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GAS PHASE DIFFUSION AND SURFACE REACTIONS IN THE CHEMICAL VAPOUR DEPOSITION OF SILICON

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Abstract - In semiconductor technology silicon is widely used as a starting material for the production of a great number of devices ranging from complicated integrated circuits to cheap solar cells. In this technology the chemical vapour deposition (CVD) of silicon plays the important role of providing the thin silicon layer in which the active devices are formed. In the growth of silicon from the vapour phase the main methods used are the hydrogen reduction of silicon halides such as $SiCl_4$ or $SiHCl_3$, or the decomposition of SiH_4. Various resistances are present to limit the growth rate, such as gas phase diffusion of reactants towards the interface and the surface reactions needed to arrive at the desired crystal structure. This paper deals with the nucleation of silicon, with models for high- and low temperature growth reactions and with the morphology of the resulting layers and the conditions are discussed under which monocrystalline, polycrystalline or amorphous layers can be expected.

INTRODUCTION

Since the discovery of the transistor by Bardeen and Brattain (Refs.1 and 2) it has been realized that the development of useful semiconductor devices depends on the properties of the materials used. In the hectic developments that took place in the early years of the semiconductor industry it was silicon that emerged as the most versatile semiconductor material. This became evident when it proved possible to turn the apparent drawback of the easy oxidation of silicon into an advantage. It was discovered that windows in an oxide layer on silicon may be used to define regions where diffusion of dopants or the growth of localized islands can take place (Ref.2). The oxide now serves as an effective mask. Photolithographic techniques provide the very high precision of position and size of regions where windows in the oxide can be opened by the etching of hydrofluoric acid, which attacks the oxide but not the silicon itself. Details smaller than 2 μm are common in this technique. To achieve reproducible doping with n- or p-type dopants the purity of the starting material has to be very high. Metallurgical grade silicon is produced in large quantities from coal and sand. Semiconductor devices, however, require a concentration of the electrically active elements in the ppb level (10^{-9} or 5.10^{13} at/cm^3). The main purification is based upon fractional distillation of silicon chlorides, followed by a chemical vapour deposition of pure silicon on a heated silicon rod to give polycrystalline bars of more than 20 cm diameter and 1 m length. This material is melted and single crystals of silicon are grown from the high purity melt, and a homogeneous doping is achieved in the same operation by adding known amounts of dopant to the melt. Slices are then cut from the crystals and, after polishing, these are used as substrates in device fabrication. During the processing and the diffusions care has to be taken to preserve the crystalline quality of the material. Imperfections such as precipitates and dislocations may seriously degrade the characteristics of the final devices. In this application the quality of the material is of prime importance, and material costs constitute only a fraction of the total end price of the finished device. In sharp contrast to this is a new, possibly large-scale, use of silicon, to meet the need for efficient and cheap solar cells for the terrestial conversion of solar energy into electricity. The solar cells produced for space vehicles have a very high efficiency, but the price of the cells and the amount of energy needed to produce them are up to a hundred times higher than is allowable in order to be competitive with other sources. This had led to a great deal of activity aimed at finding the principles and the means of producing cells of acceptable efficiency in a way suited to mass production with a minimum of material and energy costs. The situation here can be compared with the early years of the semiconductor industry where every year new ideas and technologies outdated the former ones. It took nearly twenty years to arrive at a more or less stable and accepted technology where new inventions can be incorporated more by adding to existing ideas and equipment than by totally changing them. In both applications, the integrated circuit and the solar cell,

the chemical vapour deposition of silicon plays an important role, because most devices can be made in a thin layer of material such as is obtainable from vapour deposition.

CHEMICAL VAPOUR DEPOSITION (CVD) OF SILICON

CVD is a technique to deposit solid material in which a chemical reaction produces the solid from gaseous reactants. In the following sections some aspects and results of the CVD of silicon will be presented in order to show the interplay of equilibrium and kinetics in the process.

Apparatus

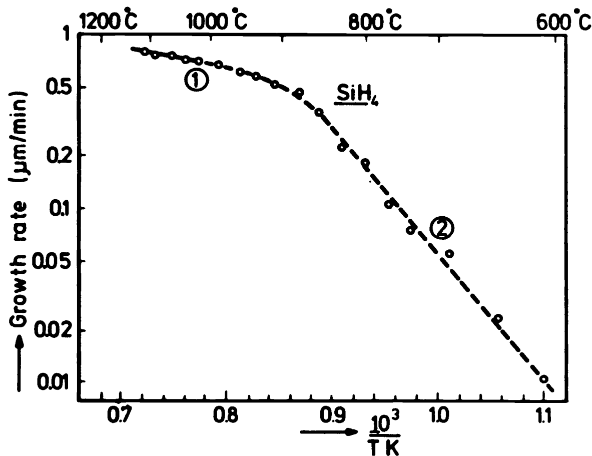

Fig.1. Growth rate of silicon as a function of temperature for 0.1% SiH_4 in hydrogen.

The growth rate of silicon for a fixed partial pressure of silane as a function of substrate temperature is shown in Fig.1. It is seen that at high temperatures the growth rate shows a slight temperature dependence characteristic of a gasdiffusion-limited growth rate. At lower growth temperatures, however, the growth rate has a much higher temperature dependence (with an apparent activation energy 35 kcal/mole). A new rate-limiting factor appears which points to a surface reaction becoming the slowest step in the chain of events. The growth of monocrystalline silicon on a single crystalline substrate (epitaxial growth of silicon on silicon or sapphire) requires a relatively high temperature ($\geqslant$ 1000°C region 1 in fig.1). A type of apparatus suited to grow such layers is shown in Fig.2.

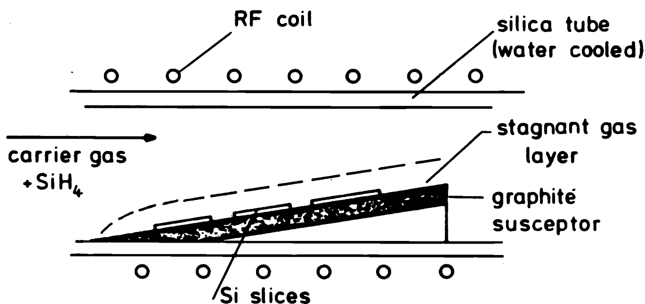

Fig.2. Horizontal epitaxial apparatus used in the high temperature CVD of silicon (cold wall apparatus).

A graphite susceptor inside a water-cooled quartz tube is heated by means of an RF coil around the tube. The substrates to be covered are placed on top of the susceptor. Hydrogen is the usual carrier gas, loaded with a small concentration of silane (SiH_4) or a silicon halide. In the gas phase adjacent to the substrates a steep temperature gradient is present, causing the formation of a boundary layer in the gas just above the substrates (Ref.3). Diffusion of reactant through this layer is therefore one of the limitations to the growth rate of the heterogeneous reaction. Typical growth rates are of the order of 1 µm per minute. At lower growth temperatures (region 2 in fig.1) another type of reactor can be used in which a higher stacking density of substrates becomes possible (Fig.3).

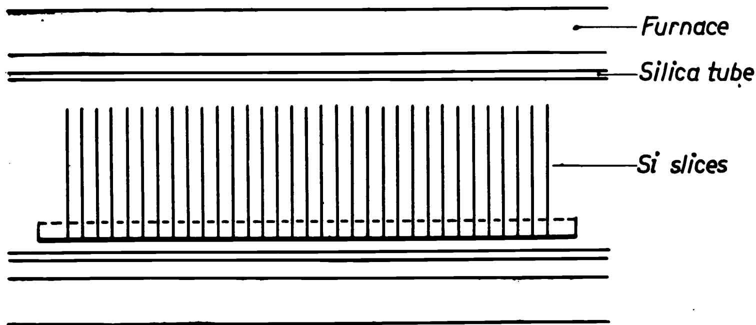

Fig.3. Hot wall reactor for the deposition of polycrystalline silicon, silicon oxide or silicon nitride. The packing density of slices is high.

Fig.3 is a schematic representation of a hot wall apparatus in which all substrates can be covered homogeneously because of the low surface reaction rate of the growth process. It is thus not only the first slice in the direction of the gas flow that begins to grow. This type of low temperature reactor in combination with a total pressure in the order of 1 Torr is becoming popular in the production of polycrystalline silicon, silicon oxide and silicon nitride layers on various substrates (Ref.4). The low temperature with the inherent low surface mobility of silicon ad-atoms makes it difficult to grow monocrystalline layers, as will be discussed in a later section.

Temperature dependence of growth rate

A typical difference has been found between the growth rate of silicon at high and low operating temperatures, as shown in Fig.1 and is explained by a diffusion-limited process at the high temperature side and a surface reaction controlled growth rate at the lower temperatures. Both steps can be defined in the following way (Ref.5): For a simple heterogeneous reaction the flux of reactant atoms (J_d) towards the growing interface can be given as:

$$J_d = \frac{D}{RT}\frac{(p_b - p_s)}{\delta} \qquad (1)$$

where D is the diffusion coefficient of reactant in the gas phase, p_b is the partial pressure of that species in the bulk of the gas phase and p_s the partial pressure near the surface, and δ is the thickness of the boundary layer in the gas phase. RT is included to convert gas phase concentrations to partial pressures via the ideal gas law (c=p/RT). On the other hand surface reactions are needed to generate growth. The nature of the surface reactions is not specified, but it is assumed, that the reaction rate is a linear function of the supersaturation and characterized by a mass transfer coefficient k_d such that the transfer flux (J_t) is given by

$$J_t = k_d \frac{(p_s - p_{eq})}{RT} \qquad (2)$$

p_{eq} denotes the value of the reactant concentration in thermodynamical equilibrium at the temperature T. In a steady state situation both fluxes have to be equal, so that the partial pressure near the surface (p_s) is given by

$$p_s = \frac{p_b + \frac{k_d\delta}{D} p_{eq}}{1 + \frac{k_d\delta}{D}} \tag{3}$$

Substitution of eq.(3) in eq.(1) or (2) leads to the general expression

$$J = \frac{p_b - p_{eq}}{RT(\frac{\delta}{D} + \frac{1}{k_d})} \tag{4}$$

From eq.(3) it is seen that the term $k_d\delta/D$ plays an important role. When the value of this parameter is high, p_s equals p_{eq}, when it is low p_s approaches p_b. The first situation is seen when diffusion control is present, all arriving reactants reach equilibrium as the surface reaction is fast. At lower temperatures the surface reaction efficiency is low and p_s will be closer to the bulk value, p_b. The dimensionless group $k_d\delta/D$ is equivalent to the Nusselt number for mass transfer in an isothermal system. When temperature gradients are present it is proposed to use the term "CVD number (Ref.5). Thus when the value of the CVD number is high one may expect diffusion controlled growth, which can best be performed in a reactor as depicted in Fig.2. At low CVD numbers the reactor shown in Fig.3. enters into the picture. The temperature dependence of the CVD number is largely determined by the temperature dependence of k_d, in the present case about 35 Kcal/mole. For the description of an CVD process it is important to have an exact knowledge of the temperature gradients near the growing interface and the relation between a possible thermal boundary layer and diffusional boundary layer. It has been shown (Ref.6 and 7) that at high hydrogen gas flow rates there is a temperature distribution between the hot substrate and the cold reactor wall as shown in Fig.4. For these higher gas flow rates a thermal boundary can be indicated.

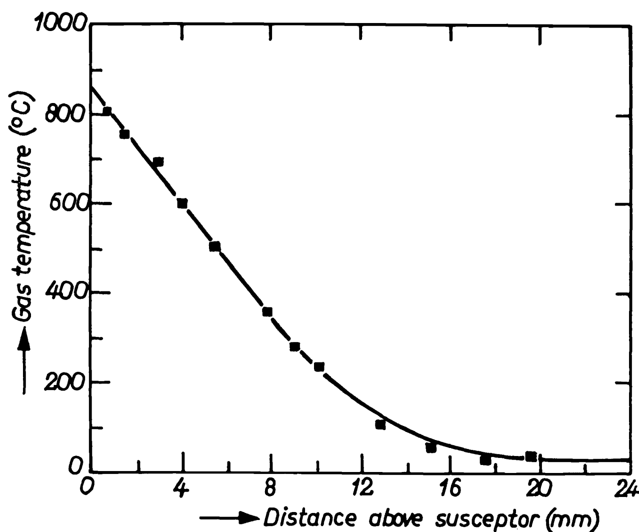

Fig.4. Temperature distribution in an epitaxial reactor as shown in Fig.2 (Ref.6 and 7).

The concentration boundary has been studied by Sedgwick (Ref.6), Ban (Ref.7) and Duchemin (Ref.8) using Raman spectroscopy, mass spectroscopy and gaschromatography respectively. The concentration gradients found above the substrate in the diffusion-limited growth region are depicted in Fig.5. The concentration boundary layer is seen to be nearly equal to the thermal boundary layer. These in situ measurements make it possible to calculate the actual growth rate in a quantitative way (Ref.9) for this diffusion-limited case.

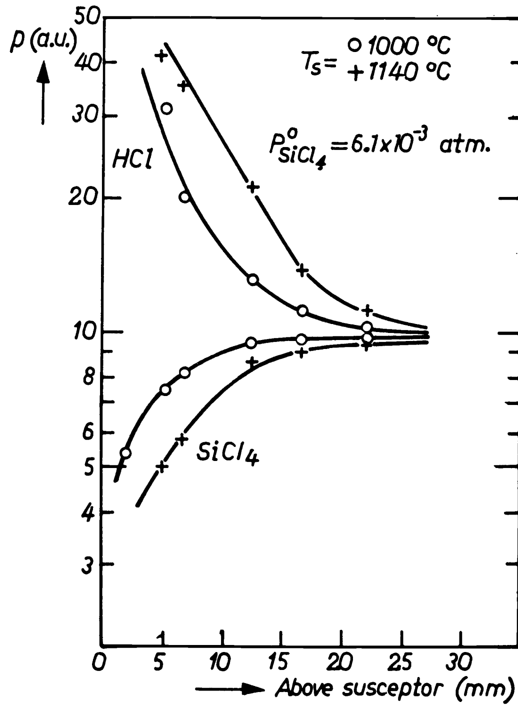

Fig.5. Concentration gradients near the growing interface indicating a concentration boundary layer in the diffusion-controlled high temperature growth (Ref.7 and 8).

At low temperatures it has been shown by Yasuda et al (Ref.10) and by Duchemin (Ref.8) that the growth rate (G) for silane as the reactant, can be represented by

$$G = \frac{k_1 \, p_b}{1 + (k_2 p_{H2})^{\frac{1}{2}}} \tag{5}$$

where $k_1/(1 + k_2 p_{H2})^{\frac{1}{2}}$ has to be compared with k_d/RT in eqs.(2) and (4). Eq.(5) indicates that possibly the adsorption of mono-atomic hydrogen on free sites of the silicon surface is responsible for the decrease in growth rate by limiting the adsorption and reaction of reactant molecules on that surface. It in interesting to note that the same activation energy is found in the kinetic region when $SiCl_4$, $SiHCl_3$ or SiH_2Cl_2 are used as reactants (Fig.6) indicating that at temperatures below 1000 K the desorption of hydrogen is rate-limiting in all these cases. The Si-H bond appears to be very strong (Ref.12) as also found in the recent studies on amorphous silicon (a-Si) (Ref.13). Photovoltaic solar cells can be made from a-Si, deposited at low temperatures on a cheap substrate. The material is only suited for the fabrication of solar cells when made in a hydrogen plasma discharge, which means that a-Si contains considerable amounts of hydrogen (≈ 20 atom %) needed to compensate all dangling silicon bonds in the amorphous structure by the formation of the strong SiH bonds (Ref.14).

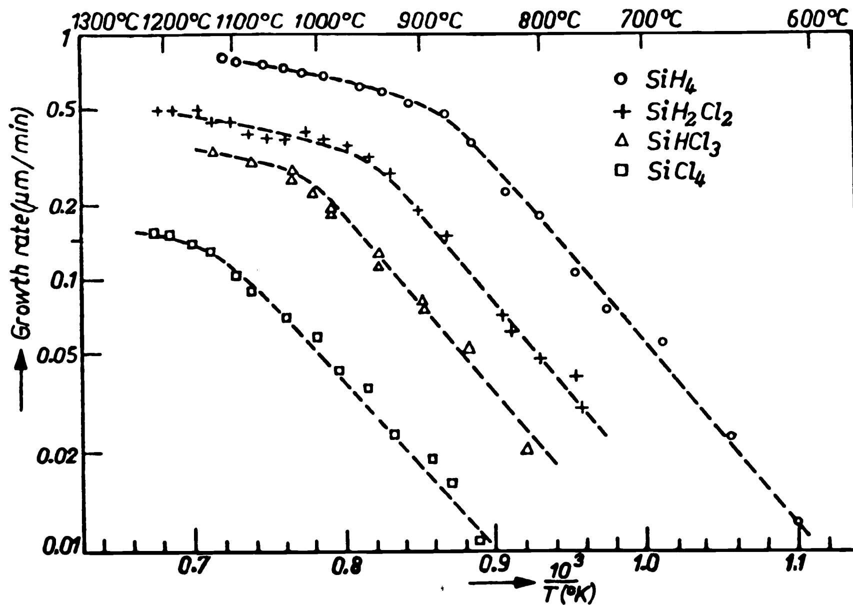

Fig.6. Growth rate as a function of reciprocal temperature for equal concentrations (0.1 volume %) of SiH_4, SiH_2Cl_2, $SiHCl_3$ and $SiCl_4$ in hydrogen as a carrier gas.

Pressure dependence of growth rate

The dependence of the silicon growth rate on hydrogen partial pressure, as given in eq.5, already points to a kind of pressure dependence of the growth rate at lower temperatures. Apart from this, however, the total gas pressure is important in that it influences the flow dynamics and gas phase transport. In general it can be stated that the gas phase diffusion constants increase with decreasing total pressure, and that the boundary layer thickness δ increases with decreasing total pressure. As δ approaches the tube radius it can be treated as being constant, The surface reaction rate will vary with the hydrogen partial pressure (Eq.5). The combined effect shows that the CVD number $k_d\delta/D$ decreases with decreasing total pressure; this means that at lower pressures the influence of surface reactions is expected to be more pronounced. Fig.7 gives experimental results reported by Duchemin (Ref.8) showing the influence of the total pressure on the growth rate. It is clearly seen that the surface reaction rate is rate-determining at the lower total pressures even at higher temperatures. The low pressure and low temperature region (1 torr at 600 ^{o}C) is mainly used for the deposition of thin polycrystalline layers as needed in various applications in the semiconductor device technology (e.g. resistors, gates, contact areas and diffusion sources). (Ref.15).

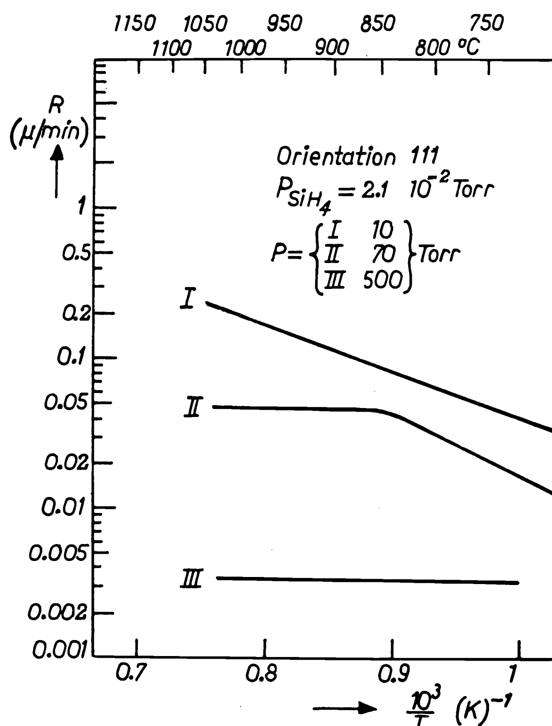

Fig.7. Temperature dependence of the silicon growth rate measured at various total pressures. At lower pressures surface reaction rate control is dominant (Ref.8).

Concentration dependence of growth rate

At small input concentrations of reactants the silicon growth rate appears to increase linearly with the input concentration. At higher input partial pressures there is a departure from linearity, caused by parasitic reactions in the gas phase or secondary reactions at the solid interface. The first type of reaction has been described by Eversteyn for the case of silane (SiH_4) in hydrogen, where gas phase nucleation leads to a cloud of small solid silicon particles that deposit on the growing interface (Ref.16). This leads to loss of the crystalline perfection of the growing layer. In this case homogeneous gas phase reactions begin to play a role above a certain gas phase concentration of the order of 0.1 volume percent of silane in hydrogen. In the epitaxial apparatus a steep temperature gradient is present near the growing interface. The critical silane concentration for the gas phase reaction now has to be compared with the actual silane concentration present in the boundary layer. The critical concentration decreases exponentially with increasing temperature, the actual silane concentration shows a linear decrease in the boundary layer in which the main temperature gradient is present. The situation in depicted in Fig.8, where it is seen that homogeneous gas phase nucleation can be avoided by a steep temperature gradient in combination with a low reactant surface concentration (diffusion-limited growth) and a not too high reactant concentration. It has been shown (Ref.17) that homogeneous gas phase decomposition of silane can be prevented by the addition of some HCl to the gas phase. In this way high growth rates of more than 10 μm/min become possible for a 1:1 mixture of silane and hydrochloric acid in hydrogen. Gas phase reactions are also less pronounced when chlorosilanes are used as a reactant (SiH_2Cl_2, $SiHCl_3$ or $SiCl_4$). In these cases, however, secondary reactions at the interface become important. Apart from silicon and HCl, other reaction products appear in the chemical equilibrium, $SiCl_2$ being the main new reaction product. An illustrative example is $SiCl_4$ in hydrogen (Ref.18) where the growth rate shows a maximum as a function of input concentration (Fig.9).

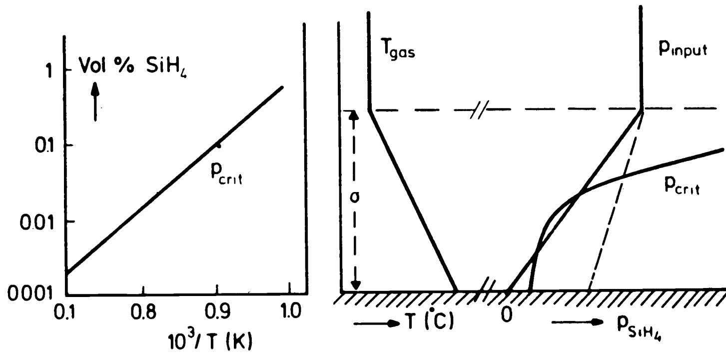

Fig.8. The actual gas phase concentration of silane in the boundary layer compared with the critical concentration for homogeneous gas phase nucleation. A low input concentration and a steep temperature gradient prevent the unwanted nucleation in the gas phase.

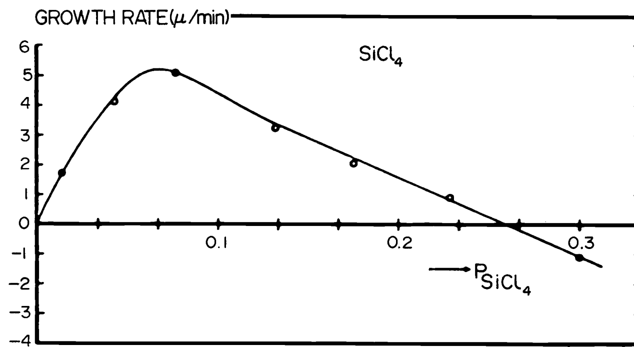

Fig.9. Silicon growth rate as a function of input concentration of $SiCl_4$ in hydrogen. At high concentrations negative growth rates occur (etching of a silicon substrate) (Ref.18).

Apart from the growth reaction

$$SiCl_4 + 2H_2 = Si + 4HCl \qquad (6)$$

the following reaction has to be considered

$$SiCl_4 + Si = 2SiCl_2 \qquad (7)$$

The latter reaction becomes increasingly important at higher input concentrations of the reactant ($SiCl_4$) and higher reaction temperatures, to an extent where even etching of a silicon substrate (negative growth rate) is found. This behaviour is in accordance with thermodynamic expectations (Ref.19,20,21). The situation at which G = 0, where etching and growth are in balance deserves special attention. It appears that the $SiCl_4$ concentration

at which this situation prevails depends strongly on the type of reactor used. The temperature gradient normal to the interface determines the diffusion of reactants and reaction products via the effect of thermodiffusion. The steeper the temperature gradient the higher the $SiCl_4$ concentration at which R = 0 (Ref.21).

Morphology of grown layers

It has been shown by Van den Brekel (Ref.5,22) that the morphology of the growing layer strongly depends on the magnitude of the dimensionless CVD number. This means that different surface structures can be expected in the diffusion-limited mode and in the surface reaction limited growth.

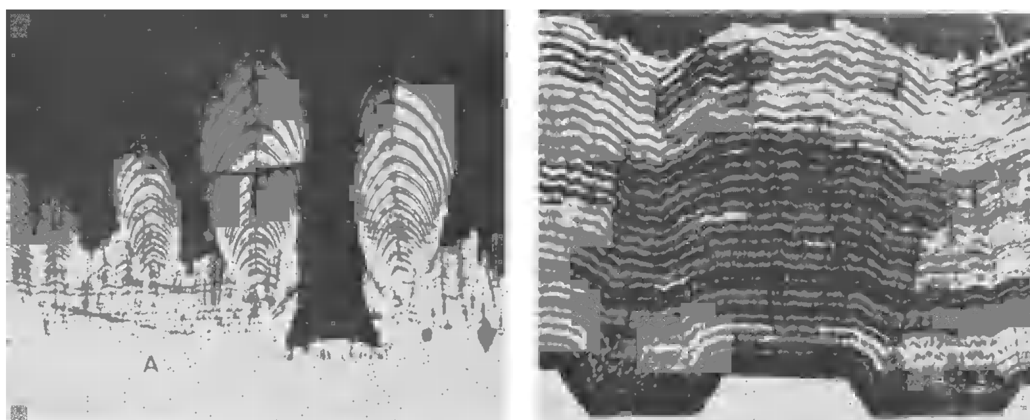

Fig.10. Growth morphologies at surface irregularities for (a) high values of the CVD number (high growth temperature) and (b) low values of CVD number (low temperature growth). In both cases $SiHCl_3$ is used in hydrogen, input concentration 0.6 vol.%. (Ref.5).

Figure 10 gives experimental results of features in the growth of polysilicon near surface irregularities both for high and low values of the CVD number. In the latter case, according to Eq.3, the surface concentration of the reactant is high and nearly constant over the whole surface. This results in a homogeneous growth rate, in contradiction to the diffusion-controlled region where shoulders in the surface receive the greatest part of the diffusion flux as explained in Ref.5. Smooth growth is expected at low temperatures, where the CVD number has a small value, and also at reduced pressures as observed experimentally. It appears, however, that smooth growth is also observed when secondary reactions at the interface become important, leading to silicon-containing reaction products other than silicon itself. Fig.11 shows that at constant temperature the surface structure dramatically depends on the input concentration of $SiHCl_3$ (Ref.22). Smooth filling of surface irregularities is found at higher concentrations, where the growth rate is reduced because of the presence of secondary reactions. It is shown by Van den Brekel and Jansen (Ref.23) that the vapour growth with respect to morphology is an essentially unstable process. Surface irregularities tend to grow out to larger dimensions. The relaxation time for the evolution of surface perturbations has to be compared with the actual growth period. It appears that the relaxation time depends on the process such that high values of the CVD number correspond to short relaxation times and vice versa. This confirms the importance of the magnitude of the CVD number of the chemical vapour deposition.

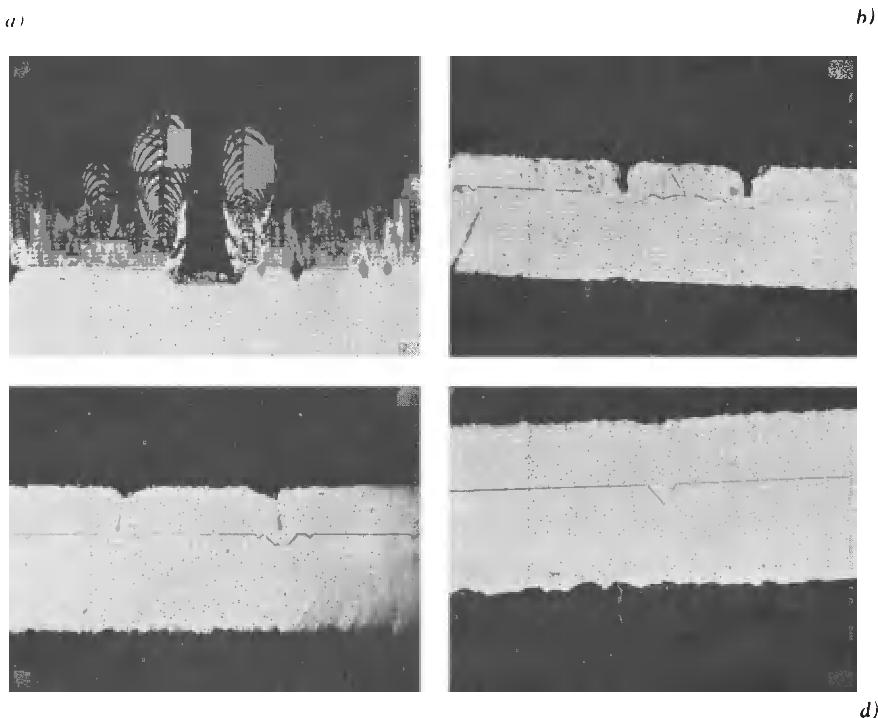

Fig.11. Growth morphologies near surface irregularities at constant temperature (1180°C) with various input concentrations of $SiHCl_3$ in hydrogen (a) 0.6 vol %, (b) 1.0 vol %, (c) 2.0 vol%, (d) 3.0 vol %. (Ref.22).

Nucleation of silicon

The phase transition from gas to solid, in most cases, does not occur spontaneously. Supersaturation in the gas phase is needed to lead to nucleation of the second phase. The nuclei have to exceed a certain critical size in order to be stable. In general the critical nucleus is smaller at higher supersaturations. Moreover, nucleation on a solid surface is favoured over homogeneous nucleation, the critical nucleus on a solid substrate having a smaller number of atoms in the nucleus. No nucleation is expected at a flat liquid surface when the reactant atoms dissolve in the liquid. The nucleation is important as it determines the crystalline structure of the growing layer. A great number of theoretical studies have been devoted to the nucleation in crystal growth. Ref.24 gives a good survey. Experimentally various modes of nucleation are observed, depending on the type of substrate and the composition of the gas phase. This will be shown in the following for three different combinations.

Nucleation of silicon on silicon

This type of nucleation is most important in the production of monocrystalline silicon layers on a single crystalline silicon surface. It has been shown (Ref.25) that silicon grows on a clean surface via the lateral movement of steps. Silicon adatoms diffuse to the steps and are incorporated there, causing the step to advance (Fig.12).

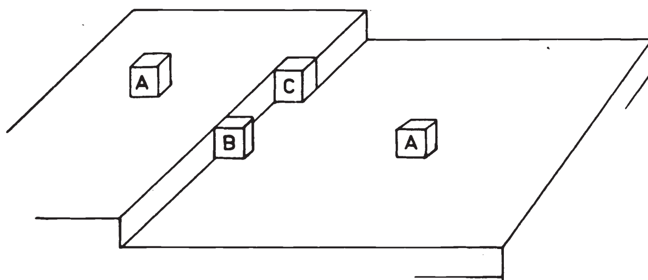

Fig.12. Schematic representation of crystal growth via the movement of adatoms (a) via steps (b) to stable kink sites (c).

Steps are present when the surface has a slight inclination with respect to a low index crystal plane. The growth rate increases with misorientation as the step density increases (Ref. 26), Nishizawa has shown that it is possible to produce facets with a very low step density. In that case secondary nucleation of adatoms leads to the formation of three-dimensional nuclei that grow out to pyramids on the surface (Ref.27). The uninterrupted movement of steps on the surface is impeded when impurities are present on the surface. It this case, too, a secondary nucleation is observed (Ref.25). At lower temperatures the reaction of silicon compounds and the nucleation of silicon on a solid surface meet with difficulties leading to polycrystalline growth even on a single crystalline substrate. Such problems are not present on a liquid surface.

Nucleation on a liquid surface

The properties of a liquid surface as a substrate for CVD are nicely revealed in the growth of silicon whiskers via the VLS (vapour-liquid-solid) process (Ref.28). Fig.13 shows the situation where a liquid alloy droplet is present on a solid silicon surface together with silane in the gas phase. The temperature is so low that solid-gas reactions are slow. The absence of any significant barrier to the reaction of silane on the liquid surface leads to solution of silicon in the liquid. As soon as supersaturation is reached, growth of silicon at the solid-liquid interface leads to the formation of a whisker with a liquid droplet on top. This growth habit can be observed when reaction rates are widely different between the solid-gas and the solid-liquid systems.

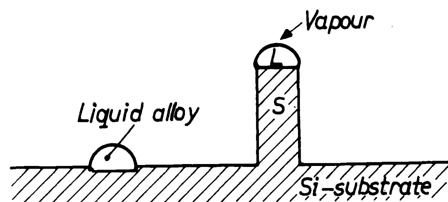

Fig.13. Principle of vapour-liquid-solid (VLS) growth of whiskers via a liquid alloy on the solid surface (Ref.28).

Another example is found in attempts to produce cheap silicon solar cells on a non-crystalline surface (Ref.29). A substrate (e.g. graphite) is coated with a 5 μm thick molten tin layer, and at about 1000°C silane is introduced via the gas phase. Reaction occurs at the liquid surface and silicon is dissolved. At a relatively high deposition rate the liquid will reach supersaturation at the top surface and silicon nuclei are formed that float on the surface. These nuclei have an additional degree of freedom and rearrange themselves to form bigger aggregates. The addition of HCl in the gas phase decreases the number of nuclei, and each nucleus may now grow out to useful dimensions (300 μm diameter at 30 μm thickness). Among the various methods used to obtain solar grade silicon this CVD method is one that deserves detailed study.

Nucleation on foreign substrates

The best studied case is the nucleation and growth of silicon on single-crystalline sapphire and spinel surfaces. Epitaxial growth is observed above 1000°C starting from differently oriented nuclei (Ref.30). It is shown that upon prolonged growth one type of nucleus overgrows the others. After about 0.5 μm of silicon growth a singly oriented layer is formed with a quality suited for the production of devices (Ref.31). Nucleation on amorphous substrates (SiO_2, Si_3N_4) leads to random nucleation. The nuclei grow out to give polycrystalline silicon. The greatest crystallite size is found at higher temperatures. The addition of HCl also helps to increase the crystallite size (Ref.32), in which case columnar growth is also observed, crystallite sizes do not exceed 10 μm. Small crystallites are often needed in smooth polycrystalline layers. Nucleation and growth at low temperatures (500°C) then leads to mirror smooth polysilicon deposits (Ref.15).

Crystal quality versus growth rate

In crystal growth a high growth rate is of economical importance, but there are several processes that limit the actual rate. Increasing the growth rate may lead to supersaturation in the gas phase, making it impossible to avoid spurious nucleation. There are several ways in which homogeneous decomposition can be reduced and growth rates up to 40 μ/min have been

reported in the CVD of silicon (Ref.17). Increasing the growth rate also inevitably leads to a loss of crystalline perfection. Fig.14 shows experimental regions of monocrystalline and polycrystalline growth on a monocrystalline silicon surface. High temperatures and low supersaturations favour smooth single crystalline growth. An increase in growth rate or a decrease in growth temperature may lead to disturbances in the single-crystalline growth and eventually poly-growth is observed.

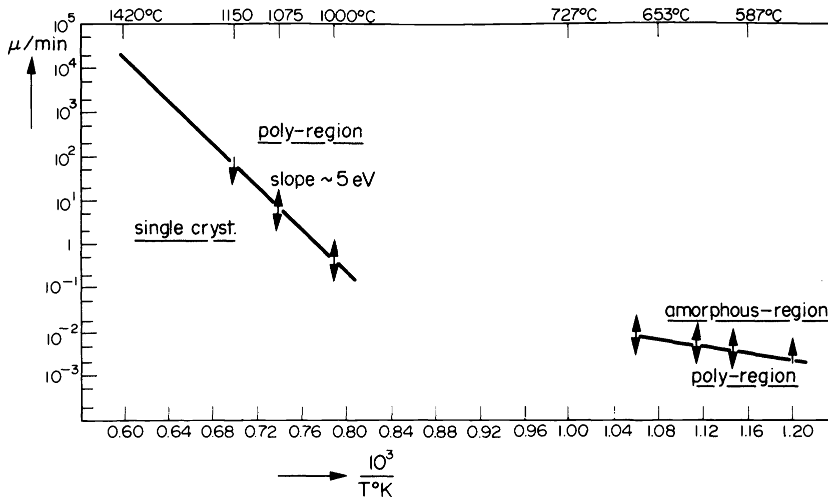

Fig.14. Regions of growth rates and temperature in which monocrystalline, polycrystalline or amorphous layers are formed on a monocrystalline silicon substrate (Ref.9).

The apparent activation energy of the dividing line shown in Fig.14 is 5 eV (115 Kcal/mole). This value corresponds to the activation energy for self-diffusion of silicon in silicon and leads to an explanation in which the factor G/D determines the degree of crystallinity. G is the growth rate and D the coefficient of self-diffusion in silicon. At high growth rates misplaced silicon atoms have no possibility of reaching the surface and cannot be eliminated so that polycrystalline growth results. It is interesting to note a second dividing line at lower temperatures; where a transition from polycrystalline to amorphous material is found (Ref.9). Here the factor G/D_2 determines the transition in which D_2 could represent the surface diffusion coefficient of silicon on silicon. Amorphous material is obtained when silicon atoms are deposited on a surface site faster than they can diffuse away on the surface. In such a case only short-range interactions determine the structure. As already mentioned, the defect-free, monocrystalline material needed for large scale integrated circuits is made at the high temperature side of Fig.14, whereas the amorphous material for possible solar cell applications is made at the extreme low temperature side of the same figure.

CONCLUSION

In a symposium on Chemistry for the Welfare of Mankind several reasons can be given for including a paper on silicon technology, in which the chemical vapour deposition of silicon plays a prominent part. One of the reasons is that the problems of today's world call for good communications between people. In systems ranging from telecommunication networks to hearing aids silicon devices help to reduce the size and the energy consumption of the apparatus. They have lent enormous impetus to the dissemination of education, information and entertainment. A further characteristic of the worlds' problems is the great complexity, and computers can do much here in helping to solve the difficulties. Large scale and very large scale integration of functions based on silicon technology will bring the next generation of computers into sight, and microprocessors will increase the safety and reliability of a large number of processes and operations. The third point is the promising outlook for the photovoltaic conversion of solar energy by silicon solar cells, which can contribute towards the supply of energy needed for the welfare of mankind.

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