

Sept. 12, 1967

T. RUMMEL
PROCESS FOR PYROLYTICALLY PRECIPITATING
ELEMENTAL SEMICONDUCTOR SUBSTANCE
Filed Aug. 7, 1963

3,341,359

Fig.1

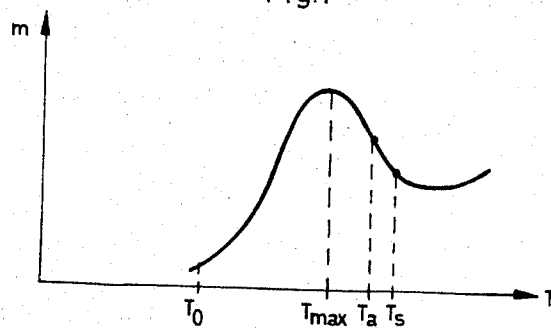
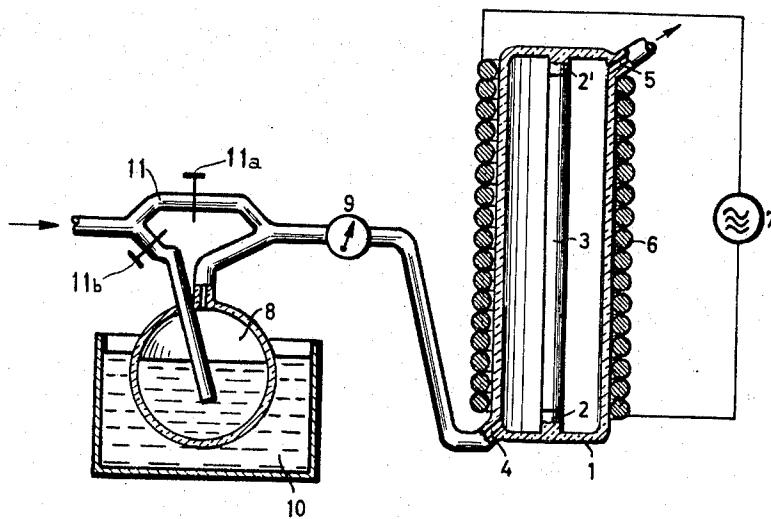


Fig.2



1

3,341,359

PROCESS FOR PYROLYTICALLY PRECIPITATING ELEMENTAL SEMICONDUCTOR SUBSTANCE

Theodor Rummel, Munich, Germany, assignor to Siemens & Halske Aktiengesellschaft, Berlin, Germany, a corporation of Germany

Filed Aug. 7, 1963, Ser. No. 300,587

Claims priority, application Germany, Aug. 24, 1962,
S 81,093

6 Claims. (Cl. 117-201)

My invention relates to the pyrolytic precipitation of elemental semiconductor substance, preferably silicon or germanium, from a reaction gas containing a compound of the substance, upon a monocrystalline rod-shaped carrier.

According to a known process of this type for the production of monocrystalline silicon, a monocrystalline carrier rod, mounted only at its ends, is subjected to a flow of a reaction gas consisting of hydrogen and silicon halogenide and is heated to incandescent, pyrolytic temperature. As a result, the halogen compound of silicon is dissociated and the evolving free silicon precipitates upon the carrier rod where it forms a growing monocrystalline layer. The resulting jacket portion of monocrystalline silicon can be grown, in principle, up to any desired thickness. Since the carrier body can be heated to a high and uniform surface temperature, for example by passing electric current from the rod holders through the carrier rod, the entire carrier surface with the exception of the mounted ends is available for the precipitation thereon so that the silicon content of the reaction gas is well utilized. A particular prerequisite for trouble-free monocrystalline growth is the maintenance of the carrier surface at a temperature below the melting temperature of the carrier because otherwise the precipitated silicon would accumulate in droplets which would interfere with the uniformity and precipitation required for monocrystalline growth on the semiconductor surface. Nevertheless, even if the formation of molten or fused localities at the carrier surface is avoided, considerable difficulties are encountered in growing monocrystalline silicon and other elemental semiconductor substances from the gaseous phase.

Various methods have been attempted for minimizing the difficulties of pyrolytically growing a monocrystalline semiconductor rod. One of these methods is known from German Patent 1,048,638. According to this known method, irregularities in the growth of the precipitating material are minimized by heating the exposed surface structure of the monocrystalline carrier body in a reaction gas flow, with or without the addition of doping substances, to a temperature below the value at which the maximum participation of semiconductor substance takes place upon the carrier body. For this purpose, the reaction gas from the turbulent flow around the surface of the carrier body, and the precipitation rate at the chosen doping temperature with the chosen reactants are so adjusted in known manner as to prevent oversaturation of the carrier rod with the precipitating semiconductor material.

In the known process just mentioned, the carrier rod is heated by directly passing electric current therethrough. However, it has also become known to heat a rod-shaped carrier for pyrolytic precipitation of semiconductor material by inductance heating. For this purpose, the carrier is disposed on the axis of an induction winding which concentrically surrounds the carrier and is energized with alternating current, particularly of high-frequency. The axial length of the coil is preferably so dimensioned that the peripheral carrier surface on which the precipitation is to take place becomes inductively heated to the pyrolytic temperature as uniformly as possible.

2

Such a method, employed for the production of particularly hyperpure silicon, is described in U.S. Patent application Ser. No. 51,630, filed Aug. 24, 1960.

It is an object of my invention to improve pyrolytic semiconductor production methods of the above-mentioned kind toward minimizing the disturbances and non-uniformities encountered in the growth of the precipitating semiconductor substance upon the monocrystalline carrier, and toward obtaining a pyrolytically grown product more closely approaching monocrystalline perfection than heretofore achievable.

It is a further object of my invention to provide a process for pyrolytically precipitating elemental semiconductor substance in which irregularities in the rate of growth of the semiconductor crystal are automatically equalized.

To this end, and in accordance with my invention, I maintain the monocrystalline rod-shaped carrier or core during the entire pyrolytic precipitation process at a proper temperature below the melting point of the elemental semiconductor substance by subjecting the carrier surface to induction heating by means of an electromagnetic field preferably of high-frequency, along the entire length that is to receive the precipitate. I further adjust the composition of the reaction gas during the entire precipitation process in such a manner that the precipitation rate of the elemental semiconductor substance has a maximal value at a temperature T_{max} which is below the pyrolytic operating temperature T_a that is maintained inductively and substantially uniformly at the carrier surface, the precipitation rate having upwardly from the temperature T_{max} at its maximum a monotonously or continuously declining range which includes the chosen pyrolytic precipitation temperature T_a of the carrier surface, so that the actually effective precipitation rate is appreciably smaller than that obtaining at the lower temperature T_{max} .

The invention will be further described with reference to the accompanying drawings in which:

FIG. 1 is a coordinate diagram of precipitation rate against carrier temperature; and

FIG. 2 shows schematically and in section an apparatus for performing the process according to the invention.

The curve shown in the diagram of FIG. 1 is typical of the precipitation characteristic required of a reaction gas suitable for performing the process according to the invention. The abscissa indicates the temperature T at the carrier surface. The ordinate indicates the quantity m of the elemental semiconductor substance, here silicon, which is precipitated upon each cm^2 of the carrier surface per minute. Consequently, the m -values indicate the rate of precipitation. The values shown in the diagram are conditioned upon maintaining a constant flowing speed of the reaction gas through the reaction vessel. The precipitation of silicon begins to be noticeable at a threshold temperature T_0 . As the carrier surface temperature increases to a temperature T_{max} , the precipitation rate also increases. With further increase in temperature, the precipitation rate monotonously or continuously declines through a range of temperatures which includes the chosen pyrolytic working temperature T_a at the carrier surface. This pyrolytic working or reaction temperature T_a should be higher than the temperature T_{max} of maximum precipitation, but must remain lower than the melting temperature T_s of the carrier. Thus, in the case of silicon, the reaction temperature at the carrier surface must be lower than $1415^\circ C$. As a rule, the temperature T_a is higher than $1100^\circ C$, and even more particularly higher than $1150^\circ C$.

The composition of the reaction gas decisively determines whether in a particular case the curve of precipita-

tion rate against carrier temperature possesses the characteristic exemplified in FIG. 1 which is necessary for the process performed in accordance with the invention. An example of an unsuitable reaction gas is one in which the semiconductor compound to be dissociated is a silane. Silanes or other pure gaseous hydrogen compounds of semiconducting elements, when used in the process, become increasingly dissociated at increasing temperature during the formation of the semiconducting element, and the precipitation curve, if plotted in accordance with the principles of FIG. 1, does not exhibit a maximum value followed by a range descending toward higher temperature values. However, the necessary precipitation-temperature characteristic can be produced and regulated by employing semiconductor-halogen compounds.

For example, when the reaction gas employed is composed of 5 mole percent SiHCl_3 and 95 mole percent hydrogen, the precipitation rate becomes a maximum at a carrier temperature $T_{\text{max}} = 1400^\circ \text{C}$. The quantity of the precipitation silicon also depends upon the pressure of the reaction gas and amounts at normal atmospheric pressure to about 2 mg. silicon per minute and per cm^2 of carrier surface. If the carrier temperature is increased above 1400°C ., the precipitation rate decreases. The value of the temperature T_{max} greatly depends upon the hydrogen content of the reaction gas. For example with molar ratio of 7 mole percent SiHCl_3 and 93 mole percent hydrogen, the temperature T_{max} of maximum precipitation is considerably above the melting point of silicon. Conversely, a reaction gas composed of 2 mole percent SiHCl_3 and 98 mole percent hydrogen produces a maximum rate of precipitation at about 1100°C ., so that the pyrolytic reaction temperature T_a can be adjusted to any value within the range from about 1150°C . up to the melting point of the carrier. Indeed, the just-mentioned operating conditions have been found to be preferable, and a reaction temperature at about 1250°C . is well applicable under these conditions.

If silicon tetrachloride SiCl_4 is used instead of silicichloroform SiHCl_3 , analogous temperature and composition ratios are applicable, except that the quantity of silicon precipitating during unit time for a given gas pressure and a given temperature is smaller than when using SiHCl_3 under the otherwise same conditions.

Consequently, when using a reaction gas consisting of a mixture of hydrogen with SiHCl_3 or SiCl_4 , the SiHCl_3 or SiCl_4 content in the reaction gas should not exceed 5 mole percent. However, when SiHCl_2 or SiH_2Cl is used, somewhat different values will result according to experience.

An example of the process performed according to the invention will be best described with reference to FIG. 2 in which there is shown a rod-shaped carrier body 3 of hyperpure silicon mounted in vertical position in a cylindrical quartz reaction vessel 1 by means of coaxially spaced holders 2 and 2' also consisting of quartz. The reaction vessel has an inlet opening 4 and an outlet opening 5 for the reaction gas. A tightly wound induction coil 6 serving to heat the carrier is mounted in the outer surface of the reaction vessel and is sufficiently long enough to extend along the entire length of the carrier 3 between the two holders. During operation, the coil is energized by alternating current supplied from a high-frequency generator 7.

The reaction gas consists of 2 mole percent SiHCl_3 and 98 mole percent H_2 . The gaseous mixture is produced by passing a current of hydrogen in the direction of the arrow as shown in FIG. 2 through an evaporator vessel 8 filled with liquid SiHCl_3 whose temperature is kept constant by means of a temperature bath 10. The hydrogen and the liquid SiHCl_3 used are available in highly pure condition.

A gas-flow speed measuring instrument 9 is provided for determining the quantity of reaction gas entering per unit time into the reaction vessel. Also provided is a bypass 11 for the evaporator vessel 8 which is controllable by valves 11a, 11b, to permit further dilution of the gas

coming from the evaporator by adding pure hydrogen. For example, flow through valve 11b can be suitably reduced while the flow through valve 11a can be increased as required.

The quantity of SiHCl_3 entering per unit time into the reaction vessel 1 is dependent upon the temperature of the evaporator vessel 8 and the flow speed of the hydrogen gas passing through the evaporator vessel. By varying these valves, therefore, the amount of SiHCl_3 in the reaction gas can be regulated. This amount, of course, also depends upon the size and shape of the evaporator vessel, and it is, therefore, not possible to make definite and broadly applicable statements with respect to the temperature of the evaporator vessel and flow speed of the gas. However, with the aid of the gas-flow meter 9 the amount of hydrogen consumed within a given time can be measured and the hydrogen flow can then be regulated at will. For determining the parameter values of evaporator temperature and flow speed of the hydrogen gas to be adjusted during pyrolytic processing, the precipitation vessel can be substituted in preliminary tests by a cooling trap in which the entire SiHCl_3 entrained by the hydrogen current is caused to freeze out. In this manner, the SiHCl_3 content in the reaction gas which is entrained by the hydrogen at a given evaporator temperature and at a given flow speed of the hydrogen gas, can readily be determined. On the basis of a few such preliminary tests made with different flow speeds and/or evaporator temperatures, a number of resulting data are obtained from which a suitable combination of the speed of the carrier gas and the evaporator temperature can be derived in order to produce a reaction gas composed of 2 mole percent SiHCl_3 and 98 mole percent hydrogen. The flow-speed and temperature data are then employed during the subsequent pyrolytic process.

For initiation the precipitation process with the equipment shown in FIG. 2, the carrier 3 is heated to the desired precipitation temperature. For this purpose and if desired, after preheating, the induction field at the coil 6 is switched on and the carrier is thus heated up to the glowing temperature corresponding to the chosen value. For example it is preferable to adjust the temperature to a value of about 1250°C . because then the descending portion of the precipitation curve according to FIG. 1, at the chosen composition of the reaction gas, has a particularly steep slope. The precipitation temperature is then controlled and kept constant in known manner. Before commencing the precipitation operation proper, it is advisable to anneal the carrier for some time in a current of hydrogen. To commence the precipitation operation thereafter, the reaction gas is introduced into the reaction vessel in accordance with the composition determined by the preliminary tests, for example in the manner heretofore explained.

Since the growth of the carrier by precipitation takes place in the radial direction, the carrier surface gradually approaches the inner periphery of the induction heater coil as the precipitation process progresses. Consequently, the inductive coupling between the coil and the carrier surface increases during the precipitation process. The temperature of the carrier surface consequently likewise increases when the power supply to the heater coil is kept constant. Similar results are produced by the so-called skin effect resulting from eddy currents induced in the surface zone of the carrier and heating the carrier. Any parts protruding at the carrier surface, for example bosses or other protuberances, are therefore hotter than the normal carrier surface or even any recesses in the surface. These conditions are just the opposite from those existing when the carrier is heated by means of alternating current or direct current supplied by electrodes or terminals.

As aforementioned, the reaction gas employed in accordance with the invention is selected with due regard to the pyrolytic precipitation temperature adjusted at the carrier surface, so that a reduction in precipitation takes

place when the surface temperature is increased, and so that the rate of precipitation is augmented when the carrier temperature decreases. Consequently, any protruding and therefore hotter localities of the carrier surface encounter a reduced amount of precipitation, and any recessed and therefore cooler localities of the carrier surface receive an increased amount of precipitation.

Since the cooler localities receive more precipitated semiconductor substance, these localities will gradually rise above the level of the normal carrier surface so that they are heated more than the surface and therefore receive a reduced amount of precipitation. Conversely, more slowly growing localities of the carrier surface will eventually become cooler than the normal carrier surface and thus receive augmented precipitation.

Since my invention requires suitable adaptation to the composition of the gas as well as to the use of inductive means for heating the carrier, automatic equalization of irregularities in the rate of growth takes place. This is one of the fundamental requirements for the production of monocrystalline silicon as well as other elemental semiconductor substances.

With the exception of the requirement to operate in the descending portion of the curve representing the precipitation rate versus carrier temperature, the process can be carried out to advantage in the manner described in the aforementioned German Patent 1,048,638. This particularly applies to the required purity at the carrier surface, as well as the preferred use of a turbulent flow of reaction gas passing around the carrier body. With respect to these known process steps, reference may be had to the German patent for further details.

Since the semiconducting compound employed in the process according to the invention is greatly diluted with hydrogen and since, furthermore, precipitation takes place either under normal atmospheric pressure or at negative pressure, supersaturation of the carrier with precipitating semiconductor material generally does not occur.

If the semiconductor rods that are to be pyrolytically produced are not to be doped during the production process, purity of the highest degree is achieved in the product when the reaction gas contains only halogen and hydrogen besides the elemental semiconductor substance. For producing doped semiconductor rods, the doping element may be added to the reaction gas either in pure condition or in the form of a halogen or hydrogen compound, if it is desired to build the dopant into the semiconductor during the pyrolytic production process. Since the fraction of the dopant in the reaction gas must be fundamentally set at a very small value, the configuration of the precipitation curve of the semiconducting element from the reaction gas is not appreciably influenced thereby.

The phenomenon of a descending range following the precipitation maximum in the temperature-precipitation characteristic is probably due to the formation of subhalogenides, this formation being increasingly promoted with increasing temperature to such an extent that the occurrence of subhalogenides becomes more strongly pronounced than the formation of free silicon above a certain temperature. There is, however, the possibility that other reactions, for example disproportioning reactions or dissolution of silicon that is already formed, may cause a range of declining precipitation in the sense of the characteristic shown in FIG. 1.

While my invention has been illustrated and described as a process for pyrolytically precipitating elemental semiconductor substance, it is not intended to be limited to the details shown, since various modifications in my proc-

ess may be made without departing in any way from the spirit of my invention. Such adaptations should and are intended to be comprehended within the meaning and range of equivalents of the following claims.

I claim:

1. With the process of thermally dissociating elemental semiconductor substance selected from the group consisting of silicon and germanium from a reaction gas, containing a component of said substance and free of undesired impurity, upon a monocrystalline carrier of said substance heated in a flow of said reaction gas to pyrolytic reaction temperature below the melting point of said substance, in combination the steps of maintaining said pyrolytic temperature at the carrier surface by directly subjecting the carrier substantially uniformly to an alternating-current induction field, and mutually adjusting during the entire precipitation process the composition of the reaction gas and said pyrolytic reaction temperature at the carrier surface so that every slight increase of said temperature produces a decrease in the deposition rate of the substance on the carrier surface and every slight decrease of said temperature from the adjusted value thereof produces an increase in the deposition rate of the substance on the carrier surface.

2. In the process of claim 1, said substance being silicon, said reaction gas being fugitive halogen silane, and said pyrolytic reaction temperature being between 1100° and 1415° C.

3. In the process of claim 2, wherein the reaction gas comprises, as another component thereof, hydrogen intermixed with the halogen silane thereof.

4. The process of pyrolytically precipitating silicon from a reaction gas containing a silicon compound onto a rod-shaped carrier of silicon heated in a flow of said reaction gas to a pyrolytic temperature below the melting point of silicon, in combination the steps of employing as reaction gas a mixture of hydrogen and a silicon compound selected from the group consisting of SiCl_4 and SiHCl_3 , maintaining said pyrolytic temperature at the carrier surface above 1100° C. but less than 1415° C. by directly subjecting the carrier substantially uniformly to an alternating-current induction field, and adjusting during the entire precipitation process the content of said silicon compound in said reaction gas to a value of up to 5 mole percent at which the precipitation rate is less than the maximum and tends to vary in inverse relation to increase and decrease of the carrier temperature.

5. In the silicon production process according to claim 4, said reaction-gas mixture consisting substantially of about 98 mole percent hydrogen and about 2 mole percent of said silicon compound, and said reaction temperature at the carrier surface being above 1150° C. but less than 1415° C.

6. In the silicon production process according to claim 4, said reaction temperature at the carrier surface being about 1250° C.

References Cited

UNITED STATES PATENTS

3,222,217	12/1965	Grabmaier	117—213
3,232,792	2/1966	Rummel et al.	117—106
3,239,372	3/1966	Sirtl	117—201

FOREIGN PATENTS

1,048,638	1/1959	Germany.
-----------	--------	----------

ALFRED L. LEAVITT, *Primary Examiner*.

WILLIAM L. JARVIS, *Examiner*.