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ELEMENTAL SEMICONDUCTORS

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INORGANIC REACTIONS AND METHODS

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17. The Formation of Ceramics

17.3. The Synthesis and Fabrication of Ceramics for Special Applications

17.3.9. Preparation of Semiconductors

17.3.9.1 Elemental Semiconductors*

The large number of applications of the elemental semiconductors silicon and germanium is reflected in the wide range of purity and crystalline perfection over which these semiconductors are presently produced. Low cost infrared lenses, for example, can be manufactured from low purity polycrystalline material while in the other extreme, nuclear radiation detectors require nearly ideal single crystals of several centimeters in diameter and length with impurity concentrations as low as 0.001 ppb (1 in 10^{12}). These widely varying requirements have led to a number of manufacturing methods/processes.

Metallurgical silicon--obtained from the reduction of various forms of quartz with carbon--is the starting material for semiconductor grade silicon. Metallurgical silicon is converted to silicon tetrachloride ($SiCl_4$) and trichlorosilane ($SiHCl_4$) which are purified by fractional distillation. Pure polycrystalline silicon is obtained by chemical vapor deposition of the silicon compounds on an electrically heated silicon rod[1]. These rods are left to grow up to ~ 15 cm diameter. The purity of such poly-silicon is typically better than 1 ppb of electrically active impurities (i.e. mainly group III B and group V B elements). For many applications, the purity of the polysilicon at this stage is sufficient, and conversion into a single crystal is obtained with either the Czochralski[2] or the floating-zone process[3].

The Czochralski method uses a melt contained in a rotating silica crucible heated by a graphite susceptor. The ambient is typically 1 atm of argon. A counter-rotating single crystal seed (usually oriented along <111> or <100>) is dipped into the melt. Heat is withdrawn through the seed which leads to crystal growth. Single crystals of almost cylindrical shape, with diameters

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up to ~ 15 cm and over 100 cm in length are routinely grown for electronic applications.

The reduction of the silica crucible by the melted silicon yields free oxygen which in turn reacts with the graphite heater elements. A large number of simultaneously occurring reactions[4] lead to a high oxygen concentration $[O] \approx 10^{18} cm^{-3}$ and a carbon concentration $[C] \approx 5 \times 10^{17-18} cm^{-3}$ in the final crystal. Although both impurities are neutral in their isolated state, they readily form electrically-active impurity complexes. It is one of the more important aspects of electronic device development and fabrication to find processes which getter the undesirable impurities outside those areas in a crystal slice which are important for device performance.

Depending on the specific application, the silicon crystal has to be doped with donors or acceptors. Because of impurity segregation between the melt and the solid, one cannot obtain a constant impurity concentration profile along the growth axis of a single crystal. Re-introduction of doping pellets (silicon pieces with a very high impurity concentration) and counterdoping during the growth process lead to more constant impurity profiles.

The floating-zone purification and crystal growing technique[3] avoids the crucible. A melted zone up to a few cm long is supported by the silicon surface tension and by radiofrequency eddy currents between two vertical silicon cylinders. The radiofrequency field is also the heating source. The liquid zone is typically kept at a fixed position. The upper silicon rod is fed downwards to the zone while the lower rod is withdrawn towards the bottom of the floating zone apparatus. The geometry can be used for zone-purification (see chapter 17.2.8.1) in which case both solid silicon cylinders are polycrystalline. After sufficient purification has been achieved, a final pass starting with a single crystal seed at the bottom yields a single crystal. Extreme

mechanical stability is required for single crystal growth in a floating zone puller. It is possible to grow crystals with diameters > 12.5 cm and lengths over 100 cm. The temperature distribution and heat flow pattern is very unfavorable for large crystal diameters in a floating zone machine. Rapid multiplication of any dislocations present turns a single crystal polycrystalline. This is the reason why dislocation-free crystals must be grown. The point defects--mainly silicon interstitials and vacancies--which are unavoidably present at the melting point condense in dislocation-free crystals into a variety of defects, distributed in spiral patterns along the crystal growth axis. Crystal growth velocity and the temperature distribution strongly affect the type and distribution of these swirl defect patterns[5]. The most prominent defects--the A-type swirls--are due to the condensation of interstitials into platelets surrounded by dislocation loops.

Germanium is, for all practical purposes, no longer used in electronic amplifying and logic devices. It is, on the other hand, a very important semiconductor for ir-optics, ir-photoconductors and nuclear radiation detectors. Germanium is found in copper, zinc and silver ores. After a number of extraction and purification steps, $GeCl_4$ is obtained. Fractionated distillation is followed by a hydrolysis step which leads to $Ge(OH)_4$. Calcination leads to GeO_2 which is reduced at 650°C in a graphite boat in a pure hydrogen atmosphere to elemental germanium. Zone purification (see chapter 17.2.8.1) is used to obtain intrinsic polycrystalline germanium (i.e., germanium with an electrically-active net-impurities less than $3.5 \times 10^{13} cm^{-3}$, the intrinsic carrier concentration at room temperature). Single crystal growth has been performed in the past in a graphite boat analogous to the floating-zone technique described for Si. The small surface tension and the high density of liquid germanium do not permit vertical floating-zone growth. The most

commonly used technique for germanium single crystal growth is the Czochralski method. A modification of the graphite crucible--the floating crucible assembly--allows the growth of crystals with nearly constant impurity profiles. Germanium single crystals used in nuclear radiation detector fabrication are ultra-pure with net-impurity concentrations below $10^{10}cm^{-3}$ (one impurity in 4×10^{12} germanium atoms). Such crystals are grown from a melt contained in a synthetic quartz crucible and a pure hydrogen atmosphere[6]. Infrared spectroscopy of such pure crystals has revealed a large number of hydrogen-related impurity complexes[7].

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