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Problems in the Melt- and Vapor Growth of Silicon for Integrated Circuits and Solar Cells

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Since the invention of the transistor in 1948 silicon has emerged as the most versatile semiconductor material, and the resulting devices have caused a revolution in the electronics industry. The crystal growth of silicon from the melt is the basis for the nearly perfect crystalline quality needed for the devices. Problems in the melt growth, the elimination of dislocations, and the prevention of the precipitation of point defects are still under study and are discussed. In addition, the growth of thin monocrystalline layers of Si on a monocrystalline substrate has become of great importance. In sharp contrast to this type of approach are the recent activities aimed at obtaining cheap silicon photovoltaic solar cells. Examples of methods based on melt or vapor growth for producing thin, almost monocrystalline layers on a cheap substrate are given. The new discovery that amorphous silicon may be a suitable candidate for this type of cells is discussed.

1. Introduction

Solids can be classified as metals or nonmetals. In the nonmetals all valence electrons participate in stable bonds with electron energies grouped in a range of filled states known as a valence band. A forbidden energy gap E_g has to be overcome thermally or optically in order to give conduction via quasi-free electrons excited to the nearest empty band, the conduction band. At the same time holes, which are often mobile and add to the conductivity, are left in the valence band. The nonmetals are divided into semiconductors and insulators, but this classification is not a fundamental one and depends on the temerature of investigation. Semiconductors may be described as nonmetals with a band gap of a few tenths of an electron volt up to, say, 5 eV.

The technical importance of semiconductors is based on the modification of the physical properties that can be achieved by the introduction of small concentrations of foreign atoms. Silicon is in group IV of the periodic table. Introduction of 1 ppm (10^{-6}) of atoms from group III or V leads to a change in resistivity by about 6 orders of magnitude; e.g., phosphorus on a Si site has one additional valence electron. At room temperature this electron is readily ionized and gives rise to electron (*n*-type) conduction. Boron as a group III dopant has one valence electron missing; this leads to holes in the valence band and thus to hole (*p*-type) conduction. Multilayer structures can be made with different types of conductivity by doping methods either during growth or afterward (diffusion, ion implantation), resulting in devices such as diodes, photodiodes, transistors, and integrated circuits. The transistor effect was first observed in monocrystalline germanium (*1*); early devices were made with this base material. Pfann (*2*) found the way to efficient purification by means of zone melting. This

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purification is of prime importance because ultrahigh purity with respect to electrically active atoms is required to ensure reliable doping.

It had been realized that devices made from silicon (energy gap, 1.1 eV) could operate up to higher temperatures than devices made from germanium (E_g = 0·7 eV), the higher-band-gap material having a lower intrinsic electron and hole concentration. The inherent difficulty of easy oxidation made silicon less attractive from a technological point of view until the disadvantage turned into an advantage. It was shown that silicon could be easily oxidized to give a thin adherent SiO_2 layer. Windows can be etched in the oxide by HF[5], and the oxide now serves as an effective mask against diffusion of gaseous dopants, such that *n*- or *p*-type diffused areas into the silicon are made only via the windows, and *p*/*n* junctions can be created. Photolithographic techniques enable the design of very fine patterns of localized diffusions. Repeated oxidations, window delineation, and diffusions are needed to arrive at an integrated circuit in which resistors, capacitors, diodes, and transistors are made, connected by an ultimate pattern of evaporated metal interconnects and contact areas.

This so-called planar technique, where all electrical contacts are made on the top side of the structure, demands the highest quality of monocrystalline silicon; defects such as dislocations or precipitates seriously hamper the reliable operation of the devices. The starting material thus deserves special care, and much study has been devoted to the growth of silicon crystals from the melt and of silicon layers from the vapor phase. In the following sections growth from the melt and growth from the vapor phase are discussed, followed by a description of materials problems in the fabrication of cheap photovoltaic cells and some remarks on the interesting properties of amorphous silicon.

2. Melt Growth of Monocrystalline Silicon

Metallurgical grade silicon is produced in large quantities from coal and sand. For semiconductor quality silicon this impure silicon is converted into silicon chlorides that can be purified by fractional distillation. Polycrystalline silicon rods are obtained by chemical vapor deposition of silicon on a heated silicon wire. In a hydrogen carrier gas the silicon chloride is reduced to silicon on the heated surface, giving rods up to 20 cm in diameter.

Single crystals of silicon are then grown from a high-purity melt, while in the same pass a homogeneous doping is achieved by adding known amounts of dopant to the melt. Slices are cut from the crystals, and these are used as substrates in device fabrication. The properties of these devices are generally adversely affected by lattice defects such as line defects (dislocations) and point defects. Dislocations are not present in thermodynamical equilibrium because they always increase the total free energy of the lattice. Their presence originates from local strain due to temperature or concentration gradients.

Point defects such as vacancies and self-interstitials may be thermodynamically stable because the entropy is significantly increased by introduction of these point defects, and this compensates, at relatively high temperatures, for the enthalpy of formation. A significant improvement in the crystal quality was introduced by Dash, who succeeded in eliminating dislocations in melt-grown silicon by growing a thin neck on top of the crystal at a relatively large pulling speed. In this neck the line defects grow out to the nearby surface. Because of the small diameter of the neck the thermal stresses are too low to cause multiplication of the dislocations. When the neck is dislocation-free the diameter can be increased, and with proper precautions a wholly dislocation-free crystal results.

The absence of dislocations does not imply that completely perfect lattice structures are obtained. In dislocation-free material, in particular, the presence and behavior of point defects may be evident. At the growth temperature a high concentration of point defects will be present. On subsequent cooling these defects become supersaturated as the equilibrium concentration decreases with decreasing temperature. Nucleation and condensation processes result in the formation of point defect clusters. The formation of such microdefects will be most pronounced in dislocation-free material because dislocations can act as effective sinks for excess mobile point defects. It is also possible that chemical impurities, either intentionally added (dopes) or residual, become supersaturated at cooling and separate from the solid solution via precipitation on dislocations which then become decorated or via another homogeneous or heterogeneous precipitation process.

Reference is made to Fig. 1 for the principle of the floating-zone growth method. In the widely used Czochralsky growth method a crystal is pulled from molten silicon contained in a fused quartz crucible, and because of the attack on the crucible by the molten silicon the oxygen content of the crystal is a factor of 100 or more higher than that in the floating-zone method in which no crucible is needed (10^{18} cm^{-3} as against 10^{16} cm^{-3}). Microdefects in dislocation-free silicon made by both processes have been studied in great detail; different types of defect are identified, and a number of models to explain their origin have been put forward (*4, 5*). Here it is sufficient to say that heterogeneous condensation of point defects on preferred sites seems to give the most probable explanation. These defects are often denoted as swirl defects because they occur in a spiral-like pattern in the crystal.

The defects can be detected by etching methods, but more convincingly by X-ray topography, infrared transmission microscopy, scanning electron microscopy, and transmission electron microscopy (TEM). The contrast is enhanced by decoration of the defect by fast-diffusing impurities with a retrograde solubility (Cu, Li) (*3*). It has been possible to eliminate the swirl defects during the crystal growth of silicon (*6, 7*). In Fig. 2 the concentration of defects is plotted versus the pulling rate of the dislocation-free crystal. The concentration of small *B*-type defects and larger *A*-type defects can be seen to depend on the growth rate. The explanation of this effect is to be found in the nucleation kinetics of the defect formation. At very low growth rates the cooling rate of the crystal is low, and the point defects can diffuse to the crystal surface such that large supersaturations are avoided. When the crystals are doped with carbon, however, both *A*- and *B*-type defects are still present at this

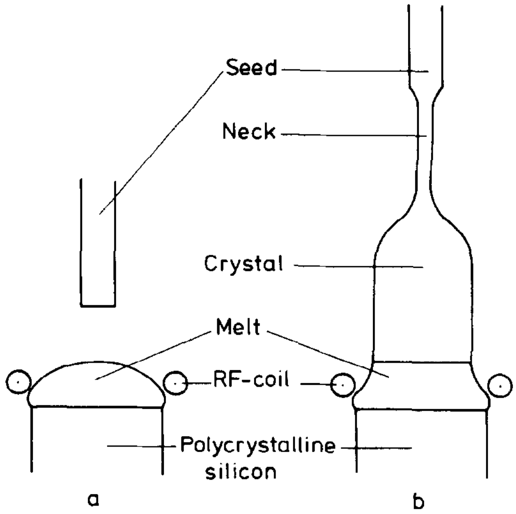

FIG. 1. Principle of crystal growth via the melt. (a) A monocrystalline seed is dipped into the melt and slowly withdrawn to originate growth at the solid–liquid interface. Control of the melt temperature gives an increase or decrease in the crystal diameter. (b) Floating-zone growth. A molten zone is created between two silicon rods. Surface tension keeps the liquid in position. Movement of the molten zone gives solidification at one interface and melting at the other. For Czochralsky growth the silicon melt is contained in a fused quartz crucible.

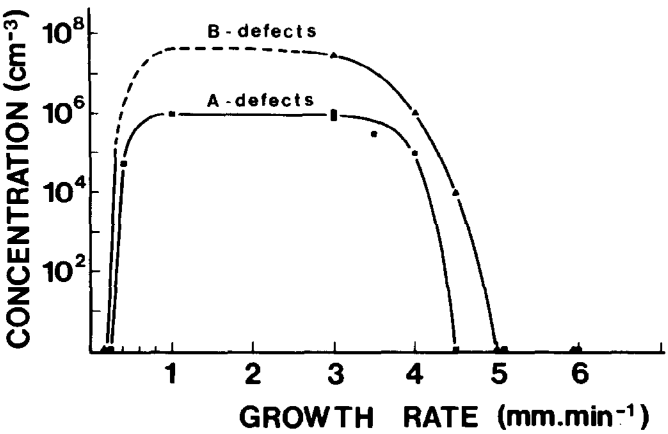

FIG. 2. The concentration of swirl defects in dislocation-free silicon crystals as a function of pulling rate.

low pulling rate. At very fast pulling rates, on the other hand, the supersaturation is high, but apparently the time is not sufficient to form larger clusters, and the point defects are frozen in or trapped. Upon slicing and reheating the crystals, the excess point defects may reach the surface again to restore an equilibrium value.

A last source of inhomogeneities is the variation in the microscopic growth rate during pulling, resulting in a striated distribution of impurities because the effective segregation coefficient depends on the growth rate. In this way local variations in resistivity can occur, as well as a striated pattern of the residual impurities such as carbon and oxygen. It has not been possible to eliminate this type of inhomogeneity. Recent results in a space laboratory confirm that convection currents in the melt also add to the formation of the striations (*8*). Much effort is concentrated nowadays on the prevention and elimination of defects during growth and subsequent processing of the silicon slices (oxidation, diffusion, ion implantation), but nearly perfect silicon technology has not yet been attained.

3. Crystal Growth from the Vapor

Most semiconductor devices can be made in a thin layer of silicon, and therefore the growth of silicon layers and multilayers from the vapor phase has found widespread application (*9*). Growth on monocrystalline substrates (sapphire, spinel, silicon) can lead to monocrystalline layers of good perfection, suited for the fabrication of high-quality devices. The growth is mostly performed in a cold wall reactor in which the input gases react on a heated substrate to form the desired deposit (Fig. 3). In this layer, growth problems arise in the first nucleation, in the growth rate attainable, and in the morphology of the resulting layer.

For the growth of silicon on a silicon substrate (mostly of a different conductivity) it is found that, to begin with, the substrate must be clean. This is achieved by gaseous HCl etching prior to the growth. Furthermore, the surface should contain atomic steps to facilitate the incorporation of silicon adatoms produced on the surface between the steps. Via surface diffusion these adsorbed atoms can reach the steps and find a stable position. The lateral flow of steps then constitutes the crystal growth process. This type of surface is obtained by cutting the substrate a few degrees out of a low index plane. After etching, the surface is then provided with atomic steps with low index surfaces in between. When the steps are far apart, or on a foreign substrate, the adatoms tend to condense into isolated nuclei that

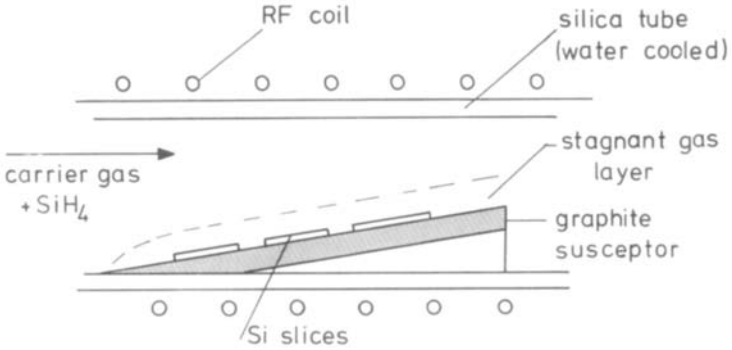

FIG. 3. Cold wall reactor for the deposition of thin layers on a heated substrate by chemical vapor deposition.

grow out until coalescence is achieved (*10, 11*).

After proper nucleation, the growth process proceeds smoothly, and it seems logical to decrease processing costs by increasing the input concentration of the reactant ($SiCl_4$, $SiHCl_3$, SiH_2Cl_2, or SiH_4) in order to increase the growth rate. In the case of $SiCl_4$ an increased concentration leads to the result given in Fig. 4. The following reactions have to be considered: the first reaction describes the production of silicon by reduction of $SiCl_4$; the second reaction gives a competing etch effect.

$$SiCl_4 + 2H_2 \rightleftharpoons Si + 4HCl,$$

$$SiCl_4 + Si \rightleftharpoons 2\,SiCl_2.$$

At higher input concentrations of $SiCl_4$ the second reaction becomes predominant, and the growth rate decreases with a further increase of the input concentration.

For SiH_4 no such etching effect is present, but in this case an increased input concentration soon leads to gas phase nucleation. Silicon is then deposited on the walls of the reactor and no longer exclusively on the heated substrates. SiH_2Cl_2 and $SiHCl_3$ as well as mixtures of SiH_4 and HCl can be used to obtain the highest growth rates, up to 40 μm/min (*12*). Here a limiting case is found in the circumstance that at higher growth rates the monocrystalline growth breaks down to give a polycrystalline growth. Defects captured in the layer can no longer

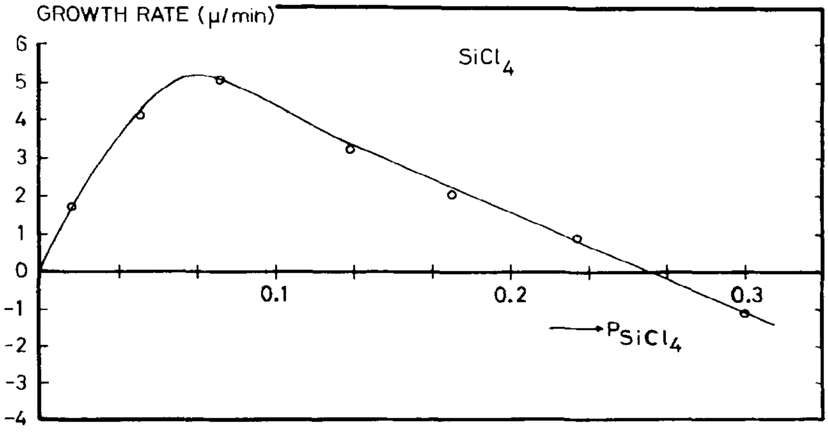

FIG. 4. Growth rate of silicon from $SiCl_4$ in hydrogen as a function of the input concentration of reactant. At high concentrations a negative growth rate, i.e., etching of a silicon substrate, occurs.

be eliminated by solid-state diffusion of the defects back to the surface, and the structure becomes polycrystalline. At temperatures below 500°C rapid growth even leads to the deposition of amorphous silicon (*9*), and in this case the surface diffusion of silicon adatoms is a slow process compared to the arrival rate of adatoms; only short-range order is established. The long-range order met in crystalline material is restored only after reheating at higher temperatures.

In the chemical vapor deposition of silicon the temperature dependence of the growth rate also deserves some attention (Fig. 5). At high temperatures a diffusion-controlled reaction mechanism, in which the supply of reactant from the bulk of the gas phase determines the growth rate, is present. At lower temperatures surface reactions are rate limiting, and it is postulated that hydrogen desorption limits the growth rate in this region. Monoatomic hydrogen is strongly absorbed on silicon surfaces. The binding energy of the Si–H bond is close to 3 eV(13), and the heat of formation of H from H_2 is about 2 eV, giving in thermal equilibrium a formation energy of SiH from H_2 equal to 1 eV.

At the lower temperatures it is difficult to grow monocrystalline silicon; yet this range is very attractive, as very homogeneous growth can be observed. At high temperatures, where the growth rate is diffusion-controlled, the growth is unstable and protrusions are easily formed, especially near surface irregularities (*14*). At lower temperatures, where surface kinetics determine the growth rate, a smooth coverage of the substrates is found, and even irregularities can be smoothed out. It is for this reason that low-temperature growth combined with a low total pressure is becoming popular for the growth of polycrystalline layers. Research into growing monocrystalline layers under comparable conditions is in progress.

4. Solar Cells

In the field of energy conversion, an important part is being played by the conversion of solar energy into heat and elec-

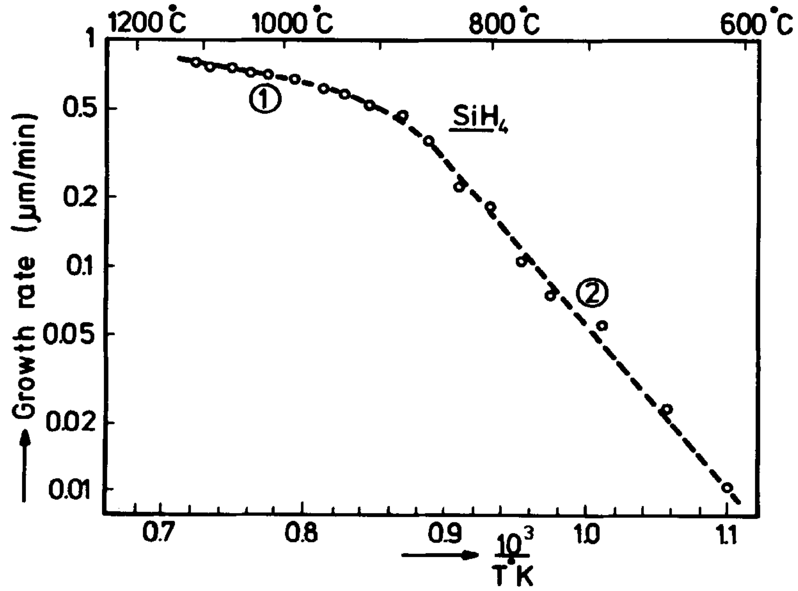

FIG. 5. Temperature dependence of the growth rate of silicon from the vapor using 0.1% SiH_4 in hydrogen.

tricity. The former part needs solar collectors, a blackbody with a high absorption coefficient for the incident light. At the same time heat losses from the blackbody have to be minimized by a low-emission coefficient for infrared radiation. This type of energy conversion is becoming widely used to assist with heating and air conditioning.

The conversion of the incident solar energy into electricity can most efficiently be done by means of photovoltaic solar cells (*15*). In this device mobile charge carriers are generated by illumination, with the charge carriers separated in the field of a p/n junction parallel to the surface. The band gap of the semiconductor has to match the photon energy distribution in the solar spectrum, and an energy gap of 1 to 1.5 eV is the most suitable. Silicon, the second-most-abundant element in the Earth's crust, with $E_g = 1.1$ eV, thus emerges as a strong candidate. Conversion efficiencies of 18% have been achieved on silicon cells made on single crystalline silicon with techniques well known in semiconductor technology. The price of these cells and the amount of energy needed to produce them are so high that they seem to be competitive with other conversion methods only for remote locations. A price reduction by a factor of 10 to 100, however, could give rise to the foundation of a new industry with a size comparable to that of present semiconductor activities. In the conventional technology nearly 80% of the price of a solar panel stems from the silicon material (*16*); therefore every detail of the process is being studied with an emphasis on the materials side. An important parameter in the silicon material is given by the mean-free path (L) of the charge carriers created by the illumination. The value of L must be of the order of the thickness of the cell ($L \approx 300\ \mu m$). For polycrystalline material, therefore, the grain size must be greater than 300 μm in order to give reasonable efficiencies. This factor appears to be the bottleneck holding back a great number of methods aimed at growing silicon layers on cheap substrates. A number of processes are being suggested for improving the purity of metallurgical silicon; an integrated process suggested by Wolf is shown in Fig. 6 (*15*). Interesting studies are being made on growing thin silicon ribbons, strips, or layers from

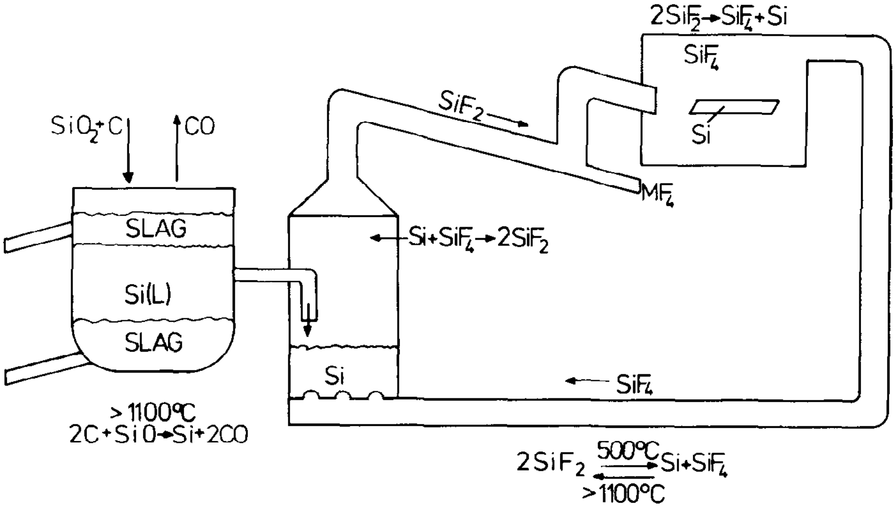

FIG. 6. Integrated process suggested for producing impure silicon. Conversion to SiF_2 and subsequent disproportionation of SiF_2 to Si and SiF_4 give a silicon deposit on the substrates in the chemical vapor deposition cell.

the melt with or without shaping guides (*17*), or casting molten silicon directly into the desired shape; controlled solidification should improve the grain size in this case. Chemical vapor deposition to grow silicon layers on cheap substrates has been studied extensively. On polycrystalline substrates the grain size appears to be rather small, and an improvement has been obtained by the growth from the vapor on a thin liquid metal film where a crystallite size of 100 to 300 μm has been found (*18*). From the multitude of processes a few will emerge as possible candidates for mass production. Emphasis will then be on cheap mass production of cells with efficiencies of at least 10%.

In view of the efforts made and the results so far achieved it can be expected that photovoltaic conversion will provide part of the energy needed in the not too distant future.

5. Amorphous Silicon (α-Si)

The properties of amorphous materials have long been a subject of study, and transport properties have been of particular interest, but practical applications were not envisaged. This situation was changed completely by the discovery of Spear and Le Comber (*19*) that amorphous silicon is a semiconductor that can be *n*- and *p*-type doped and has interesting optical properties. Carlson and Wronski (*20*) showed that solar cells can be made from amorphous silicon, and it became clear (*21*) that the useful properties of amorphous silicon originate from the presence of large amounts of hydrogen in the amorphous structure. Amorphous silicon can be made by chemical vapor deposition at relatively low temperatures or by evaporation or sputtering of silicon on a substrate. It then appears as a semiconductor with a multitude of bulk trapping states, known from silicon surfaces. These broken or dangling bonds determine the transport properties to a great extent. When the α-Si is prepared in a plasma from SiH_4 or in the presence of hydrogen, enough monoatomic hydrogen is formed to saturate the dangling bonds, and the electronic transport properties resemble those of a crystalline solid. Amorphous silicon has an absorption coefficient for visible light that is nearly a factor of 100 greater than that of crystalline silicon. Solar cells made from α-Si therefore need only to be 2 μm thick as compared to 200 μm for crystalline silicon.

These inventions spurred considerable research activity, and now the literature on α-Si is increasing explosively. It should be noted that α-Si is unstable, and heating above 500°C and laser radiation bring it back to the crystalline state. Given a certain stability and performance α-Si can appear to be a very interesting candidate for low-cost devices requiring large areas of material as solar cells or flat screen displays.

Conclusion

Some aspects of the growth of silicon from the melt and from the vapor phase to give monocrystalline, polycrystalline, or amorphous material have been discussed. The optical and electrical properties of these materials are used to make a great number of devices, but it should be emphasized that the growth of the material and the possible defects in the structure in particular are understood only in a qualitative way at present, and thus a large field of study is still open.

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