June 13, 1967 T. RUMMEL 3,325,392

METHOD OF PRODUCING MONOCRYSTALLINE LAYERS OF SILICON ON MONOCRYSTALLINE SUBSTRATES

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Fig.1

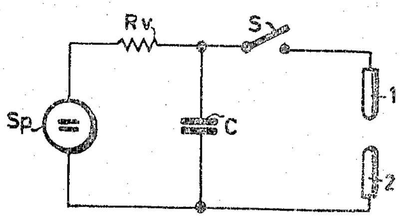


Fig.2

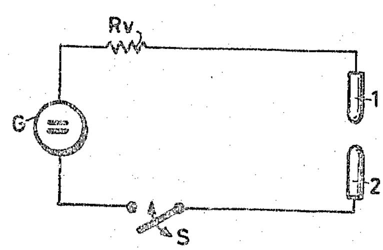


Fig.4

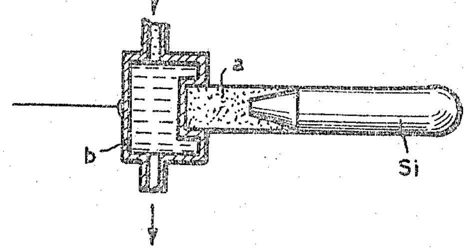
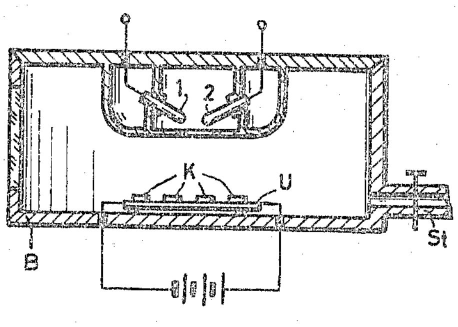


Fig.5



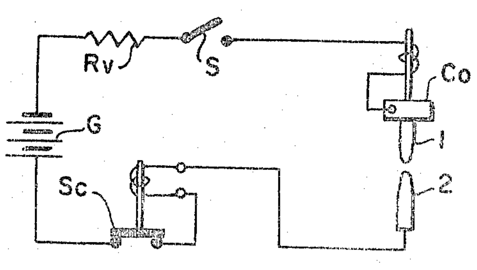


Fig.3

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METHOD OF PRODUCING MONOCRYSTALLINE LAYERS OF SILICON ON MONOCRYSTALLINE SUBSTRATES

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10 Claims. (Cl. 204—192)

My invention relates to methods and apparatus for the vapor-deposition of epitaxial layers upon substrates of monocrystalline silicon for use in electronic and related semiconductor devices. In a more particular aspect, my invention concerns a method and means according to which the required silicon vapor is produced with the aid of an electric discharge between electrodes.

Monocrystals, particularly those of semiconductor material, have been formed by producing an electron beam in an evacuated vessel between an incandescent cathode and an anode consisting of refractory metal, the electron beam being used for vaporizing the material from which the monocrystal is to be produced by causing the vapor to condense upon a monocrystalline seed of the same material. In such a method, the crystal seed may be heated by additional means, for example an infrared lamp, and the amount of heat applied can thus control the rate of monocrystalline growth. This method has been tested with a number of different substances and for several of them has resulted in monocrystals of satisfactory properties. However, the application of the method to silicon has heretofore failed to produce monocrystals such as are required for electronic semiconductor purposes because the growth of the precipitating silicon upon the crystal seed is generally not monocrystalline but rather has polycrystalline and irregular constitution even when the carrier or substrate receiving the precipitation consists of monocrystalline silicon and is provided with a highly purified surface.

It is an object of my invention to devise a method along the principles of the one mentioned above for the epitaxial production of monocrystalline silicon layers of any desired thickness upon carriers or substrates of monocrystalline silicon.

To this end, and in accordance with my invention, I pass within an evacuated vessel an electric pulse-wise or intermittent discharge through the gap between the tips of two electrodes that consist of hyperpure silicon, i.e. silicon of the extreme purity required for electronic purposes, so that silicon from the electrodes is vaporized by the electric discharge. Simultaneously, I expose to the evolving vapor the cleaned surface of a monocrystalline silicon substrate or carrier in the same evacuated vessel and heat the substrate surface to a temperature below the melting point of silicon but at least 800° C.

The research which resulted in the present invention has led to the conclusion that the difficulties heretofore encountered in attempts to produce monocrystalline silicon layers by vapor deposition upon substrates in accordance with the above-mentioned known method are predominantly due to the fact that with the evacuation of the processing space by presently known techniques an excessive amount of foreign substances is built or incorporated into the vapor-deposited silicon which more readily results in polycrystalline growth of the precipitating silicon than would be the case if the silicon were pyrolytically precipitated from a gaseous silicon compound, particularly a halogen-containing compound, upon the heated monocrystalline carrier body. This applies to a great extent when the silicon vapor is produced by prolonged overheating of silicon in an evaporator or by the action of an electron beam. Furthermore, these known methods of generating silicon vapor require the use of devices, for example evaporator vessels or hot cathodes, which contribute considerable impurities that prevent monocrystalline formation and also produce uncontrollable doping effects. In attempting to reduce such contamination of the products in the known vapor-deposition methods, one must invariably use relatively low vaporization temperatures which cause an unfavorable ratio of the silicon vapor pressure, to the vapor pressure of the foreign substances that are contained even in the best obtainable vacuum, with the result that the vapor-deposited silicon layers become polycrystalline and are besides uncontrollably contaminated. For example, under the mentioned circumstances, the silicon vapor contacting the carrier or substrate surface still contains a foreign-substance partial pressure of at least 10^{-5} or 10^{-6} mm. Hg, in comparison with a silicon vapor pressure of at most 10^{-2} mm. Hg.

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A more specific object of my invention, therefore, relates to increasing the silicon vapor pressure without simultaneously increasing the vapor pressure of the foreign substances contained in the vapor. This object is attained by the above-mentioned method in accordance with the invention because in the practice of this method the electrodes which serve as the carrier of the electric discharge and which consist of hyperpure silicon also function simultaneously as the source of the silicon vapor required for epitaxial deposition. Furthermore, by the above-mentioned cleaning and heating of the substrate surface, the operating conditions are such that the effect of precipitating impurities upon the monocrystalline growth is greatly suppressed.

Silicon monocrystals are preferably used as carrier bodies or substrates although other carrier bodies or substrates coated with a monocrystalline layer of silicon in accordance with known methods, are likewise applicable. Such surface disturbances as oxidation localities, soiling and the like are removed to a great extent from the surface of the substrate that is to receive the vapor-deposited layer, prior to performing the deposition process proper. Known surface cleaning methods for treatment of semiconductor bodies may be employed for this purpose. Examples of cleaning methods that are applicable are an etching treatment or annealing the substrate in an etching gas that does not produce any oxide spots at the semiconductor surface, for example annealing in Cl_2.

During the deposition process, the temperature of the carrier or substrate is preferably maintained as high as feasible and for this reason should at least be 800° C. On the other hand, melting of the precipitated silicon must be avoided because, aside from the danger posed by the dripping of the melted silicon, the high surface tension of liquid silicon can cause the formation of drops and hence non-uniformity of the vapor-deposited layer. It is, therefore, preferable to adjust the heating of the carrier or substrate to a surface temperature of about 1200° C.

For practicing the invention, the cleaned substrate, or a multiplicity thereof, is placed into an evacuable and cleaned processing vessel of quartz for example. After evacuation of the vessel, the substrate is heated to at least the above-mentioned minimum temperature of 800° C., but preferably to 1200° C. If a number of relatively small silicon monocrystals are to be processed, they are preferably placed upon a thermally stable support of silicon, molybdenum or the like through which an electric current is passed so as to heat it to the required temperature. Heating may also be effected by high-frequency induction or capacitively.

At least one pair of electrodes consisting of hyperpure silicon are mounted in the processing vessel. A high-voltage source is applied between the electrodes in order to produce a sequence of high-temperature discharge surges or impacts, preferably of individually short duration.

According to a preferred feature of the invention, the silicon electrodes are located within an additional housing of highly heat resistant material, for example molybdenum, and provided with a diaphragm opening from which the silicon vapor resulting from the electric discharges will emerge in a direction toward the crystal surfaces to be coated. For confining and orienting the vapor jet, additional diaphragms may be mounted between the electrodes and the crystal substrates. The rate of epitaxial growth can be adjusted or modified by a corresponding selection of the distance between the vapor source and the substrate surfaces. It has been found that an optimum result is obtained if the crystal surfaces are spaced a distance of approximately 7 cm. from the vapor source, i.e. the tips of the silicon electrodes. The vacuum in the processing vessel is preferably made as high as feasible and hence should be at least 10^{-5} mm. Hg. In the past practical performance of the invention, a vacuum of 10^{-6} and even greater vacuum has been employed. It is further advisable to cool the walls of the processing vessel and in some cases also the holders for the electrodes. If desired, the vapor source, including the pair of electrodes, can be moved periodically back and forth over the substrate surfaces that are to receive the silicon deposition.

Since the electric discharge between the two originally cold or at best only moderately warm silicon electrodes takes place in high vacuum, a field strength of at least 10^{-6} v./cm. is required for initiating the discharge. With a correspondingly high voltage, the breakthrough field-strength is first reached or exceeded at the mutually facing tips of the electrodes. Accordingly, the electric discharge commences at the electrode tips and remains essentially limited to the tip areas. The discharge is either a spark discharge or an arc discharge if the current source furnishes sufficient power. When selecting the voltage between the two electrodes and the power rating of the current source, attention must be given to the fact that the vaporization temperature of silicon, which is approximately 2700° C., must be exceeded at the electrode tips at least for short intervals of time.

The invention will be further described with reference to the accompanying drawings showing by way of example, various embodiments of apparatus according to the invention.

FIG. 1 is a schematic circuit diagram relating to the operation of the above-mentioned silicon electrodes with alternating voltage.

FIG. 2 is a schematic circuit diagram of another electrode system operating with direct-current arc discharges.

FIG. 3 is a schematic circuit diagram of a modified electrode system operating with direct-current arc discharges.

FIG. 4 shows in section an embodiment of a holder and cooling device for one of the silicon electrodes; and

FIG. 5 shows schematically and in section a processing apparatus according to the invention.

It has been found experimentally that sufficiently high discharge temperatures can readily be produced by impact spark discharges. Such spark discharges are obtainable in a relatively simple manner by means of electrostatic devices. For example, when a capacitor charged to a high voltage is discharged through the highly evacuated discharge gap between the tips of the silicon electrodes, then the high gap voltage causes sparks of extremely high temperature which have the property of vaporizing silicon to a great extent without noticeably melting the silicon.

The circuit diagram shown in FIG. 1 relates to such a device for the production of high-temperature sparks by surges of capacitive discharges. The two terminals of a high-voltage capacitor C preferably given a capacitance in the order of 0.01 microfarad, are connected with the respective silicon electrodes **1** and **2**. The capacitor C is charged from a high-voltage source S_p, for example a generator of the electrostatic type such as an induction machine or a machine of the Wimshurst or Van de Graaff type. The charging circuit preferably includes a series resistor R_v for example of 10 megohms. Consequently the capacitor C can be charged up to several hundred thousand volts in this manner. When the equipment is in operative condition, the normally open switch S is kept closed continuously. As soon as the increase in voltage of the capacitor reaches the ignition value between the electrodes **1** and **2**, a discharge through the electrode gap commences and continues until the voltage between the electrode tips has dropped below the extinction value. No discharge takes place during the subsequent period T in which the capacitor C is again charged up to the critical ignition voltage, this interval being in accordance with the equation $T=R_v \cdot C$. The duration of this interval must be sufficiently long that the electrodes will cool down and dripping of molten electrode material is prevented. The spacing between the electrodes for obtaining a spark discharge in the embodiment described is preferably a few millimeters and generally between approximate limits of 1 and 10 mm. The spark discharges are of extremely short duration and of extremely high temperature.

However, as mentioned, the method according to the invention can also be performed with the aid of arc-discharge pulses. For this purpose, the electrodes **1** and **2** in the embodiments shown in FIGS. 2 and 3 are axially movable relative to each other. It is assumed that the electrode **2** is stationary, whereas the electrode **1** in the embodiment of FIG. 2 is movable away from electrode **2** manually or mechanically by any suitable means. In the embodiment of FIG. 3, the electrode **1** is mounted in a control device C_o whose coil, when excited pulls the electrode **1** upwardly away from the electrode **2** a given arcing distance. A direct-voltage source G of about 100 volts is connected through a resistor R_v with the two silicon electrodes **1** and **2**. When the switch S is closed, the electrode **1** is pulled upwardly manually or mechanically in the embodiment of FIG. 2 or by the electromagnetic control device C_o of the embodiment in FIG. 3 a distance of a few millimeters and thereby ignites the discharge which is then maintained despite the relatively low voltage. The discharge has the character of an arc and is accompanied by appreciable vaporization as well as by melting of the silicon. Since the melting may rapidly cause the silicon to drip, the arc discharge must be switched off intermittently at a sufficiently early moment. This can be done by manually opening the switch S in the embodiment of FIG. 2 but is preferably effected by means of a contactor S_c connected in the circuit of the discharge as shown in FIG. 3. The time constant of the contactor S_c is chosen in accordance with the desired burning and extinction intervals of the periodic arc discharges.

It is preferable that the electrodes have a diameter at least in the order of 1 to 2 cm. because this minimizes the progressive shortening of the electrodes due to vaporization and has also the effect that the internal resistance of the electrodes is not excessive in comparison with that of the discharge gap. It is further preferable to give the electrodes a pointed shape at the respective tips, although the tip angle of each electrode may be relatively large. The general viewpoint to be kept in mind with respect to the dimensioning of the electrodes is the aim to minimize the amount of material that can be melted.

A preferred type of holder for the electrodes is shown in FIG. 4. The silicon electrode S_1 is fastened in a holder *a* of carbon which is embedded in a copper sleeve *b*. The electrode can be of any desired length, for example about 3 cm. The copper sleeve *b* is connected with a conductor for attachment to the source of operating voltage. The sleeve is preferably designed as a hollow body to receive liquid coolant for the electrode as shown.

It is advisable to pre-heat the electrodes when initiating the process in order to reduce the specific resistance of the electrodes for facilitating the ignition of the discharge.

The need for additional equipment to mount and control the electrodes depends essentially upon whether or not a variation or regulation of the electrode spacing is required during performance of the process. This is contingent mainly on the quantity of electrode material to be evaporated and also on whether the discharge is to be ignited by direct contact between the electrode tips. In the latter case it is necessary to provide means, as exemplified in FIGS. 2 and 3, that permit changing or controlling the electrode spacing during the operation of the processing apparatus without appreciably impairing the vacuum.

In the apparatus shown in FIG. 5, the silicon electrodes **1** and **2** are to be energized in a circuit according to FIG. 1. The discharge gap is adjusted to 5 mm., for example. The monocrystalline substrates K are located approximately 7 cm. beneath the discharge gap. They are placed upon a supporting carrier U of silicon-coated graphite. The carrier is heated by passing therethrough a current from a suitable source. The monocrystalline substrates K are thus heated by the carrier supporting them to a temperature maintained at 1200° C., for example. The walls of the processing vessel C consist of quartz and the vessel is connected through a suction duct S_t to a high-vacuum pump. During the vapor-deposition process, the vacuum pump is kept in continuous operation to maintain the desired vacuum.

The capacitor C used in the arrangement of FIG. 1, had a capacitance of about 0.01 μf. and was each time charged to about 40,000 v. and discharged through the electrodes in intervals of about 1 minute, thus producing a spark surge through the electrode gap. The surface of the substrates K subjected to the silicon vapor was coated within a period of about one-half hour with a monocrystalline silicon layer of 3 micron thickness.

The epitaxially precipitated layer of silicon can be given any desired doping by adding a doping substance, such as boron, gallium or phosphorus, in suitable quantity to the silicon material of which the electrodes are made. The doping substance then evaporates and precipitates together with the silicon under the effect of the high-temperature electric discharge.

The electrodes can be kept in rotation about their axis to cause the silicon electrodes to burn off more uniformly. This also has the effect that the vaporization spark remains at the same locality in space so that the atom jets passing through the masks or diaphragms always impinge upon the same area of the carrier.

The processing vessel B in the arrangement of FIG. 4 comprises a separate housing D in which the discharge gap is located and which has a diaphragm opening E through which the jet of silicon vapor passes toward the substrates.

To those skilled in the art, it will be obvious upon a study of this disclosure that with respect to details of the processing equipment, my invention permits of a variety of modifications and hence can be given embodiments other than particularly illustrated and described herein, without departing from the essential features of my invention and within the scope of the claims annexed hereto.

I claim:

1. The method of precipitating a layer of silicon upon

a monocrystalline substrate of silicon, which comprises passing within an evacuated vessel an electric discharge pulsewise through a gap between the tips of electrodes of hyperpure silicon and thereby vaporizing silicon from the electrodes, and simultaneously heating a cleaned surface of the silicon substrate in the vessel to a temperature of at least about 800° C. but below the melting point of silicon, whereby the vaporized silicon precipitating upon the substrate causes a monocrystalline layer to grow on the substrate surface.

2. The method of precipitating a layer of silicon upon a monocrystalline substrate of silicon, which comprises passing within an evacuated vessel a sequence of electric spark discharges between two electrodes of hyperpure silicon and thereby vaporizing silicon from the electrodes, and simultaneously heating the substrate in the vessel to a temperature below the melting point of silicon but at least about 800° C., whereby the vaporized silicon precipitating upon the substrate causes a monocrystalline layer to grow on the substrate surface.

3. The silicon precipitating method according to claim 2, which comprises producing the sequence of spark discharges by charging a capacitance with high direct voltage and periodically discharging the capacitance through the silicon electrodes.

4. The silicon precipitating method according to claim 1, which comprises producing the pulsewise discharges by intermittently burning and extinguishing an electric arc between the electrode tips.

5. The silicon precipitating method according to claim 1, which comprises producing the pulsewise discharges by moving the electrode tips into contact with each other, then temporarily separating them from each other to cause an electric arc discharge to burn between them, then interrupting the arc discharge and thereafter periodically repeating the same sequence.

6. The silicon precipitating method according to claim 1, wherein the silicon substrates are maintained at a temperature of about 1200° C. during precipitation.

7. The silicon precipitating method according to claim 1, which comprises moving the silicon substrates along the electrodes during vapor deposition.

8. The silicon precipitating method according to claim 1, wherein the vacuum in the vessel during precipitation is maintained at a pressure of not more than 10^{-6} mm. Hg.

9. The silicon precipitating method according to claim 1, which comprises directing the evolving silicon vapor through diaphragm means from the silicon electrodes toward the silicon substrate.

10. The silicon precipitating method according to claim 1, wherein the silicon of the electrodes contains doping substance to be vaporized and precipitated upon the substrate together with the silicon.

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