United States Patent [19]

Hara

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[54] **METHOD OF DEPOSITION OF SILICON BY USING PYROLYSIS OF SILANE**

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[30] **Foreign Application Priority Data**

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Dec. 29, 1970 Japan 45-123814

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[51] **Int. Cl.** **C23c 11/00**
[58] **Field of Search** ..... 117/106, 107, 107.2 R, 117/135.1

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[57] **ABSTRACT**

An improved method of deposition of silicon by using pyrolysis of silane, which employs a carrier gas of a mixture of hydrogen gas and an inert gas such as argon, helium, neon, krypton, xenon, radon and nitrogen.

1 Claim, 7 Drawing Figures

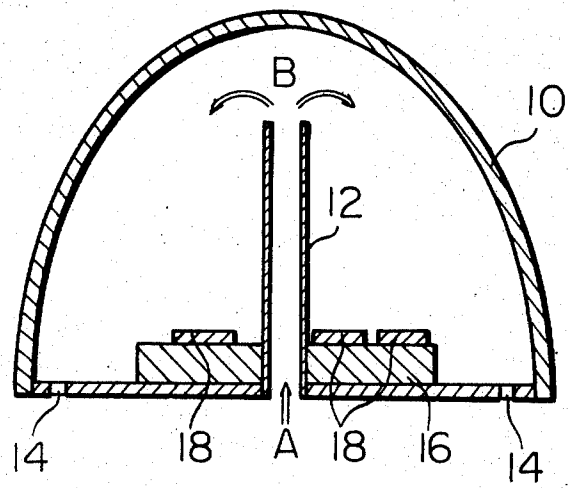
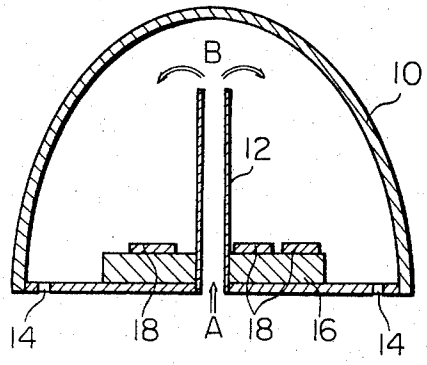


Fig. 1



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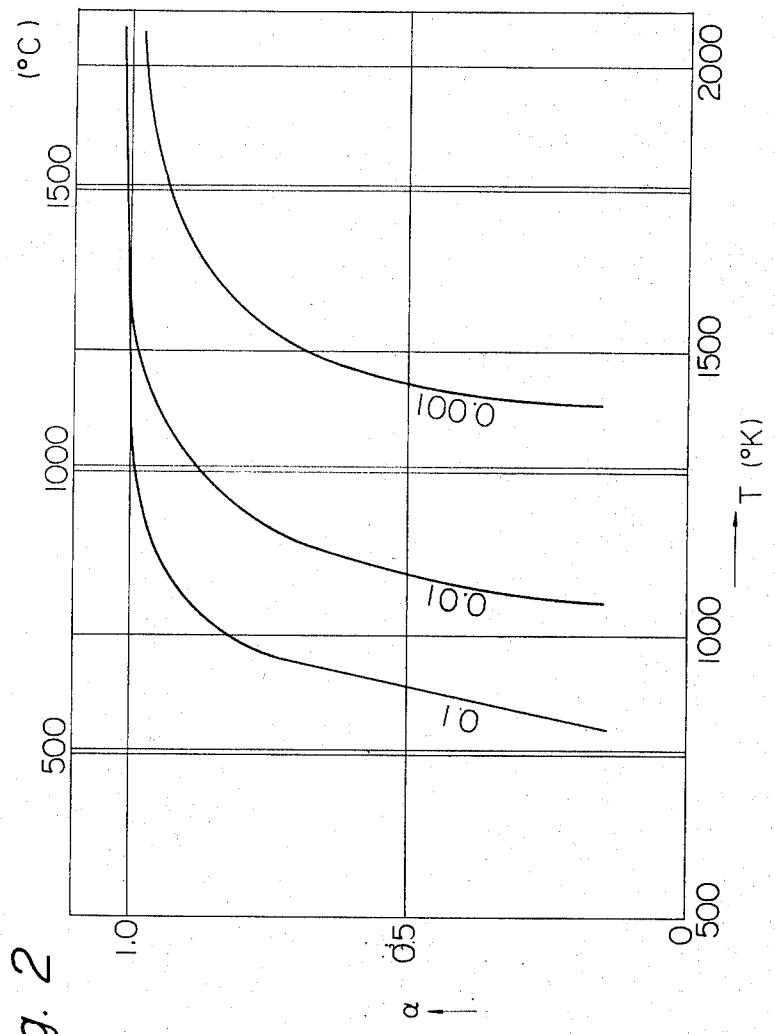


Fig. 2

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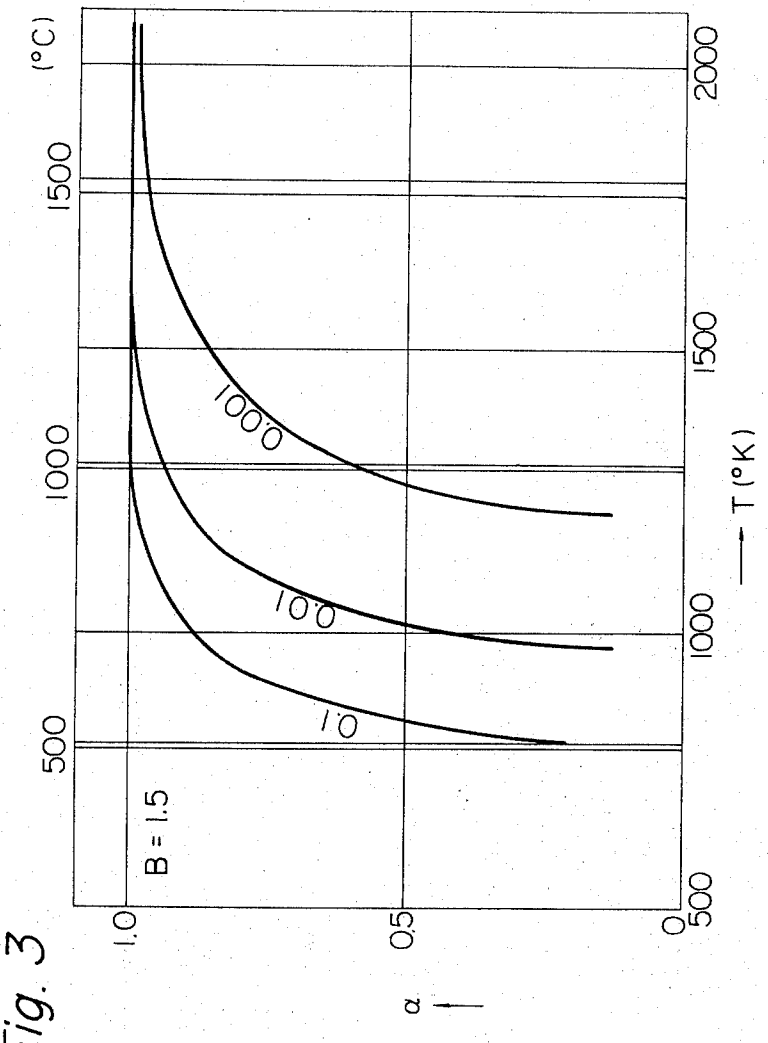


Fig. 3

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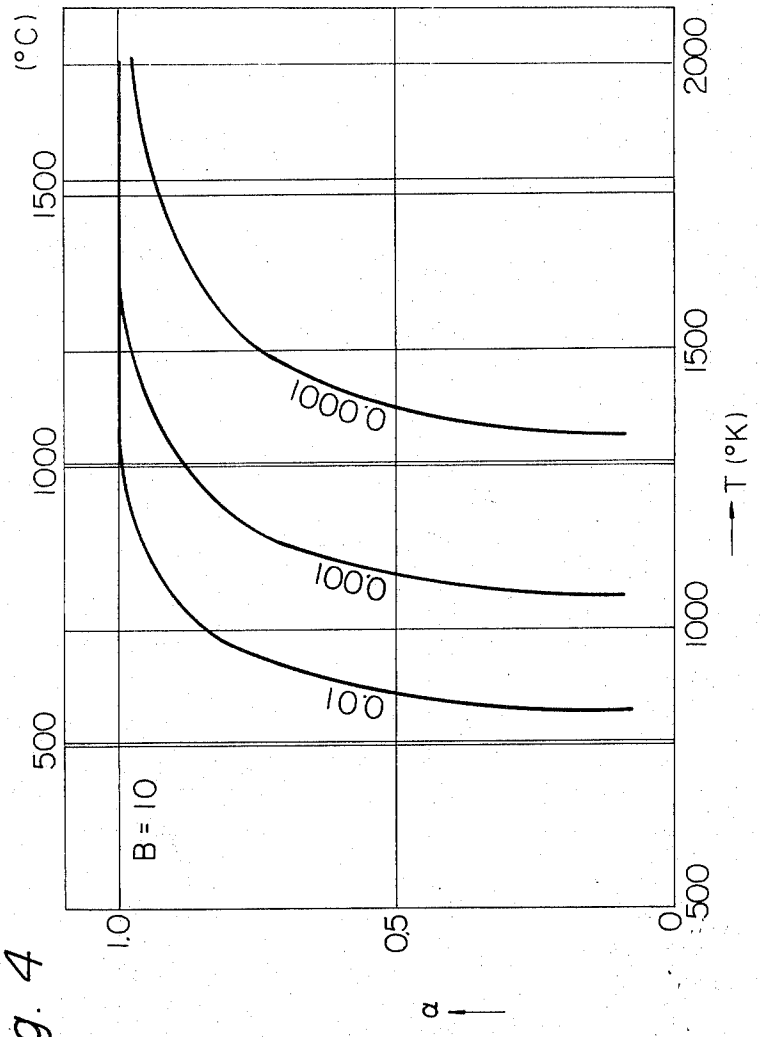


Fig. 4

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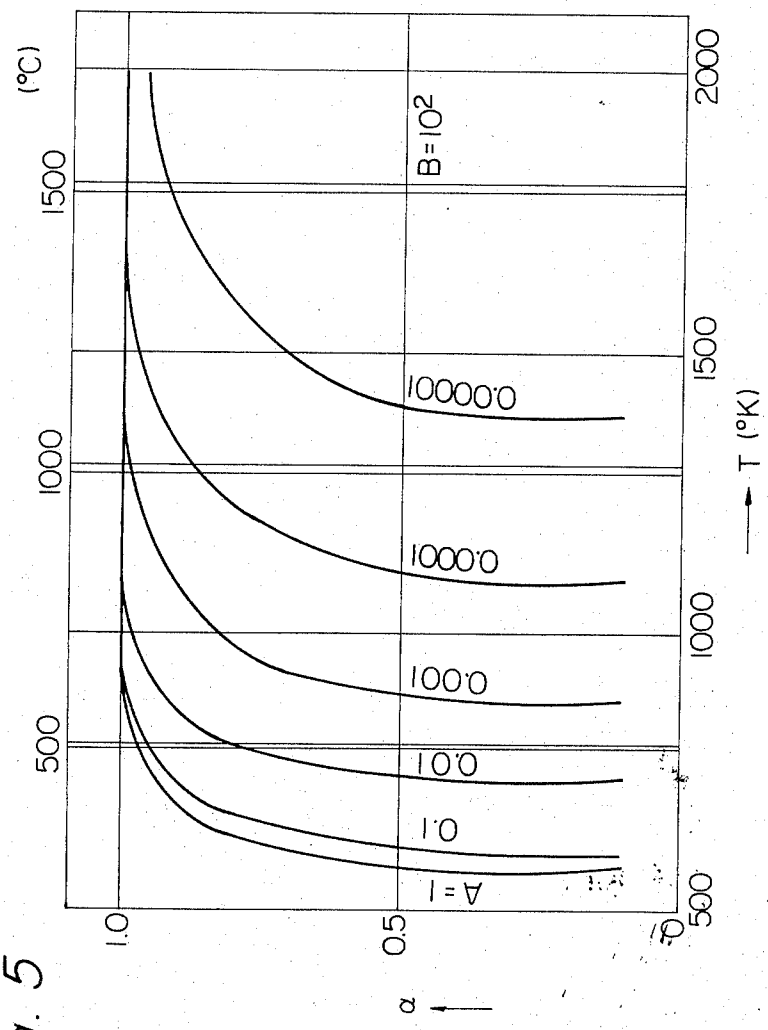


Fig. 5

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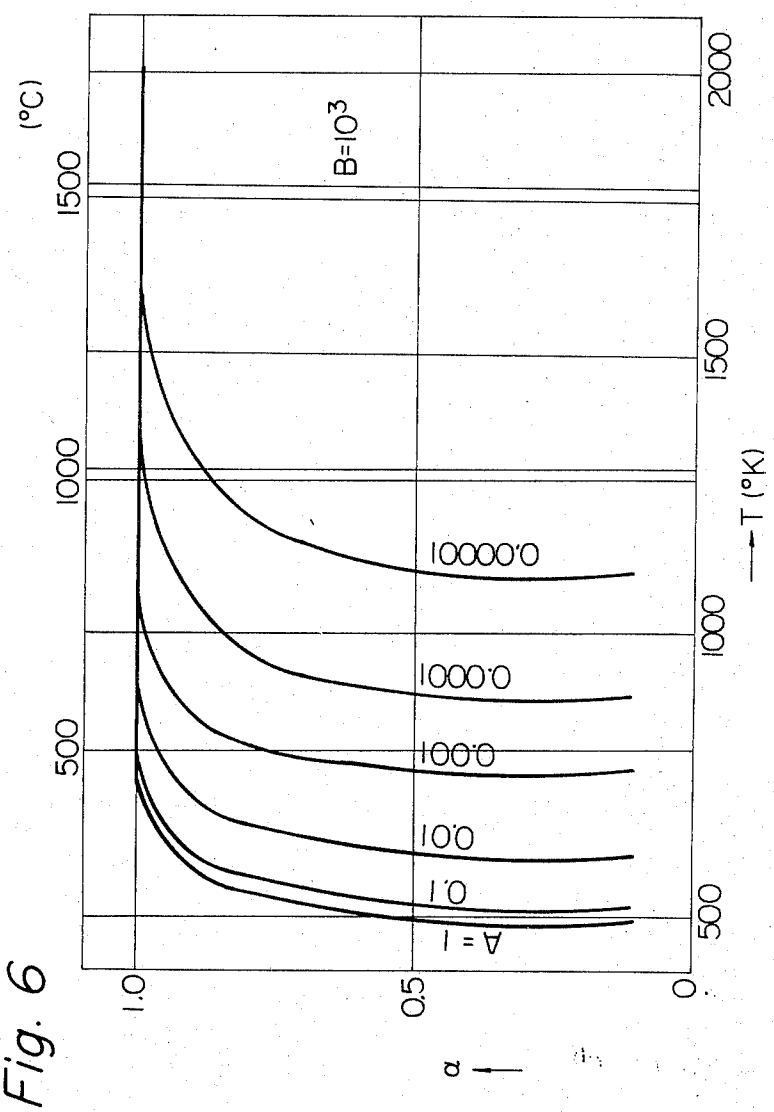
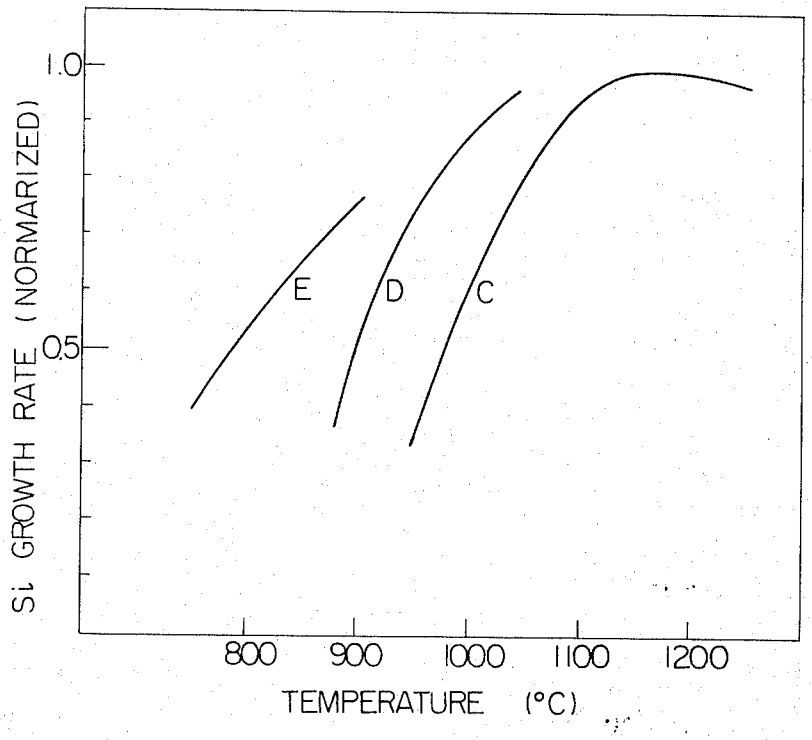


Fig. 6

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Fig. 7



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METHOD OF DEPOSITION OF SILICON BY USING PYROLYSIS OF SILANE

This invention relates to a method for producing a silicon wafer and more particularly to a method for epitaxially growing silicon crystals by using pyrolysis of silane.

Various method for growing silicon crystals are known in the art, one of which utilizes a reaction of reduction of silicon chrolide with hydrogen. Another is the one using pyrolysis of silane (SiH_4). The latter method is superior to the former since the latter can be achieved at a considerably lower temperature than the former. Furthermore, the latter is suitable for producing a silicon epitaxial wafer especially with a steep with uniform impurity concentration, because the carrier gas in the process of the method does not include gaseous chlorides which invites the undesired vapour etching and auto-doping.

The method however is not fully acceptable because the method still necessitates so a high temperature that the property of the resultant silicon wafer does not completely meet the requirements of high-frequency or low-noise transistors.

It is therefore an object of this invention to provide improved method of growing silicon crystals by using pyrolysis of silane, at a relatively low temperature.

In the drawings

FIG. **1** is a sectional view of a growth apparatus employed for the method of this invention;

FIG. **2** is a graphic illustration showing variations of growth rate of silane in terms of temperature;

FIGS. **3** through **6** are graphic illustrations showing variations of ratio of decomposed silane to hydrogen-argon mixed carrier gas; and

FIG. **7** is a graphic illustration showing variations of ratio of decomposed silane to carrier hydrogen gas.

In FIG. **1**, a vertical type reaction apparatus which is generally used in the growth of silicon is illustrated, which includes a quartz bell-jar reactor **10** having a gas feed tube **12** and outlet port **14.** In the chamber **10** is placed one or more succeptor **16** on which substrate crystals **18** are mounted. A conventional method of silicon deposition by using pyrolysis of silane is described hereinbelow. The conventional method is performed by admitting gaseous silane carried by a carrier hydrogen gas to the feed tube **12** of the chamber **10,** as indicated by an arrow A. The gaseous silane carried by hydrogen gas enters via the tube **12** the chamber **10** as indicated by arrows B. Since the substrate **16** is heated to a high temperature for example 1,150°C, the silane gas thus entered the reaction **10** thermally decomposes through the following reaction:

$$SiH_4\ (g) \rightleftarrows Si\ (s) + 2H_2\ (g) \qquad 1$$

The solid silicon produced through the above reaction deposits on the surface of the substrate **16** and, namely, a silicon wafer epitaxially grows on the surface of the substrate **16.**

FIG. **2** is a graph showing the variation of the decomposition rate α of the gaseous silane in the process of the reaction (1) against temperature of the substrate T in terms of ratios A in gram molecule of the silane gas to the carrier gas, wherein absicissa and ordinate axes

respectively represents the temperature T and the decomposition rate α.

If, in this instance, the activity of the solid is assumed to be unity, then the equilibrium constant K of the reaction (1) is expressed as:

$$K = P_H{}^2/P_{SiH} \qquad 2$$

where P_H and P_{SiH} respectively represent partial pressure of the hydrogen gas and the silane gas when equilibrium established.

It should be noted that since not only the silane gas but the carrier hydrogen gas are introduced into the reaction chamber **10,** the partial pressure of the hydrogen gas in the chamber **10** increases so that the rightward shift of equilibrium of the reaction (1) is undesirably suppressed.

In order to solve this problem, a method according to this invention employs as the carrier gas for the silane gas, a mixture of hydrogen gas and an inert gas such as argon, helium, neon, krypton, xenon, radon or nitrogen gas. When the silane gas is carried by such a carrier gas as above mentioned, the partial pressure of hydrogen in the carrier gas introduced into the reaction chamber is considerably smaller whereby the decomposition of the silane gas is preferably promoted even at a relatively low temperature. The method according to this invention may therefore be performed at such a low temperature as not to affect the property of the resultant silicon wafer.

FIGS. **3** and **6** respectively show graphs of the variation of the decomposition rate α against the temperature T of the substrate in terms of the ratio A when the carrier gas includes an inert gas in a ratio B in gram molecule of an inert gas to hydrogen gas. The proportions A and B are varied from 0 to 1 and from 0 to 10^3, respectively.

It can be seen from FIGS. **3** and **6** that the larger the proportion B becomes, the more readily the decomposition of silane gas takes place. For instance, when the proportions A and B are equal to 0.001 and 10^2, respectively, the decomposition of silane gas sufficiently arises even when the substrate is at such a low temperature as 850°C.

It can be also seen from the figures that in the process of the present method the substrate may be heated at from 450°C to 1,300°C. However, it is preferable to keep the temperature of the substrate as high as possible to obtain a desired monocrystalline. When, on the other hand, it is required to prevent the vapour nucliation of the silane gas, the temperature of the substrate should be kept as low as possible. Therefore the optimum temperature of the substrate is about 900°C when the ratios A and B are 0.001 and 10^2, respectively.

FIG. **7** is a graphic illustration showing variations of the growth rate of silicon crystals, wherein a curve C represents the variation when the carrier gas made of only hydrogen gas is fed at a feed rate 40 (*l*/min.). Curve D represents the variation when the argon and hydrogen gases are equally fed at a rate of 20 (*l*/min.), respectively, and curve E, **18** and **2** (*l*/min.), respectively. These measurements were conducted at a feed rate of 40 (cc/min.) of silane gas.

It is apparent from the graph discussed above that growth temperature of silicon crystals becomes low as the mole ratio of argon in the carrier gas increases.

According to this invention, the substrate on which an epitaxial layer is to be formed is kept at a relatively low temperature such as 900°C whereby the resultant silicon layer has a property suitable for high-frequency or low-noise transistor.

In addition, the method of this invention can be usable for growing silicon polycrystals on a suitable substrate such as silicon-oxide glass by keeping the temperature of the substrate as low as 650°C, for example. The resultant silicon polycrystal layer has a property suitable for a low threshold MOS transistor.

The invention will be more fully understood with reference to the following illustrative specific embodiments:

EXAMPLE I

This example illustrates the formation and deposition of an epitaxial film of Si on substrate crystal. A polished seed crystal of phosphor doped n-type Si of 2 inches in diameter and 500mg in weight and having a carrier concentration of 3×10^{18} carriers/cc is placed on a graphite succeptor located in a quartz chamber. The susceptor is heated to 900°C with radio frequency heating and a stream of silane is introduced together with carrier gas through the tube. Here the feed rate of silane employed is 40cc/min. Carrier gas is a mixture of hydrogen and argon and the feed rates of hydrogen and argon are 8*l*/min. and 12*l*/min., respectively.

Deposition of epitaxial layer takes place on the substrate as a result of pyrolysis of silane. The growth rate of the layer is about 0.5μ/min. X-ray diffraction patterns show that the deposited layer is a single crystal and has the same crystalline orientation as the substrate.

EXAMPLE II

The same procedure outlined in Example I is repeated but the substrate of silicon single crystal is substituted for a surface oxidized silicon wafer. The substrate is heated to 700°C. Gas feed rates of silane, hydrogen and argon are **20**cc/min., 2*l*/min. and 8*l*/min., respectively. Polycrystal silicon layer of 2,000A in thickness is deposited by carrying out the reaction for about **10** minutes.

What is claimed is:

1. In a method of growing a silicon epitaxial layer on a substrate by pyrolysis of silane (SiHy) in an atmosphere containing hydrogen gas, the improvement comprising mixing a inert gas selected from the group consisting of argon, helium, neon, krypton, xenon, radon and nitrogen with said hydrogen gas at a gram molecule ratio of inert gas to hydrogen of up to 1,000 and heating said substrate to a temperature in the range from 450° to 700° C., whereby the partial pressure of the hydrogen may be controlled so as to control the equilibrium of the reaction toward formation of silicon.

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