 3.4: Typical impurity concentrations found in metallurgical-grade silicon (MGS).

Element	Concentration (ppb)	Element	Concentration (ppb)
arsenic	< 0.001	gold	< 0.00001
antimony	< 0.001	iron	0.1-1.0
boron	≤ 0.1	nickel	0.1-0.5
carbon	100-1000	oxygen	100-400
chromium	< 0.01	phosphorus	≤ 0.3
cobalt	0.001	silver	0.001
copper	0.1	zinc	< 0.1

Table 3.5: Typical impurity concentrations found in electronic-grade silicon (EGS).

3.2.2.1 Metallurgical-grade silicon (MGS)

The typical source material for commercial production of elemental silicon is quartzite gravel; a relatively pure form of sand (SiO_2). The first step in the synthesis of silicon is the melting and reduction of the silica in a submerged-electrode arc furnace. An example of which is shown schematically in Figure 3.1, along with the appropriate chemical reactions. A mixture of quartzite gravel and carbon are heated to high temperatures (ca. 1800 °C) in the furnace. The carbon bed consists of a mixture of coal, coke, and wood chips. The latter providing the necessary porosity such that the gases created during the reaction (SiO and CO) are able to flow through the bed.

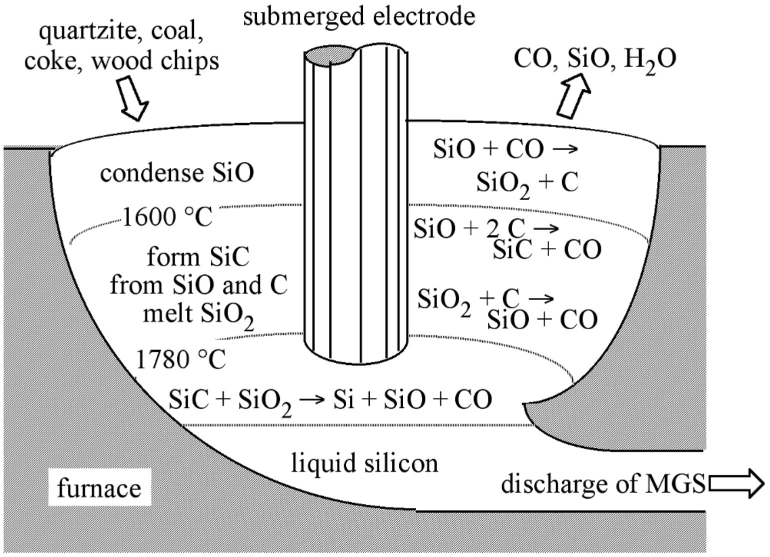

Figure 3.1: Schematic of submerged-electrode arc furnace for the production of metallurgical-grade silicon (MGS).

The overall reduction reaction of SiO_2 is expressed in (3.1), however, the reaction sequence is more complex than this overall reaction implies, and involves the formation of SiC and SiO intermediates. The initial reaction between molten SiO_2 and C ((3.2)) takes place in the arc between adjacent electrodes, where the local temperature can exceed 2000 °C. The SiO and CO thus generated flow to cooler zones in the furnace where SiC is formed ((3.3)), or higher in the bed where they reform SiO_2 and C ((3.2)). The SiC reacts with molten SiO_2 ((3.4)) producing the desired silicon along with SiO and CO. The molten silicon formed is drawn-off from the furnace and solidified.

$$SiO_2(\text{liquid}) + 2\,C(\text{solid}) \rightarrow Si(\text{liquid}) + 2\,CO\ (\text{gas}) \tag{3.1}$$

$$SiO_2 + 2\,C \underset{<1600\ °C}{\overset{>1700\ °C}{\rightleftharpoons}} SiO + CO \tag{3.2}$$

$$SiO + 2\,C \rightarrow SiC + CO\ \ (1600 - 1700\ °C) \tag{3.3}$$

$$SiC + SiO_2 \rightarrow Si + SiO + CO \tag{3.4}$$

The as-produced MGS is approximately 98-99% pure, with the major impurities being aluminum and iron (Table 3.4), however, obtaining low levels of boron impurities is of particular importance, because it is difficult to remove and serves as a dopant for silicon. The drawbacks of the above process are that it is energy and raw material intensive. It is estimated that the production of one metric ton (1,000 kg) of MGS requires 2500-2700 kg quartzite, 600 kg charcoal, 600-700 kg coal or coke, 300-500 kg wood chips, and 500,000 kWh of electric power. Currently, approximately 500,000 metric tons of MGS are produced per year, worldwide. Most of the production (ca. 70%) is used for metallurgical applications (e.g., aluminum-silicon alloys are commonly used for automotive engine blocks) from whence its name is derived. Applications in a variety of chemical products such as silicone resins account for about 30%, and only 1% or less of the total production of MGS is used in the manufacturing of high-purity EGS for the electronics industry. The current worldwide consumption of EGS is approximately 5 x 10^6 kg per year.

3.2.2.2 Electronic-grade silicon (EGS)

Electronic-grade silicon (EGS) is a polycrystalline material of exceptionally high purity and is the raw material for the growth of single-crystal silicon. EGS is one of the purest materials commonly available, see Table 3.5. The formation of EGS from MGS is accomplished through chemical purification processes. The basic concept of which involves the conversion of MGS to a volatile silicon compound, which is purified by distillation, and subsequently decomposed to re-form elemental silicon of higher purity (i.e., EGS). Irrespective of the purification route employed, the first step is physical pulverization of MGS followed by its conversion to the volatile silicon compounds.

A number of compounds, such as monosilane (SiH_4), dichlorosilane (SiH_2Cl_2), trichlorosilane ($SiHCl_3$), and silicon tetrachloride ($SiCl_4$), have been considered as chemical intermediates. Among these, $SiHCl_3$ has been used predominantly as the intermediate compound for subsequent EGS formation, although SiH_4 is used to a lesser extent. Silicon tetrachloride and its lower chlorinated derivatives are used for the chemical vapor deposition (CVD) growth of Si and SiO_2. The boiling points of silane and its chlorinated products (Table 3.6) are such that they are conveniently separated from each other by fractional distillation.

Compound	**Boiling point (°C)**
SiH_4	-112.3
SiH_3Cl	-30.4
SiH_2Cl_2	8.3
$SiHCl_3$	31.5
$SiCl_4$	57.6

Table 3.6: Boiling points of silane and chlorosilanes at 760 mmHg (1 atmosphere).

The reasons for the predominant use of $SiHCl_3$ in the synthesis of EGS are as follows:

1. $SiHCl_3$ can be easily formed by the reaction of anhydrous hydrogen chloride with MGS at reasonably low temperatures (200 - 400 °C);
2. it is liquid at room temperature so that purification can be accomplished using standard distillation techniques;
3. it is easily handled and if dry can be stored in carbon steel tanks;
4. its liquid is easily vaporized and, when mixed with hydrogen it can be transported in steel lines without corrosion;
5. it can be reduced at atmospheric pressure in the presence of hydrogen;
6. its deposition can take place on heated silicon, thus eliminating contact with any foreign surfaces that may contaminate the resulting silicon; and
7. it reacts at lower temperatures (1000 - 1200 °C) and at faster rates than does $SiCl_4$.

3.2.2.2.1 Chlorosilane (Seimens) process

Trichlorosilane is synthesized by heating powdered MGS with anhydrous hydrogen chloride (HCl) at around 300 °C in a fluidized-bed reactor, (3.5).

$$\mathrm{Si(solid)} + 3\,\mathrm{HCl(gas)} \underset{>900\ ^\circ\mathrm{C}}{\overset{\mathrm{ca.}\ 300\ ^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{SiHCl_3(vapor)} + \mathrm{H_2\ (gas)} \qquad (3.5)$$

Since the reaction is actually an equilibrium and the formation of $SiHCl_3$ highly exothermic, efficient removal of generated heat is essential to assure a maximum yield of $SiHCl_3$. While the stoichiometric reaction is that shown in Eq. 5, a mixture of chlorinated silanes is actually prepared which must be separated by fractional distillation, along with the chlorides of any impurities. In particular iron, aluminum, and boron are removed as $FeCl_3$ (b.p. = 316 °C), $AlCl_3$ (m.p. = 190 °C subl.), and BCl_3 (b.p. = 12.65 °C), respectively. Fractional distillation of $SiHCl_3$ from these impurity halides result in greatly increased purity with a concentration of electrically active impurities of less than 1 ppb.

EGS is prepared from purified $SiHCl_3$ in a chemical vapor deposition (CVD) process similar to the epitaxial growth of Si. The high-purity $SiHCl_3$ is vaporized, diluted with high-purity hydrogen, and introduced into the Seimens deposition reactor, shown schematically in Figure 3.2. Within the reactor, thin silicon rods called slim rods (ca. 4 mm diameter) are supported by graphite electrodes. Resistance heating of the slim rods causes the decomposition of the $SiHCl_3$ to yield silicon, as described by the reverse reaction shown in Eq. 5.

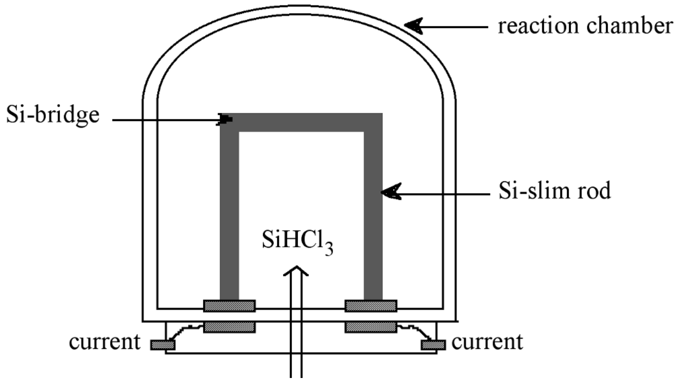

Figure 3.2: Schematic representation of a Seimens deposition reactor.

The shift in the equilibrium from forming $SiHCl_3$ from Si at low temperature, to forming Si from $SiHCl_3$ at high temperature is as a consequence of the temperature dependence ((3.6)) of the equilibrium constant ((3.7), where ρ = partial pressure) for (3.5). Since the formation of $SiHCl_3$ is exothermic, i.e., $\Delta H < 0$, an increase in the temperature causes the partial pressure of $SiHCl_3$ to decrease. Thus, the Siemens process is typically run at ca. 1100 °C, while the reverse fluidized bed process is carried out at 300 °C.

$$\ln K_p = \frac{-\Delta H}{RT} \qquad (3.6)$$

$$K_p = \frac{\rho_{SiHCl_3}\ \rho_{H_2}}{\rho_{HCl}} \tag{3.7}$$

The slim rods act as a nucleation point for the deposition of silicon, and the resulting polycrystalline rod consists of columnar grains of silicon (polysilicon) grown perpendicular to the rod axis. Growth occurs at less than 1 mm per hour, and after deposition for 200 to 300 hours high-purity (EGS) polysilicon rods of 150-200 mm in diameter are produced. For subsequent float-zone refining the polysilicon EGS rods are cut into long cylindrical rods. Alternatively, the as-formed polysilicon rods are broken into chunks for single crystal growth processes, for example Czochralski melt growth.

In addition to the formation of silicon, the HCl coproduct reacts with the $SiHCl_3$ reactant to form silicon tetrachloride ($SiCl_4$) and hydrogen as major byproducts of the process, (3.8). This reaction represents a major disadvantage with the Seimens process: poor efficiency of silicon and chlorine consumption. Typically, only 30% of the silicon introduced into CVD reactor is converted into high-purity polysilicon.

$$HCl + SiHCl_3 \rightarrow SiCl_4 + H_2 \tag{3.8}$$

In order to improve efficiency the HCl, $SiCl_4$, H_2, and unreacted $SiHCl_3$ are separated and recovered for recycling. Figure 3.3 illustrates the entire chlorosilane process starting with MGS and including the recycling of the reaction byproducts to achieve high overall process efficiency. As a consequence, the production cost of high-purity EGS depends on the commercial usefulness of the byproduct, $SiCl_4$. Additional disadvantages of the Seimens process are derived from its relatively small batch size, slow growth rate, and high power consumption. These issues have lead to the investigation of alternative cost efficient routes to EGS.

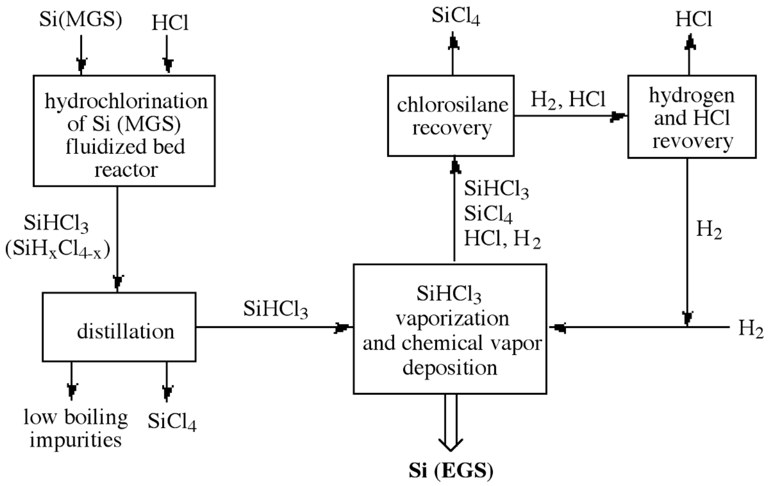

Figure 3.3: Schematic representation of the reaction pathways for the formation of EGS using the chlorosilane process.

3.2.2.2.2 Silane process

An alternative process for the production of EGS that has begun to receive commercial attention is the pyrolysis of silane (SiH_4). The advantages of producing EGS from SiH_4 instead of $SiHCl_3$ are potentially lower costs associated with lower reaction temperatures, and less harmful byproducts. Silane decomposes < 900 °C to give silicon and hydrogen, (3.9).

$$SiH_4(vapor) \rightarrow Si(solid) + 2\ H_2\,(gas) \tag{3.9}$$

Silane may be prepared by a number of routes, each having advantages with respect to purity and production cost. The simplest process involves the direct reaction of MGS powders with magnesium at 500 °C in a hydrogen atmosphere, to form magnesium silicide (Mg_2Si). The magnesium silicide is then reacted with ammonium chloride in liquid ammonia below 0 °C, (3.10).

$$Mg_2Si + 4\ NH_4Cl \rightarrow SiH_4 + 2\ MgCl_2 + 5\ NH_3 \tag{3.10}$$

This process is ideally suited to the removal of boron impurities (a p-type dopant in Si), because the diborane (B_2H_6) produced during the reaction forms the Lewis acid-base complex, $H_3B(NH_3)$, whose volatility is sufficiently lower than SiH_4, allowing for the purification of the latter. It is possible to prepare EGS with a boron content of $\leq$ 20 ppt using SiH_4 synthesized in this manner. However, phosphorus (another dopant) in the form of PH_3 may be present as a contaminant requiring subsequent purification of the SiH_4.

Alternative routes to SiH_4 involve the chemical reduction of $SiCl_4$ by either lithium hydride ((3.11)), lithium aluminum hydride ((3.12)), or via hydrogenation in the presence of elemental silicon ((3.13) - (3.16)). The hydride reduction reactions may be carried-out on relatively large scales (ca. 50 kg), but only batch processes. In contrast, Union Carbide has adapted the hydrogenation to a continuous process, involving disproportionation reactions of chlorosilanes ((3.14) - (3.16)) and the fractional distillation of silane (Table 3.6).

$$SiCl_4 + 4\ LiH \rightarrow SiH_4 + 4\ LiCl \tag{3.11}$$

$$SiCl_4 + 4\ LiAlH_4 \rightarrow SiH_4 + LiCl + AlCl_3 \tag{3.12}$$

$$SiCl_4 + 2\ H_2 + Si(98\%) \rightarrow 4\ SiHCl_3 \tag{3.13}$$

$$2\ SiHCl_3 \rightarrow SiH_2Cl_2 + SiCl_4 \tag{3.14}$$

$$3\ SiH_2Cl_2 \rightarrow SiH_3Cl + 2\ SiHCl_3 \tag{3.15}$$

$$2\ SiH_3Cl \rightarrow SiH_4 + SiH_2Cl_2 \tag{3.16}$$

Pyrolysis of silane on resistively heated polysilicon filaments at 700-800 °C yields polycrystalline EGS. As noted above, the EGS formed has remarkably low boron impurities compared with material prepared from trichlorosilane. Moreover, the resulting EGS is less contaminated with transition metals from the reactor container because SiH_4 decomposition does not cause as much of a corrosion problem as is observed with halide precursor compounds.

3.2.2.2.3 Granular polysilicon deposition

Both the chlorosilane (Seimens) and silane processes result in the formation of rods of EGS. However, there has been increased interest in the formation of granular polycrystalline EGS. This process was developed in 1980's, and relies on the decomposition of SiH_4 in a fluidized-bed deposition reactor to produce free-flowing granular polysilicon.

Tiny silicon particles are fluidized in a SiH_4/H_2 flow, and act as seed crystal onto which polysilicon deposits to form free-flowing spherical particles. The size distribution of the particles thus formed is over the range from 0.1 to 1.5 mm in diameter with an average particle size of 0.7 mm. The fluidized-bed seed particles are originally made by grinding EGS in a ball (or hammer) mill and leaching the product with acid, hydrogen peroxide, and water. This process is time-consuming and costly, and tended to introduce undesirable impurities from the metal grinders. In a new method, large EGS particles are fired at each other by a high-speed stream of inert gas and the collision breaks them down into particles of suitable size for a fluidized bed. This process has the main advantage that it introduces no foreign materials and requires no leaching or other post purification.

The fluidized-bed reactors are much more efficient than traditional rod reactors as a consequence of the greater surface area available during CVD growth of silicon. It has been suggested that fluidized-bed reactors require $^1/_5$ to $^1/_{10}$ the energy, and half the capital cost of the traditional process. The quality of fluidized-bed polysilicon has proven to be equivalent to polysilicon produced by the conventional methods. Moreover, granular EGS in a free-flowing form, and with high bulk density, enables crystal growers to obtain the high, reproducible production yields out of each crystal growth run. For example, in the Czochralski crystal growth process, crucibles can be quickly and easily filled to uniform loading with granular EGS, which typically exceed those of randomly stacked polysilicon chunks produced by the Siemens silane process.

3.2.2.3 Zone refining

The technique of zone refining is used to purify solid materials and is commonly employed in metallurgical refining. In the case of silicon may be used to obtain the desired ultimate purity of EGS, which has already been purified by chemical processes. Zone refining was invented by Pfann, and makes use of the fact that the equilibrium solubility of any impurity (e.g., Al) is different in the solid and liquid phases of a material (e.g., Si). For the dilute solutions, as is observed in EGS silicon, an equilibrium segregation coefficient (k_0) is defined by $k_0 = C_s/C_l$, where C_s and C_l are the equilibrium concentrations of the impurity in the solid and liquid near the interface, respectively.

If k_0 is less than 1 then the impurities are left in the melt as the molten zone is moved along the material. In a practical sense a molten zone is established in a solid rod. The zone is then moved along the rod from left to right. If $k < 1$ then the frozen part left on the trailing edge of the moving molten zone will be purer than the material that melts in on the right-side leading edge of the moving molten zone. Consequently the solid to the left of the molten zone is purer than the solid on the right. At the completion of the first pass the impurities become concentrated to the right of the solid sample. Repetition of the process allows for purification to exceptionally high levels. Table 3.7. lists the equilibrium segregation coefficients for common impurity and dopant elements in silicon; it should be noted that they are all less than 1.

Element	**k_0**	**Element**	**k_0**
aluminum	0.002	iron	8×10^{-6}
boron	0.8	oxygen	0.25
carbon	0.07	phosphorus	0.35
copper	4×10^{-6}	antimony	0.023

Table 3.7: Segregation coefficients for common impurity and dopant elements in silicon.

3.2.3 Gallium arsenide

In contrast to electronic grade silicon (EGS), whose use is a minor fraction of the global production of elemental silicon, gallium arsenide (GaAs) is produced exclusively for use in the semiconductor industry. However, arsenic and its compounds have significant commercial applications. The main use of elemental arsenic is in alloys of Pb, and to a lesser extent Cu, while arsenic compounds are widely used in pesticides and wood preservatives and the production of bottle glass. Thus, the electronics industry represents a minor user of arsenic. In contrast, although gallium has minor uses as a high-temperature liquid seal, manometric fluids and heat transfer media, and for low temperature solders, its main use is in semiconductor technology.

3.2.3.1 Isolation and purification of gallium metal

At 19 ppm gallium (L. *Gallia*, France) is about as abundant as nitrogen, lithium and lead; it is twice as abundant as boron (9 ppm), but is more difficult to extract due to the lack of any major gallium-containing ore. Gallium always occurs in association either with zinc or germanium, its neighbors in the periodic table, or with aluminum in the same group. Thus, the highest concentrations (0.1-1%) are in the rare mineral germanite (a complex sulfide of Zn, Cu, Ge, and As), while concentrations in sphalerite (ZnS), diaspore [AlO(OH)], bauxite, or coal, are a hundred-fold less. Industrially, gallium was originally recovered from the flue dust emitted during sulfide roasting or coal burning (up to 1.5% Ga), however, it is now obtained as side product of vast aluminum industry and in particular from the Bayer process for obtaining alumina from bauxite.

The Bayer process involves dissolution of bauxite, AlO_xOH_{3-2x}, in aqueous NaOH, separation of insoluble impurities, partial precipitation of the trihydrate, $Al(OH)_3$, and calcination at 1,200 °C. During processing the alkaline solution is gradually enriched in gallium from an initial weight ratio Ga/Al of about 1/5000 to about 1/300. Electrolysis of these extracts with a Hg cathode results in further concentration, and the solution of sodium gallate thus formed is then electrolyzed with a stainless steel cathode to give Ga metal. Since bauxite contains 0.003-0.01% gallium, complete recovery would yield some 500-1000 tons per annum, however present consumption is only 0.1% of this about 10 tons per annum.

A typical analysis of the 98-99% pure gallium obtained as a side product from the Bayer process is shown in Table 3.8. This material is further purified to 99.99% by chemical treatment with acids and O_2 at high temperatures followed by crystallization. This chemical process results in the reduction of the majority of metal impurities at the ppm level, see Table 3.8. Purification to seven nines 99.9999% is possible through zone refining, however, since the equilibrium distribution coefficient of the residual impurities $k_0 \approx 1$, multiple passes are required, typically > 500. The low melting point of gallium ensures that contamination from the container wall (which is significant in silicon zone refining) is minimized. In order to facilitate the multiple zone refining in a suitable time, a simple modification of zone refining is employed shown in Figure 3.4. The gallium is contained in a plastic tube wrapped around a rotating cylinder that is half immersed in a cooling bath. A heater is positioned above the gallium plastic coil. Thus, establishing a series of molten zones that pass upon rotation of the drum by one helical segment per revolution. In this manner, 500 passes may be made in relatively short time periods. The typical impurity levels of gallium zone refined in this manner are given in Table 3.8.

Element	**Bayer process (ppm)**	**After acid/base leaching (ppm)**	**500 zone passes (ppm)**

continued on next page

aluminum	100-1,000	7	< 1
calcium	10-100	not detected	not detected
copper	100-1,000	2	< 1
iron	100-1,000	7	< 1
lead	< 2000	30	not detected
magnesium	10-100	1	not detected
mercury	10-100	not detected	not detected
nickel	10-100	not detected	not detected
silicon	10-100	≈ 1	not detected
tin	10-100	≈ 1	not detected
titanium	10-100	1	< 1
zinc	30,000	≈ 1	not detected

Table 3.8: Typical analysis of gallium obtained as a side product from the Bayer process.

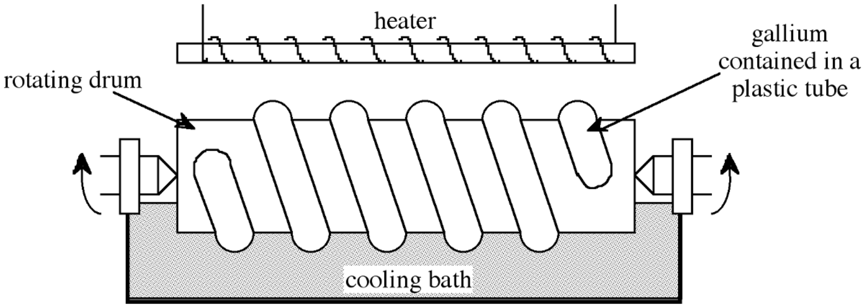

Figure 3.4: Schematic representation of a zone refining apparatus.

3.2.3.2 Isolation and purification of elemental arsenic

Elemental arsenic (L. arsenicum, yellow orpiment) exists in two forms: yellow (cubic, As_4) and gray or metallic (rhombohedral). At a natural abundance of 1.8 ppm arsenic is relatively rare, however, this is offset by its presence in a number of common minerals and the relative ease of isolation. Arsenic containing minerals are grouped into three main classes: the sulfides realgar (As_4S_4) and orpiment (As_2S_3), the oxide arsenolite (As_2O_3), and the arsenides and sulfaresenides of the iron, cobalt, and nickel. Minerals in this latter class include: loellinginite ($FeAs_2$), safforlite (CoAs), niccolite (NiAs), rammelsbergite ($NiAs_2$), ansenopyrite or mispickel (FeAsS), cobaltite (CoAsS), enargite (Cu_3AsS_4), gerdsorfite (NiAsS), and the quarturnary sulfide glaucodot [(Co,Fe)AsS]. Table 3.9 shows the typical impurities in arsenopyrite.

Element	**Concentration (ppm)**	**Element**	**Concentration (ppm)**
silver	90	nickel	< 3,000
gold	8	lead	50
cobalt	30,000	platinum	0.4
copper	200	rhenium	50
germanium	30	selenium	50
manganese	3,000	vanadium	300
molybdenum	60	zinc	400

Table 3.9: Typical impurities in arsenopyrite.

Arsenic is obtained commercially by smelting either $FeAs_2$ or FeAsS at 650-700 °C in the absence of air and condensing the sublimed element ($T_{sub} = 613$ °C), (3.17).

$$\text{FeAsS} \xrightarrow{650\text{-}700\ ^\circ\text{C}} \text{FeS} + \text{As(vapor)} \xrightarrow{<613\ ^\circ\text{C}} \text{As(solid)} \tag{3.17}$$

The arsenic thus obtained is combined with lead and then sublimed ($T_{sub} = 614$ °C) which binds any sulfur impurities more strongly than arsenic. Any residual arsenic that remains trapped in the iron sulfide is separated by forming the oxide (As_2O_3) by roasting the sulfide in air. The oxide is sublimed into the flue system during roasting from where it is collected and reduced with charcoal at 700-800 °C to give elemental arsenic. Semiconductor grade arsenic (> 99.9999%) is formed by zone refining.

3.2.3.3 Synthesis and purification of gallium arsenide.

Gallium arsenide can be prepared by the direct reaction of the elements, (3.18). However, while conceptually simple the synthesis of GaAs is complicated by the different vapor pressures of the reagents and the highly exothermic nature of the reaction. Furthermore, since the synthesis of GaAs at atmospheric pressure is accompanied by its simultaneous decomposes due to the loss by sublimation, of arsenic, the synthesis must be carried out under an overpressure of arsenic in order to maintain a stoichiometric composition of the synthesized GaAs.

$$\text{Ga(liquid)} + \text{As(vapor)} \xrightarrow{>1240\ ^\circ\text{C}} \text{GaAs(solid)} \tag{3.18}$$

In order to overcome the problems associated with arsenic loss, the reaction is usually carried out in a sealed reaction tube. However, if a stoichiometric quantity of arsenic is used in the reaction a constant temperature of 1238 °C must be employed in order to maintain the desired arsenic overpressure of 1 atm. Practically, it is easier to use a large excess of arsenic heated to a lower temperature. In this situation the pressure in the tube is approximately equal to the equilibrium vapor pressure of the volatile component (arsenic) at the lower temperature. Thus, an over pressure of 1 atm arsenic may be maintained if within a sealed tube elemental arsenic is heated to 600-620 °C while the GaAs is maintained at 1240-1250 °C.

Figure 3.5 shows the sealed tube configuration that is typically used for the synthesis of GaAs. The tube is heated within a two-zone furnace. The boats holding the reactants are usually made of quartz, however, graphite is also used since the latter has a closer thermal expansion match to the GaAs product. If higher purity is required then pyrolytic boron nitride (PBN) is used. One of the boats is loaded with pure gallium the other with arsenic. A plug of quartz wool may be placed between the boats to act as a diffuser. The tube is then evacuated and sealed. Once brought to the correct reaction temperatures (Figure 3.5), the arsenic vapor is transported to the gallium, and they react to form GaAs in a controlled manner. Table 3.10 gives the typical impurity concentrations found in polycrystalline GaAs.

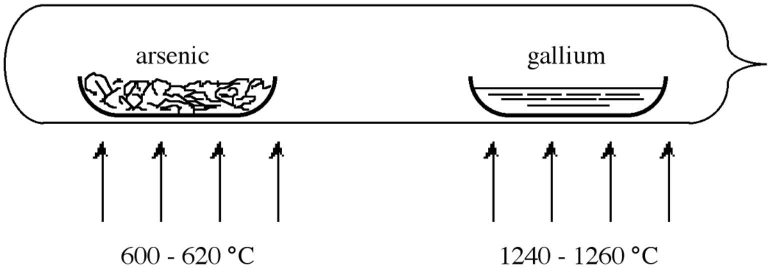

Figure 3.5: Schematic representation of a sealed tube synthesis of GaAs.

Element	**Concentration (ppm)**	**Element**	**Concentration (ppm)**
boron	0.1	silicon	0.02
carbon	0.7	phosphorus	0.1
nitrogen	0.1	sulfur	0.01
oxygen	0.5	chlorine	0.08
fluorine	0.2	nickel	0.04
magnesium	0.02	copper	0.01
aluminum	0.02	zinc	0.05

Table 3.10: Impurity concentrations found in polycrystalline GaAs.

Polycrystalline GaAs, formed in from the direct reaction of the elements is often used as the starting material for single crystal growth *via* Bridgeman or Czochralski crystal growth. It is also possible to prepare single crystals of GaAs directly from the elements using in-situ, or direct, compounding within a high-pressure liquid encapsulated Czochralski (HPLEC) technique.

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3.3 Growth of Gallium Arsenide Crystals[3]

3.3.1 Introduction

When considering the synthesis of Group 13-15 compounds for electronic applications, the very nature of semiconductor behavior demands the use of high purity single crystal materials. The polycrystalline materials synthesized above are, therefore, of little use for 13-15 semiconductors but may, however, serve as the starting material for melt grown single crystals. For GaAs, undoubtedly the most important 13-15 (III - V) semiconductor, melt grown single crystals are achieved by one of two techniques: the Bridgman technique, and the Czochralski technique.

3.3.2 Bridgman growth

The Bridgman technique requires a two-zone furnace, of the type shown in Figure 3.6. The left hand zone is maintained at a temperature of *ca.* 610 °C, allowing sufficient overpressure of arsenic within the sealed system to prevent arsenic loss from the gallium arsenide. The right hand side of the furnace contains the polycrystalline GaAs raw material held at a temperature just above its melting point (*ca.* 1240 °C). As the furnace moves from left to right, the melt cools and solidifies. If a seed crystal is placed at the left hand side of the melt (at a point where the temperature gradient is such that only the end melts), a specific orientation of single crystal may be propagated at the liquid-solid interface eventually to produce a single crystal.

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[3] This content is available online at <http://cnx.org/content/m40280/1.1/>.

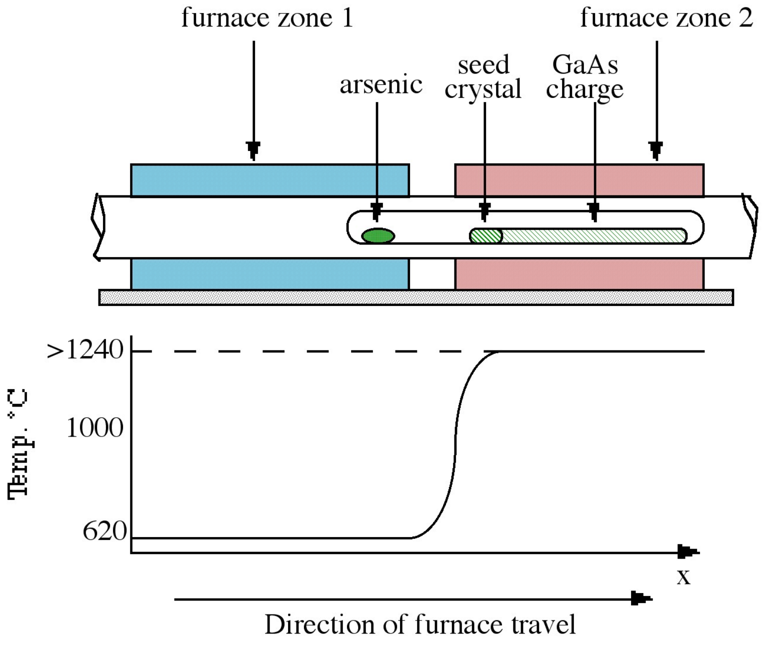

Figure 3.6: A schematic diagram of a Bridgman two-zone furnace used for melt growths of single crystal GaAs.

3.3.3 Czochralski growth

The Czochralski technique, which is the most commonly used technique in industry, is shown in Figure 3.7. The process relies on the controlled withdrawal of a seed crystal from a liquid melt. As the seed is lowered into the melt, partial melting of the tip occurs creating the liquid solid interface required for crystal growth. As the seed is withdrawn, solidification occurs and the seed orientation is propagated into the grown material. The variable parameters of rate of withdrawal and rotation rate can control crystal diameter and purity. As shown in Figure 3.7 the GaAs melt is capped by boron trioxide (B_2O_3). The capping layer, which is inert to GaAs, prevents arsenic loss when the pressure on the surface is above atmospheric pressure. The growth of GaAs by this technique is thus termed liquid encapsulated Czochralski (LEC) growth.

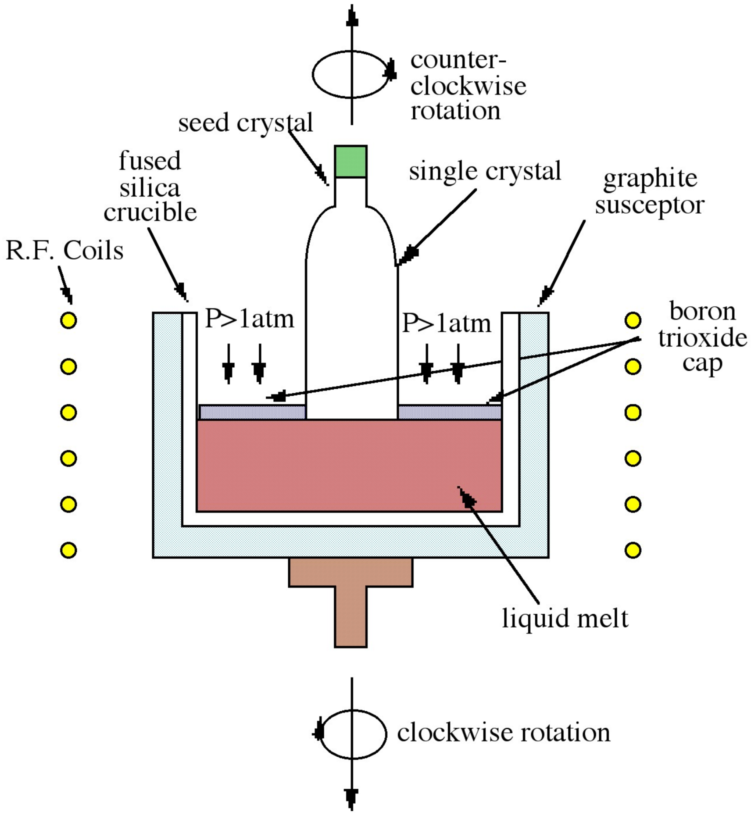

Figure 3.7: A schematic diagram of the Czochralski technique as used for growth of GaAs single crystal bond.

While the Bridgman technique is largely favored for GaAs growth, larger diameter wafers can be obtained by the Czochralski method. Both of these melt techniques produce materials heavily contaminated by the crucible, making them suitable almost exclusively as substrate material. Another disadvantage of these techniques is the production of defects in the material caused by the melt process.

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3.4 Ceramic Processing of Alumina[4]

3.4.1 Introduction

While aluminum is the most abundant metal in the earth's crust (*ca.* 8%) and aluminum compounds such as alum, $K[Al(SO_4)_2].12(H_2O)$, were known throughout the world in ancient times, it was not until the

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[4] This content is available online at <http://cnx.org/content/m22376/1.6/>.

isolation of aluminum in the late eighteenth century by the Danish scientist H. C. Öersted that research into the chemistry of the Group 13 elements began in earnest. Initially, metallic aluminum was isolated by the reduction of aluminum trichloride with potassium or sodium; however, with the advent of inexpensive electric power in the late 1800's, it became economically feasible to extract the metal *via* the electrolyis of alumina (Al_2O_3) dissolved in cryolite, Na_3AlF_6, (the Hall-Heroult process). Today, alumina is prepared by the Bayer process, in which the mineral bauxite (named for Les Baux, France, where it was first discovered) is dissolved with aqueous hydroxides, and the solution is filtered and treated with CO_2 to precipitate alumina. With availability of both the mineral and cheap electric power being the major considerations in the economical production of aluminum, it is not surprising that the leading producers of aluminum are the United States, Japan, Australia, Canada, and the former Soviet Union.

3.4.2 Aluminum oxides and hydroxides

The many forms of aluminum oxides and hydroxides are linked by complex structural relationships. Bauxite has the formula $Al_x(OH)_{3-2x}$ ($0 < x < 1$) and is thus a mixture of Al_2O_3 (α-alumina), $Al(OH)_3$ (gibbsite), and $AlO(OH)$ (boehmite). The latter is an industrially important compound which is used in the form of a gel as a pre-ceramic in the production of fibers and coatings, and as a fire retarding agent in plastics.

Heating boehmite and diaspore to 450 °C causes dehydration to yield forms of alumina which have structures related to their oxide-hydroxide precursors. Thus, boehmite produces the low-temperature form γ-alumina, while heating diaspore will give α-alumina (corundum). γ-alumina converts to the hcp structure at 1100 °C. A third form of Al_2O_3 forms on the surface of the clean aluminum metal. The thin, tough, transparent oxide layer is the reason for much of the usefulness of aluminum. This oxide skin is rapidly self-repairing because its heat of formation is so large (ΔH = -3351 kJ/mol).

$$4\,Al + 3\,O_2 \rightarrow 2\,Al_2O_3 \tag{3.19}$$

3.4.2.1 Ternary and mixed-metal oxides

A further consequence of the stability of alumina is that most if not all of the naturally occurring aluminum compounds are oxides. Indeed, many precious gemstones are actually corundum doped with impurities. Replacement of aluminum ions with trace amounts of transition-metal ions transforms the formerly colorless mineral into ruby (red, Cr^{3+}), sapphire (blue, $Fe^{2+/3+}$, Ti^{4+}), or topaz (yellow, Fe^{3+}). The addition of stoichiometric amounts of metal ions causes a shift from the α-Al_2O_3 hcp structure to the other common oxide structures found in nature. Examples include the perovskite structure for ABO_3 type minerals (e.g., $CeTiO_7$ or $LaAlO_3$) and the spinel structure for AB_2O_4 minerals (e.g., beryl, $BeAl_2O_4$).

Aluminum oxide also forms ternary and mixed-metal oxide phases. Ternary systems such as mullite ($Al_6Si_2O_{13}$), yttrium aluminum garnet (YAG, $Y_3Al_5O_{12}$), the β-aluminas (e.g., $NaAl_{11}O_{17}$) and aluminates such as hibonite ($CaAl_{12}O_{19}$) possessing β-alumina or magnetoplumbite-type structures can offer advantages over those of the binary aluminum oxides.

Applications of these materials are found in areas such as engineering composite materials, coatings, technical and electronic ceramics, and catalysts. For example, mullite has exceptional high temperature shock resistance and is widely used as an infrared-transparent window for high temperature applications, as a substrate in multilayer electronic device packaging, and in high temperature structural applications. Hibonite and other hexaluminates with similar structures are being evaluated as interfacial coatings for ceramic matrix composites due to their high thermal stability and unique crystallographic structures. Furthermore, aluminum oxides doped with an alkali, alkaline earth, rare earth, or transition metal are of interest for their enhanced chemical and physical properties in applications utilizing their unique optoelectronic properties.

3.4.3 Synthesis of aluminum oxide ceramics

In common with the majority of oxide ceramics, two primary synthetic processes are employed for the production of aluminum oxide and mixed metal oxide materials:

1. The traditional ceramic powder process.
2. The solution-gelation, or "sol-gel" process.

The environmental impact of alumina and alumina-based ceramics is in general negligible; however, the same cannot be said for these methods of preparation. As practiced commercially, both of the above processes can have a significant detrimental environmental impact.

3.4.3.1 Traditional ceramic processing

Traditional ceramic processing involves three basic steps generally referred to as powder-processing, shape-forming, and densification, often with a final mechanical finishing step. Although several steps may be energy intensive, the most direct environmental impact arises from the shape-forming process where various binders, solvents, and other potentially toxic agents are added to form and stabilize a solid ("green") body (Table 3.11).

Function	**Composition**	**Volume (%)**
Powder	alumina (Al_2O_3)	27
Solvent	1,1,1-trichloroethane/ethanol	58
Deflocculant	menhaden oil	1.8
Binder	poly(vinyl butyrol)	4.4
Plasticizer	poly(ethylene glycol)/octyl phthalate	8.8

Table 3.11: Typical composition of alumina green body

The component chemicals are mixed to a slurry, cast, then dried and fired. In addition to any innate health risk associated with the chemical processing these agents are subsequently removed in gaseous form by direct evaporation or pyrolysis. The replacement of chlorinated solvents such as 1,1,1-trichloroethylene (TCE) must be regarded as a high priority for limiting environmental pollution. The United States Environmental Protection Agency (EPA) included TCE on its 1991 list of 17 high-priority toxic chemicals targeted for source reduction. The plasticizers, binders, and alcohols used in the process present a number of potential environmental impacts associated with the release of combustion products during firing of the ceramics, and the need to recycle or discharge alcohols which, in the case of discharge to waterways, may exert high biological oxygen demands in the receiving communities. It would be desirable, therefore, to be able to use aqueous processing; however, this has previously been unsuccessful due to problems associated with batching, milling, and forming. Nevertheless, with a suitable choice of binders, etc., aqueous processing is possible. Unfortunately, in many cast-parts formed by green body processing the liquid solvent alone consists of over 50 % of the initial volume, and while this is not directly of an environmental concern, the resultant shrinkage makes near net shape processing difficult.

3.4.3.2 Sol-gel

Whereas the traditional sintering process is used primarily for the manufacture of dense parts, the solution-gelation (sol-gel) process has been applied industrially primarily for the production of porous materials and coatings.

Sol-gel involves a four stage process: dispersion, gelation, drying, and firing. A stable liquid dispersion or *sol* of the colloidal ceramic precursor is initially formed in a solvent with appropriate additives. By changing the concentration (aging) or pH, the dispersion is "polymerized" to form a solid dispersion or *gel*. The excess liquid is removed from this gel by drying and the final ceramic is formed by firing the gel at higher temperatures.

The common sol-gel route to aluminum oxides employs aluminum hydroxide or hydroxide-based material as the solid colloid, the second phase being water and/or an organic solvent, however, the strong interactions of the freshly precipitated alumina gels with ions from the precursor solutions makes it difficult to prepare these gels in pure form. To avoid this complication, alumina gels are also prepared from the hydrolysis of aluminum alkoxides, $Al(OR)_3$.

$$Al(OR)_3 + H_2O/H^+ \rightarrow \text{Al-gel} \tag{3.20}$$

$$\text{Al-gel} \xrightarrow{\Delta} Al_2O_3 \tag{3.21}$$

The exact composition of the gel in commercial systems is ordinarily proprietary, however, a typical composition will include an aluminum compound, a mineral acid, and a complexing agent to inhibit premature precipitation of the gel, e.g., Table 3.12.

Function	**Composition**
Boehmite precursor	ASB [aluminum *sec*-butoxide, $Al(OC_4H_9)_3$]
Electrolyte	HNO_3 0.07 mole/mole ASB
Complexing agent	glycerol *ca.* 10 wt.%

Table 3.12: Typical composition of an alumina sol-gel for slipcast ceramics.

The principal environmental consequences arising from the sol-gel process are those associated with the use of strong acids, plasticizers, binders, solvents, and *sec*-butanol formed during the reaction. Depending on the firing conditions, variable amounts of organic materials such as binders and plasticizers may be released as combustion products. NO_x's may also be produced in the off-gas from residual nitric acid or nitrate salts. Moreover, acids and solvents must be recycled or disposed of. Energy consumption in the process entails "upstream" environmental emissions associated with the production of that energy.

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3.5 Piezoelectric Materials Synthesis[5]

This module was developed as part of the Rice University course CHEM-496: *Chemistry of Electronic Materials*. This module was prepared with the assistance of Ilse Y. Guzman-Jimenez.

3.5.1 Introduction

Piezoelectricity is the generation of an electric moment by a change of stress applied to a solid. The word piezoelectricity literally means “pressure electricity”; the prefix piezo is derived from the Greek word *piezein*, “to press”. The piezoelectric effect was discovered in 1880 by the brothers Jacques and Pierre Curie. Not only did they demonstrate the phenomenon, but they also established the criteria for its existence in a given crystal. Of the thirty-two crystal classes, twenty-one are non-centrosymmetric (not having a centre of symmetry), and of these, twenty exhibit direct piezoelectricity.

The first practical application of the piezoelectric effect was developed when ground quartz crystals were placed between the plates of a tuning capacitor in order to stabilize oscillating circuits in radio transmitters and receivers; however, the phenomenon of piezoelectricity was not well exploited until World War I, when Langevin used piezoelectrically excited quartz plates to generate sounds waves in water for use in submarine detection.

Piezoelectricity can also occur in polycrystalline or amorphous substances which have become anisotropic by external agents. Synthetic piezoelectric materials became available near the end of World War II, with the accidental discovery of the fact that materials like barium titanate and rare earth oxides become piezoelectric when they are polarized electrically. During the postwar years, when germanium and silicon were revolutionizing the electronics industry, piezoceramics appeared for a while to be joining the revolution, but the limited availability of materials and components, made the piezoelectric phenomenon failed to lead mature applications during the 1950s. It is only now that a variety of piezoelectric materials are being synthesized and optimized. As a consequence piezoelectric-based devices are undergoing a revolutionary development, specially for medicine and aerospace applications.

3.5.2 Piezoelectric ceramics

Most piezoelectric transducers are made up of ceramic materials for a broad range of electromechanical conversion tasks as transmitters, ranging from buzzers in alarm clocks to sonars, and as receivers, ranging from ultra high frequency (UHF) filters to hydrophones.

Most of the piezoelectric materials in usage are from the lead zirconate titanate (PZT) family, because of their excellent piezoelectric parameters, thermal stability, and dielectric properties. Additionally the properties of this family can be modified by changing the zirconium to titanium ratio or by addition of both metallic and non-metallic elements. PZT ($PbZr_{1-x}Ti_xO_3$) ceramics and their solid solutions with several complex perovskite oxides have been studied; among the various complex oxide materials, niobates have attracted special attention. Ternary ceramic materials, lead metaniobate, as well as, barium and modified lead titanates complete the list of piezoceramic materials.

Selective parameters for piezoceramic materials are given in Table 3.13, where Q_m is the mechanical quality factor, T_c is the Curie point, d_{31} is the the transverse charge coefficient, and k_p, k_t and k_{31} are the electromechanical coupling factors for planar, thickness, and transversal mode respectively.

Material property	**PZT modified**	**Lead metaniobate**	**PSZNT 31/40/29**	**PZT, x = 0.5**	**PSN-PLT**	**TsTS-42-1 50/50**	**PZT, x = 0.48**

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[5] This content is available online at <http://cnx.org/content/m25441/1.2/>.

Q_m	350	40	222	74	41	887	
T_c (°C)	290	462		369	152		355
d_{31} (x10^{-12} C/N)					-79	50	
k_p	0.5		60	0.428	30.7	46.5	
k_t		0.32		0.438	-		
k_{31}		0.21		0.263	17.9		

Table 3.13: Selective parameters for illustrative piezoceramic materials.

Recently, sol-gel processing has been used to prepare ceramics, making possible the preparation of materials that are difficult to obtain by conventional methods. Both, inorganic and organic precursor have been reported. Additionally, new techniques for the production of ceramic fibers have been developed. Better processing and geometrical and microestructural control are the main goals in the production of fibers.

The latest development in piezoceramic fibers is the modification of the viscous-suspension-spinning process (VSSP) for the production of continuos piezoelectric ceramic fibers for smart materials and active control devices, such as transducers, sensor/actuators and structural-control devices. The VSSP utilizes conventional synthesized ceramic powders and cellulose, as the fugitive carrier, to produce green ceramic fiber at a reasonable cost. Figure 3.8 shows the schematic representation of the VSSP.

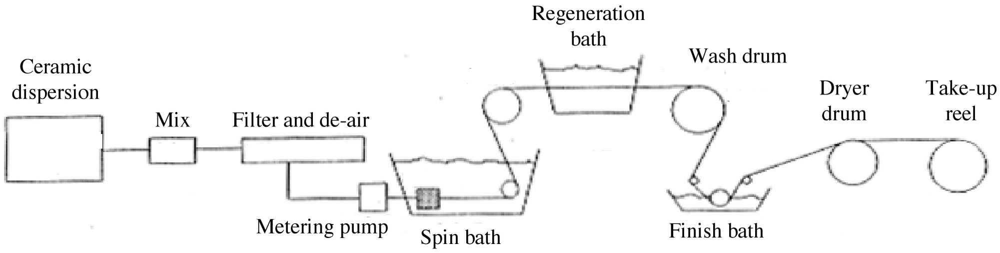

Figure 3.8: The viscous-suspension-spinning process (VSSP) for the production of continuous piezoceramic fiber.

Synthesis of reactive PZT precursor powder by the oxalate coprecipitation technique has also been developed. The precursor transforms to phase pure PZT at or above 850 °C the PZT obtained by this technique showed a Curie temperature of 355 °C. The advantages of the coprecipitation technique are the lack of moisture sensitive and special handling precursors.

Although new materials have been investigated with the purpose of create replacements for ceramics, there has been a great improvement in their properties and, current research is focused in the development of new techniques for both synthesis and processing.

3.5.3 Piezoelectric single crystals.

The recent progress of the electronic technology requires new piezoelectric crystals with a high thermal stability and large electromechanical coupling factors. Single-crystal materials have been considered as replacements for polycrystalline ceramics. Ideally single-crystals of lead zirconate titanate (PZT) itself would be the main choice as it is the most prevailing piezoelectric material, but it is difficult to grow large single crystals. On the other hand, the fact that single-crystals offer many advantages over polycrystalline systems has been recognized. Materials such as lithium niobate present essentially no aging, no mechanical creep and excellent performance in high temperature conditions.

New piezoelectric single crystals grown by conventional RF-heating Czochralski (CZ) technique have been synthesized. High purity starting materials, mainly oxides powders, and Ar atmosphere are required. $La_3Ga_5SiO_{14}$, $La_3Nb_{0.5}Ga_{5.5}O_{14}$ and $La_3Ta_{0.5}Ga_{5.5}O_{14}$ single crystals have been grown by using this method. However, the CZ technique can be applied only to materials that can be synthesized by ordinary solid-state reaction and can undergo the pulling method.

$BaBe_2Si_2O_7$ (barylite) has been known as material with a strong piezoelectricity, however, it can not be obtained by solid-state reaction and CZ technique therefore is not applicable. As an alternative for piezoelectric crystals growth hydrothermal synthesis has been developed. Figure 3.9 shows the experimental apparatus for the growth of barylite. Eventhough, crystals can be obtained using this technique, high pressure (500 - 1000 bar) and a solvent for the raw materials are required.

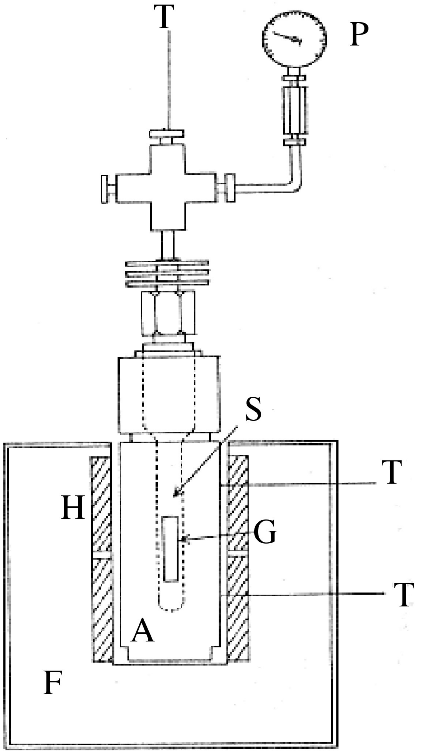

Figure 3.9: Experimental apparatus for the hydrothermal synthesis of barylite. H = heater, F = furnace, S = specimen vessel, G = growth capsule, P = pressure gauge, and T = thermocouples. Adapted from M. Maeda, T. Uehara, H. Sato and T. Ikeda, *Jpn. J. Appl. Phys.*, 1991, **30**, 2240.

While the piezoceramics dominate the single crystal materials in usage, single crystals piezoelectrics continue to make important contributions both in price-conscious consumer market and in performance-driven defense applications. Areas such as frequency stabilized oscillators, surface acoustic wave devices and filters with a wide pass band, are still dominated by single crystals.

3.5.4 Piezoelectric thin films

Recently, there has been great interest in the deposition of piezoelectric thin films, mainly for microelectronical systems (MEMS) applications; where the goal is to integrate sensors and actuators based on PZT films with Si semiconductor-based signal processing; and for surface acoustic wave (SAW) devices; where the goal is to achieve higher electromechanical coupling coefficient and temperature stability. Piezoelectrical microcantilevers, microactuators, resonators and SAW devices using thin films have been reported.

Several methods have been investigated for PZT thin films. In the metallo-organic thin film deposition, alkoxides are stirred during long periods of time (up to 18 hours). After pyrolisis, PZT amorphous films are formed and then calcination between 400 – 600 °C for 80 hours leads to PZT crystallization (perovskita phase) by a consecutive phase transformation process, which involves a transitional pyrochlore phase.

A hybrid metallorganic decomposition (MOD) route has also been developed to prepare PZT thin films. Lead and titanium acetates and, zirconium acetylacetonate are used. The ferroelectric piezoelectric and dielectric properties indicate that the MOD route provides PZT films of good quality and comparable to literature values. In addition to being simple, MOD has several advantages which include: homogeneity at molecular level and ease composition control.

Metalorganic chemical vapor deposition (MOCVD) has been applied to PZT thin films deposition also. It has been proved that excellent quality PZT films can be grown by using MOCVD, but just recently the control of microstructure the deposition by varying the temperature, Zr to Ti ratio and precursors flow has been studied. Recent progress in PZT films deposition has led to lower temperature growth and it is expected that by lowering the deposition temperature better electrical properties can be achieved. Additionally, novel techniques such as KrF excimer laser ablation and, ion and photo-assisted depositions, have also been used for PZT films synthesis.

On the other hand, a single process to deposit PZT thin film by a hydrothermal method has been reported recently. Since the sol-gel method, sputtering and chemical vapor deposition techniques are useful only for making flat materials, the hydrothermal method offers the advantage of making curved shaped materials. The hydrothermal method utilizes the chemical reaction between titanium and ions melted in solution. A PZT thin film has been successfully deposited directly on a titanium substrate and the optimum ion ratio in the solution is being investigated to improve the piezoelectric effect.

Among the current reported piezoelectric materials, the $Pb(Ni_{1/3}Nb_{2/3})_{0.2}Zr_{0.4}Ti_{0.4}O_3$ (PNNZT, 2/4/4) ferroelectric ceramic has piezoelectric properties that are about 60 and 3 times larger than the reported values for ZnO and PZT. A sol-gel technique has been developed for the deposition of a novel piezoelectric PNNZT thin film. A 2-methoxyethanol based process is used. In this process precursors are heated at lower temperature than the boiling point of the solvent, to distill off water. Then prior high temperature annealing, addition of excess Pb precursor in the precursor solution is required to compensate the lead loss. The pure perovskite phase is then obtained at 600 °C, after annealing.

Thin films of zinc oxide (ZnO), a piezoelectric material and n-type wide-bandgap semiconductor, have been deposited. ZnO films are currently used in SAW devices and in electro-optic modulators. ZnO thin films have been grown by chemical vapor deposition and both d.c. and r.f. sputtering techniques. Recently, optimization of ZnO films by r.f. magnetron sputtering has been developed. However, homogeneity is one of the main problems when using this technique, since films grown by this optimized method, showed two regions with different piezoelectric properties.

DC magnetron sputtering is other technique for piezoelectric thin film growth, recently aluminum nitride, a promising material for use in thin-film bulk acoustic wave resonators for applications in RF bandpass filters, has been grown by this method. The best quality films are obtained on Si substrates. In order to achieve the highest resonator coupling, the AlN must be grown directly on the electrodes. The main problem in the AlN growth is the oxygen contamination, which leads to the formation of native oxide on the Al surface, preventing crystalline growth of AlN.

3.5.5 Piezoelectric polymers

The discovery of piezoelectricity in polymeric materials such as polyvinylidene difluoride (PVF), was considered as an indication of a renaissance in piezoelectricity. Intensive research was focused in the synthesis and functionalization of polymers. A potential piezoelectric polymer has to contain a high concentration of dipoles and also be mechanically strong and film-forming. The degree of crystallinity and the morphology of the crystalline material have profound effects on the mechanical behavior of polymers. Additionally, in order to induce a piezoelectric response in amorphous systems the polymer is poled by application of a strong electric field at elevated temperature sufficient to allow mobility of the molecular dipoles in the polymer. Recent approaches have been focused in the development of cyano-containing polymers, due to the fact that cyano polymers could have many dipoles which can be aligned in the same direction.

Phase transfer catalyzed reaction has been used for piezoelectric polymer preparation from malonitrile, however this method leads to low molecular weight, and low yield of impure vinylidene cyanide units containing material. The use of solid K_2CO_3 and acetonitrile without added phase transfer catalyst shows excellent yields for polyester possessing backbone gem-dinitriles and for polyamide synthesis. The polyester and polyamide obtained contained a dinitrile group net dipole which can be align in the same direction as the carbonyl groups.

The pursuit for better piezoelectric polymers has led to molecular modeling which indicates that one cyano substituent should be almost as effective as two geminal cyano substituents, opening a new area of potential materials having an acrylonitrile group as the basic building block. However, polyacrilonitrile itself is not suitable because it forms a helix. Thus acrylonitrile copolymers have been investigated.

Most of the piezoelectric polymers available are still synthesized by conventional methods such as polycondensation and radical polymerization. Therefore piezoelectric polymer synthesis has the same problems as the commercial polymer preparation, such as controlling the degree of polymerization and crystallinity.

A novel technique of vapor deposition polymerization has been reported as an alternative method to copolymeric thin films. Aliphatic polyurea 9 was synthesized by evaporating monomers of 1,9-diaminononano and 1,9-diisocyanatononano onto glass substrate in vacuum. Deposition rates were improved at temperatures below 0 °C. After poling treatment films showed fairly large piezoelectric activities. Additionally, a completely novel approach to piezoelectric polymers has been presented. This approach, consists in the synthesis of ordered piezoelectric polymer networks via crosslinking of liquid-crystalline monomers. The main goal in this approach is to achieve a polymer network which combines the long term stability of piezoelectric single-crystals with the ease of processability and fabrication of conventional polymers. Figure 3.10 shows the schematic representation of this approach.

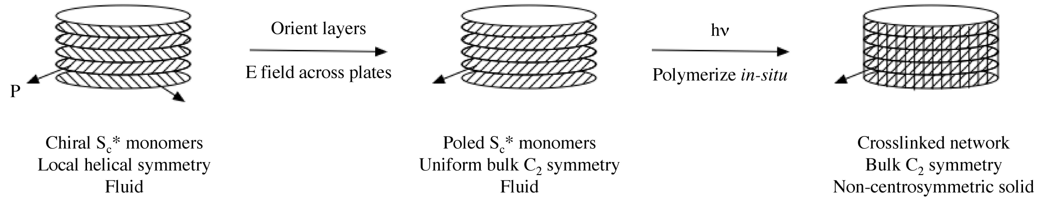

Figure 3.10: Scheme of a ordered piezoelectric networks via a liquid-crystalline monomer strategy. Adapted from D. L. Gin and B. C. Baxter, *Polymer Preprints*, 1996, **38**, 211.

Piezoelectric polymers are becoming increasingly important commercially because of their easier processability, lower cost, and higher impact resistance than ceramics, but the lack of high temperature stability and the absence of a solid understanding of the molecular level basis for the electrical properties are limitations.

The requirements for strong piezoelectricity in a polymer are: the polymer chain has a larger resultant dipole moment normal to the chain axis; polymer crystallizes into a polar crystal with the polar axis perpendicular to the chain axis, has a high crystallinity and finally the polymer polar axis aligns easily in the thickness direction during poling.

3.5.6 Piezoelectric composites

Piezocomposites have been obtained by the combination of piezoelectric ceramics and polymers, the resulting material posses both the high piezoelectric properties of ceramics and the processability of polymers. 1-3 type piezocomposites have found wide applications as medical and industrial ultrasonic transducers.

The current method for piezocomposite production is the dice-and-fill technique, which consists in cutting two sets of grooves in a block of piezoceramic at right angles each other, then a polymer is cast into these grooves and the solid ceramic base is ground off. Polishing and poling are the following steps in order to achieve the final thickness and properties. This method is expensive, time consuming and size limited.

As an alternative for the dice-and-fill technique, continuos green fibers obtained by the modified viscous-suspension-spinning process, can be bundled into a cottonball-like shape, then burned and sintered. The sintered bundle impregnated with epoxy resin can be sliced into discs and then polarized. Recent results have yielded 1-3 type composites with excellent piezoelectric properties.

On the other hand, an innovative process has been developed for $Sr_2(Nb_{0.5}Ta_{0.5})_2O_7$/PVDF composites, in this new fabrication method, appropriate amounts of oxides are mixed, pressed and sintered. The porous resulting material is subsequently infiltrated with PVDF solution and then poled. This new method for composites preparation is simple and offers a lead-free alternative smart material.

Another kind of piezocomposites can be achieved by spinning films of piezoceramic onto metal alloys, such as TiNi. The resulting materials is a hybrid composite that can utilize the different active and adaptive properties of the individual bulk materials. Due to the shape memory nature of TiNi, a possible application for this new heterostructures could be smart active damping of mechanical vibrations. DC sputtering and spin coating are the techniques necessary for the smart thin film TiNi/piezoelectric heterostructures fabrication. However, eventhough the films had a fine grain structure and high mechanical qualities, the ferroelectric properties were poor compared to literature values.

In the future, the properties of piezocomposites will be tailored, by varying the ceramic, the polymer and their relative proportions. Adjustments in the material properties will lead to fulfillment of the requirements for a particular device. Table 3.14 shows a comparison among piezoelectric ceramics, polymers and composites parameters where Z is the impedance, $\varepsilon^t{}_{33}$ is the dielectrical constant, and ρ is the density.

Material parameter	**Piezoceramics**	**Piezopolymers**	**Piezocomposites**
k_t (%)	45 - 55	20 - 30	60 - 75
Z (10^6 Rayls)	20 - 30	1.5 - 4	4 - 20
$\varepsilon^t{}_{33}/\varepsilon_0$	200 - 5000	~10	50 - 2500
tan γ (%)	<1	1.5 - 5	<1
Q_m	10 - 1000	5 - 10	2 - 50
ρ (10^3 kg/m^3)	5.5 - 8	1 - 2	2 - 5

Table 3.14: Parameter ranges for piezoelectric ceramics, polymers and composites.

3.5.7 Piezoelectric coatings.

Many potential applications exist which require film thickness of 1 to 30 μm. Some examples of these macroscopic devices include ultrasonic high frequency transducers, fiber optic modulators and for self controlled vibrational damping systems.

ZnO and PZT have been used for piezoelectric fiber optic phase modulators fabrication. The piezoelectric materials have been sputter deposited using dc magnetron source and multimagnetron sputtering systems. Coatings of 6 μm thick of ZnO and 0.5 μm of PZT are possible to achieve using these systems. However, thickness variation of approximately 15% occurs between the center and the end of ZnO coatings, results on affected modulation performance. Although PZT coatings achieved by sputtering posses uniformity and do not exhibit cracking, the PZT is only partially crystallized and it is actually a composite structure consisting of crystalline and amorphous material, diminishing the piezoelectric properties.

Sol-gel technique for thick PZT films have been developed. It is now possible to fabricate PZT sol-gel films of up to 60 μm. The electrical and piezoelectrical properties of the thick films reported are comparable with ceramic PZT.

Piezoelectric polymer coatings for high-frequency fiber-optic modulators have been also investigated. Commercial vinylidene fluoride and tetrafluoroethylene copolymer has been used. The advantage of using polymer coatings is that the polymer jacket (coating) can be easily obtained by melt extrusion on a single-mode fiber. Thus, uniformity is easily achieved and surface roughness is not present. Furthermore, if annealing of the polymer is made prior poling, a high degree of crystallinity is enhanced, leading to better piezoelectric properties.

3.5.8 Bibliography

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