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METHOD FOR PRODUCING SEMICONDUCTOR SINGLE CRYSTALS

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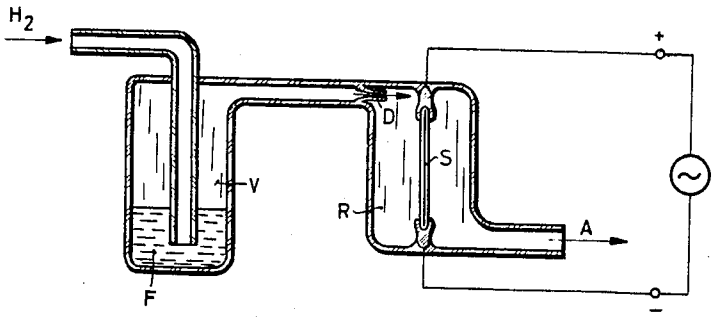

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METHOD FOR PRODUCING SEMICONDUCTOR SINGLE CRYSTALS

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This invention is concerned with a method and apparatus for producing semiconductor single crystals.

Great difficulties have until now been experienced in directly producing single crystals by the use of known methods designed to produce semiconductor crystals by separation of semiconductor material from the gaseous phase and deposit thereof upon a heated seed crystal made of the same substance. The reasons for these difficulties appear to reside in a number of disturbances, until now only partially recognized, which render the cohesive organic growth of separated material to a single crystalline phase difficult or impossible. These disturbances become particularly pronounced in the presence of the high temperatures required for the production of silicon single crystals, so that it was until now impossible to obtain completely satisfactory silicon single crystals by the use of the known method.

The object of the invention is to avoid these disturbances and to show a way which permits the use of the above mentioned method and results in disturbance-free semiconductor single crystals, particularly in completely satisfactory silicon single crystals.

The invention provides a method of producing semiconductor single crystals, preferably silicon single crystals, for use in semiconductor devices such as crystal diodes, transistors, etc., by deposition of semiconductor material of highest purity containing doping substances if desired, upon a heated carrier body made of the same material, by thermal decomposition or reduction or by other suitable chemical conversion, bringing about the separation of purest semiconductor material wherein the above mentioned disturbances are avoided, resulting in the production of completely satisfactory single crystals, by cleaning the surface structure of the single crystalline carrier body, for example, by suitable etching, and heating such cleaned surface structure to a temperature lying below the temperature at which maximum separation of the semiconductor material and deposition thereof upon the carrier body is effected at the corresponding reaction from the gaseous phase, causing the reaction gas to flow turbulently about the surface of the carrier body, and setting the velocity of separation of the material at the operatively effective working temperature applied in the reaction, so as to avoid over-saturation of the carrier body with separated semi-conductor material.

As has been ascertained in the course of investigations underlying the invention, the curve denoting the amount of silicon deposited upon a silicon carrier body in a unit of time, rises initially with increasing temperature (more accurately "surface temperature") T_0 of the carrier body, than passes at a temperature T_{max} through a more or less flat maximum, and thereupon drops steadily above this temperature T_{max}. This qualitative course of the separation velocity of a material from the gaseous phase and deposition thereof upon a carrier body of the same material, as a function of the surface temperature of the carrier body, can also be ascertained in connection with other semiconductor material, regardless of the particular semiconductor material to be produced and regardless of the gaseous initial compounds which are being employed. However, in the case of one and the same semiconductor material, the quantitative curve will depend upon the kind of the gaseous semiconductor compound used as

an initial material, and, accordingly, different initial materials will result in a different T_{max} and different rise and drop of the curve denoting the separation velocity as a function of the temperature T_0 of the surface of the carrier body and will also lead to different separation velocities with reference to a predetermined temperature value T_0.

If the surface of the carrier body is in a condition allowing the building-in of the separated semiconductor material in mono crystalline form, such material will be correspondingly built-in provided that all disturbances are carefully avoided. In case disturbances appear, the mono crystalline growth will be affected and the crystal will continue to grow in poly-crystalline manner. Such poly-crystalline degenerate semiconductor crystal requires remelting, for example, by zone melting, so as to obtain recrystallization to the mono crystalline phase. The teaching of the present invention avoids this disadvantage.

In the method according to the invention, the carrier body which is heated, for example, by passage of current therethrough or by high-frequency induction, delivers the energy required for the course of the reaction; the surface temperature T_0 of the carrier will accordingly correspond to the reaction temperature and the liberated semiconductor material will be preferentially produced respectively directly upon the surface of the carrier crystal and in the gaseous layer directly neighboring thereto.

Non-uniform heating of the surface of the carrier crystal will cause non-uniform separation velocities and therewith non-uniform crystal growth. This represents a phenomenon which disturbs the organic mono crystal formation considerably, because the faster growing surface particles cannot unite with the slower growing particles to produce an organic mono crystal structure. Another disturbance for the single crystal formation is caused by local areas along the surface of the carrier which are lean with respect to content of gas adapted for reaction. This again means that some surface parts will grow slower than other respectively neighboring parts. A third cause for impeding the single crystalline growth resides in contaminations and other inhomogeneities of the surface of the carrier body. As has been recognized, it is for these reasons necessary that the surface of the carrier body be thoroughly cleaned and the single crystalline surface structure carefully exposed. A further cause for the disturbance of the single crystal formation resides in excess production of semiconductor material separated from the gaseous phase; in other words, when the surface of the carrier is over-saturated with separated material, such material cannot be completely absorbed for single crystalline growth.

These causes which disturb the single crystal formation are with certainty avoided by the invention. It is for this purpose necessary to provide for careful initial preparation of the surface of the single crystal carrier body. Known measures for cleaning the single crystal carrier body to expose the surface structure thereof may be applied; for example, the surface may be prepared by grinding and polishing or by chemical or electro chemical etching with a suitable etching liquid. The carrier may also be prepared for the single crystalline deposit of semiconductor material by the use of a glow discharge or by cathode vaporization or vapor-removal of crystal layers disposed near the surface. Such surface layers may also be etched off by treating the carrier crystal, which may be heated if desired, with hot chlorine gas, chlorine hydrogen gas, or the like.

The carrier crystal, after being prepared as indicated above, is exposed to an atmosphere turbulently flowing thereabout, consisting respectively of purified reaction gas or a mixture of purified reaction gases, and is heated in such atmosphere to the temperature T_0 which is below

the temperature T_{max} at which is effected the maximum separation of the semiconductor material from the gas phase and maximum deposit thereof upon the carrier body. The application of this working temperature, that is, of the surface temperature T_0 of the single crystalline carrier body and the turbulent flow of the reaction gas about such body, effect uniform deposit of semiconductor material along the entire carrier surface, avoiding irregularities in growth, for example, formation of wart-like protuberances or groove-like depressions. Such irregularities along the surface of the growing crystal result in poly-crystalline degeneration which until now appeared to be unavoidable.

The appearance of wart-like protuberances at the surface of the growing crystal is always a sign that the temperature T_0 of the carrier surface was too high and above the value of T_{max} of the reaction applied. The velocity of separation and therewith the amount of separated and deposited material drops within the temperature range with increasing temperature T_0 and, accordingly, more material is separated and deposited at a colder area along the carrier surface than along neighboring hotter areas, thus causing along such areas an increased crystal growth. The increase of the surface occasioned by the increased growth along such portions of the carrier causes due to increased heat transfer gradual dropping of the temperature down to the temperature T_{max}, thus steadily increasing, the local material deposit. (Another cause for the cooling of such parts, acting in the same sense, namely, the increased heat consumption of the reaction at such colder portion, necessitated by increased material deposit, is of lesser importance.) The result is formation of a wart. However, the direction of growth and the growth velocity differ in such wart from the direction of growth and growth velocity of neighboring surface parts, and the wart therefore cannot be built into the remaining crystal structure in mono crystalline manner.

The conditions are different when the temperature T_0 of the surface of the carrier crystal is according to the invention below the temperature T_{max}. Within this temperature range, a slower crystal growth will be initially effected at colder parts as compared with neighboring parts, resulting initially in the formation of a minute depression. However, this depression, due to radiation and convection, loses less heat than adjacent parts, and its temperature will again approximate the temperature of neighboring surface parts. The material separation and deposit are accordingly automatically stabilized in the corresponding temperature range.

While disturbances caused by faulty matching of temperature will result in wart formation, a local lack of reaction gas will lead to surface disturbances in the form of depressions or grooves, especially transverse grooves. These disturbances are in accordance with the invention avoided with certainty by causing the reaction gas to flow turbulently about the carrier crystal. Investigations have proved that a laminated gas flow is for this purpose insufficient. The turbulence of the reaction gas may be conveniently produced, for example, by injecting the gas into the reaction chamber with a sufficiently high velocity or by stirring means employed within the reaction chamber. A high temperature differential or an electrical wind may also act to produce turbulence.

Investigations underlying the invention have revealed that a clean carrier surface, free of disturbance, turbulently acting reaction gases, and application of a working temperature $T_0<T_{max}$, are not always sufficient to produce silicon single crystals which are completely satisfactory. For, if the production of liberated semiconductor material exceeds a certain value which depends upon the employed reaction (especially upon the initial substances) and the working temperature T_0, the surface of the carrier will not be in a condition to accept the separated material fully in single crystalline form, and such excess material will be deposited in poly crystalline form. Accordingly, there arises in accordance with the invention the further requirement for setting or adjusting the velocity of separation and deposit of the material, at the applied reaction and working temperature, so that over-saturation of the carrier with separated semiconductor material is avoided.

As has been found, the separation velocity of a predetermined semiconductor material upon the carrier body depends not only upon the surface temperature T_0 but also upon the type of the initial gaseous compound. It may thus happen, in using certain initial substances, that the carrier may be very highly heated without exceeding its absorbability for the semiconductor material separated from the gaseous phase, while the carrier, in the case of other initial compounds of the same semiconductor may be over-saturated already at relatively low temperatures. In such a case, in accordance with a feature of the invention, the molecular concentration of the gaseous semiconductor compound must be reduced, for example, by dilution with a purified reducing or inert gas (such as a hydrogen, helium, argon, etc.) or by reduction of the gas pressure, so as to avoid the over-saturation of the surface of the carrier.

The value of the maximum separation velocity which is permissible at a working temperature T_0, must be empirically determined from case to case. Thus, it was found in the production of silicon single crystals from silicontetrachloride ($SiCl_4$) or silicochloroform ($SiHCl_3$) that the specific separation velocity, at a working temperature of 950° C. which is favorable in accordance with the requirements of the invention, must not exceed 10 mg./h. cm.^{2}, so as to make undisturbed single crystal formation possible. Accordingly, in the production of silicon single crystals from $SiCl_4$ and/or $SiHCl_3$, at a working temperature of 950° C., the specific separation velocity is maintained at a value equal to at the most 10 mg./h. cm.^{2}. When using dichlorinesilan (SiH_2Cl_2), the working temperature may be increased up to the melting point of the carrier body without causing over-saturation thereof. The use of SiH_2Cl_2 is, however, advantageous for another reason which is explained below.

In accordance with a further feature of the invention, the temperature of the carrier surface is to be as high as possible so as to obtain high mobility of the carrier surface for the single crystalline acceptance of the semiconductor material separated from the gas phase. For, the higher T_0 is, the greater is the probability for the organic building-in of the separated semiconductor material in single crystalline phase, provided that the absorbability of the carrier surface is not exceeded. It is in this connection especially important that the formation of the liberated semiconductor material is effected as much as possible at the carrier surface, because the semiconductor atoms separated from the semiconductor compound are in statu nascendi easier built into the grid of the carrier than semiconductor atoms liberated in layers of the reaction atmosphere more remote from the carrier and already bound in larger complexes. These favorable effects for the single crystalline building-in of the separated semiconductor material are augmented by a high temperature of the carrier surface. Since it is in case of SiH_2Cl_2 as initial compound in view of the high temperature thereof which exceeds the temperature T_{max} lying above the melting point of silicon, possible to heat the carrier to the melting point of silicon, without violating the basic requirement $T_0<T_{max}$, dichlorinesilan is according to the invention particularly advantageous to serve as initial compound, whereby the single crystalline carrier is heated to a temperature just below the melting point of silicon.

If desired, the method according to the invention may be combined with doping steps. For the doping of the semiconductor crystal to be produced, doping substance (in gaseous form), for example, in the form of purest gaseous compounds which decompose at the applied

working temperature, may be added to the reaction gas. Such measure does not affect the single crystal formation due to the low concentration of foreign substances required for the doping.

An embodiment of an apparatus for practicing the invention in the production of silicon single crystals is schematically shown in the accompanying drawing.

Purified hydrogen gas (for example, 0.15 l. H_2/min.) is caused to flow through a highly pure liquid silicon compound F, for example, $SiHCl_3$ or $SiCl_4$, contained in an evaporation vessel V and held at relatively low temperature, for example, 6–8° C., thereby transporting an amount of semiconductor compound, corresponding to the velocity of the flow, into a reaction vessel R containing at least one single crystalline carrier body S made of silicon, which is after preheating heated to the reaction temperature (for example, 950° C.) by an electric current flowing therethrough or by high-frequency induction. The turbulent flow of the reaction gas is effected by inflow thereof into the reaction chamber R through a nozzle D. If desired, turbulent gas flow may be effected by a mechanical gas stirrer or by maintaining the wall of the reaction vessel at a temperature which is considerably below the temperature of the carrier crystal body. The turbulent gas flow may also be effected by an electrical wind produced by the action of an alternating or direct voltage connected between the crystal carrier body and the outer vessel wall which in such case is conductive. The spent gases leave the reaction vessel at A.

It is immaterial for the invention whether the carrier crystal is a thin single crystal core which is in the operation of the new method uniformly coated with the separated semiconductor material or whether the separation is effected upon a particularly large plane surface of the carrier crystal from which the single crystal to be produced grows in accordance with the rate of separation. The invention makes it possible to produce always completely satisfactory semiconductor single crystals which are free of internal stresses, even in connection with a difficult material such as silicon, and which are at least of the same quality as single crystals drawn from a melt, frequently even superior thereto. This may be proved by the number of etching groups present per cm.^{2}, which is in the case of semiconductor single crystals, produced from the gas phase according to the invention, always considerably lower than in the case of semiconductor crystals produced by other methods. The method according to the invention, as contrasted with these other methods, offers the advantage of utmost technological simplicity so far as the apparatus and also the operation are concerned. The crystal formation does not require any particular supervision or guidance, thereby also benefitting increased output. The semiconductor single crystals produced in accordance with the invention may be cut without requiring remelting and, if desired after suitable surface treatment, may be further processed to produced diodes, transistors, etc.

The method according to the invention may also be sensibly and analogously applied for the production of semiconductor single crystals from SiC, $A^{III}B^{IV}$-compounds and $A^{II}B^{III}$-compounds (for example, CdS). The concentration of the initial gaseous components and the operating temperatures must thereby be individually set or adjusted according to the teaching of the invention. It is understood, therefore, that unless otherwise limited, silicon is referred to in an exemplary rather than in a strictly limiting sense.

Changes may be made within the scope and spirit of the appended claims.

I claim:

1. A method of producing semiconductor single crystals by separation, in a separation vessel, of highly pure semiconductor material from a gas phase, comprising the steps of exposing the single crystalline surface structure of a solid carrier consisting of the identical semiconductor material involved, heating said carrier to a temperature below the melting point thereof but sufficiently high to effect crystallization in free condition of said semiconductor material on the solid single crystal carrier surface from a gaseous compound of the semiconductor contained in reaction gas flowing through such separation vessel in which is disposed the carrier, effecting a turbulent flow of the reaction gas about the single crystal structure exposed on the surface of the carrier, maintaining the separation temperature at the carrier surface so low that an increase thereof would result in the increase of the separation velocity at such surface, and maintaining the separation velocity so low that an over-saturation of the carrier surface with available semiconductor material, which would hinder the single crystal growth, does not take place.

2. A method according to claim 1, wherein said carrier body is a silicon single crystal and wherein highly pure silicon is separated from said gas phase to grow upon said carrier body in single crystalline manner.

3. A method according to claim 1, comprising the step of reducing the molecular concentration of the semiconductor compound in said gas phase.

4. A method according to claim 1, comprising the step of reducing the molecular concentration of the semiconductor compound in said gas phase by dilution thereof with a purified gas selected from the class of gases consisting of hydrogen, helium and argon.

5. A method according to claim 1, comprising the step of reducing the molecular concentration of the semiconductor compound in said gas phase by reduction of the gas pressure applied thereto.

6. A method according to claim 1, for producing silicon single crystals from silicon tetrachloride at an operating temperature of 950° C., wherein the separation of the material to be deposited upon said carrier is effected with a specific velocity at a value which is maintained at the most at 10 mg./h. cm.^{2}.

7. A method according to claim 1, for producing silicon single crystals from dichlorinesilan in gas phase, wherein said single crystal carrier is heated to a temperature approaching the melting point of silicon.

8. A method according to claim 1, comprising the steps of maintaining at a relatively low temperature a liquid highly pure semiconductor compound contained in an evaporation vessel, said compound being selected from the class of compounds consisting of silicontetrachloride and silicochloroform, driving purified hydrogen gas through said liquid semiconductor compound for conducting amounts thereof into said reaction vessel corresponding to the flow velocity of said hydrogen, said carrier body contained in said reaction vessel being a single crystalline silicon body, said body being heated to a temperature corresponding at least to the temperature at which is effected reaction of the compound in gas phase to cause separation of said highly pure semiconductor material driven into said reaction vessel and deposit thereof upon said carrier body.

9. A method according to claim 8, comprising the step of maintaining the outer wall of said reaction vessel at a temperature considerably below the temperature of said carrier body so as to produce a temperature difference which is effective to impart turbulence to the stream of the gas phase conducted into said reaction vessel.

10. A method according to claim 8, comprising the step of producing by an electrical voltage connected between the outer wall of said reaction vessel and said carrier body an electrical wind to impart turbulence to the gas phase conducted into said reaction vessel.

11. A method according to claim 8, comprising the step of heating said carrier body by current conducted therethrough.

12. A method according to claim 1, for producing silicon single crystals from silicochloroform at an operating temperature of 950° C., wherein the separation

of the material to be deposited upon said carrier is effected with a specific velocity at a value which is maintained at the most at 10 mg./h. cm.^{2}.

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