Description

Background of the invention

This invention relates to boron doping of semiconductors, and more specifically to the achievement of a high degree of uniformity and reproducibility in the boron doping of many large diameter silicon semiconductor wafers at the same time.

Various dopant impurities are used to alter the electrical properties of silicon so that different device and circuit functions can be achieved. It is essential that the doping process give reproducible and uniform results, that is, reproducible from manufacturing run to manufacturing run, and uniform within a given manufacturing run so that, insofar as possible, each location on the semiconductor wafer and each semiconductor wafer receives substantially the same concentration of dopant and the same penetration depth into the wafer. The element boron has been found to have useful and convenient properties as an impurity dopant in silicon and is much used. Prior art techniques for boron doping of silicon are described for example in "Silicon Semiconductor Technology", McGraw Hill, New York, 1965 pages 147—149. Therefore, manufacturing methods which provide boron doping of silicon to a high degree of reproducibility and uniformity are of great technical and practical utility.

A useful technique for impurity doping of silicon is the open-tube system wherein a batch of wafers is inserted into a furnace tube or reaction chamber placed within a high temperature furnace having a temperature near 1000°C. A controlled atmosphere is maintained within the tube. The tube is open in the sense that various gases can be introduced, flow through the tube or reaction chamber, and be extracted. A gaseous species containing boron is either introduced directly into the tube, or generated within the tube by reaction or evaporation of a boron compound. The gas stream may also contain relatively inert carrier gases such as N_2, Ar or He, and/or active species such as O_2, H_2 or H_2O, for example, capable of oxidizing or reducing the boron dopant source compound and/or the silicon material within the diffusion tube. Alternatively the inert carrier gas may be omitted and the active gases used without dilution at various pressures. BCl_3 is a typical boron source gas and is used to illustrate the reactions which can occur.

Reaction of BCl_3 in a reducing atmosphere produces elemental boron as a doping impurity source for the silicon, and HCl which reacts with Si to form $SiCl_4$. The $SiCl_4$ is gaseous at the temperatures of interest, so the reaction also etches the silicon, an effect generally desired to be avoided. In oxidizing atmospheres, BCl_3 reacts to produce B_2O_3 and SiO_2 as reaction products, which deposit or form on the silicon wafers. HCl is also produced and can etch or pit the silicon through formation of $SiCl_4$, but this reaction is less likely than the formation of SiO_2, so that the problem is less severe than in reducing atmospheres. Hence, oxidizing ambients have generally been preferred in the prior art, and a large excess of oxidant typically used, for example, ten times or more of the amount needed for stoichiometric productions of B_2O_3.

The boron oxide deposited on the silicon surface provides the primary source of boron dopant atoms rather than the gas stream itself. This permits the doping process to be divided into two sequential steps which, for reasons of control, are carried out at slightly different temperatures; (a) "deposition" typically carried out in the range 700—900°C in which a $B_2O_3+SiO_2$ mixture is formed on the silicon wafers; and (b) "drive" in which the boron source gas is removed and the silicon wafers raised to a higher temperature (typically 900—1100°C) in order to accelerate solid-solid diffusion of the boron from a B_2O_3/SiO_2 glassy layer into the silicon semiconductor body. The deposition step provides primary control of the surface impurity concentration, and the drive step provides primary control of the depth in which diffusion is achieved. The above-described reactions are well known per se in the art.

In the open tube method, the boron source gas and other reactant gases (hereinafter the composite gas) pass continuously through the tube. As the composite gas stream passes over the silicon wafers and the deposition-oxidization reactions occur, there is depletion of the active species from within the gas stream. The thickness of the dopant source oxide formed on the first wafers (nearer the gas source end) may be many times that formed on the last wafers in the batch, nearer the exhaust or pump end. There will also be depletion of the reactants from the periphery to the center of the wafers. These depletion effects give rise to non-uniformity in the formation of the boron dopant source oxide layer and consequently on the resultant impurity concentration and distribution within the silicon.

The smaller the spacing between wafers and the larger the diameter, the more severe the depletion. Thus in the prior art, wafers could not be clearly spaced within the reaction chamber in order to process large numbers in a single run without suffering significant depletion and non-uniform deposition effects. Conversely, if greater uniformity was desired, larger wafer spacings were mandatory, and production efficiency suffered. As wafer diameter has increased from two inches (5.1 cm) to four inches (10.2 cm) or larger, these spacing and uniformity problems have become especially troublesome.

It is also known that B_2O_3 can dissociate in the presence of silicon at high temperatures (>800°C) to form what is believed to be an intermetallic boron-silicon compound SiB_x that is soluble only in solvents which attack silicon. The SiB_x can be advantageously used to enhance doping uniformity, but its undesirable etch properties must be avoided in some way so that subsequent process steps may be accomplished without etching the silicon.

In the prior art, a variety of approaches have been utilized to achieve uniform doping by the minimization of the reactant depletion effects. For example, (a) use of high composite gas flow rate (e.g. 0.1—10 liters per minute), (b) use of large wafer spacing (e.g. 0.5—10 cm), which limits the number of

wafers that can be treated in a single batch, and (c) use of low pressures (e.g. <1 Torr, 0.13 kPa) so as to increase the mean free path of gas molecules within the reaction chamber and enhance surface reaction. However, none of these approaches has proved entirely satisfactory. A need continues to exist for a process capable of producing uniform and reproducible boron doping of silicon which is both economical with respect to gas usage, able to handle batches of a hundred or more silicon wafers of four inch (10.2 cm) diameter or larger in a single uninterrupted diffusion run, and which is also compatible with other desired process steps.

Boron is a p-type impurity in silicon and, when diffused into an n-type silicon body, forms a p-n junction. In this circumstance, a convenient method of evaluating the results of the diffusion operation is to measure the sheet resistance R_s in ohms per square and the junction depth X_j in micro-meters (microns). The methods for performing these measurements are well known per se in the art.

In view of the foregoing, it is an object of this invention to provide an improved method for uniform and reproducible boron doping of silicon.

Preferably such a method is a low pressure method with smaller reactant gas consumption and which prevents undesirable etching of the silicon surface.

Preferably, also the method allows for the formation and subsequent removal of a boron-silicon intermediate layer at the surface of the silicon semiconductor as an aid to obtaining improved uniformity and reproducibility of boron doping in silicon without disruption of subsequent process steps.

The method preferably provides uniform and reproducible boron doping of large diameter silicon wafers which are closely spaced in the reaction chamber so that relatively large members can be processed simultaneously in a single batch to reduce manufacturing costs.

Summary of the invention

Accordingly, the invention provides a method for substantially uniformly and reproducibly boron doping a silicon body within a reaction chamber characterised by the steps of:

forming a protective layer of silicon oxide on said silicon body, wherein said layer of silicon oxide has a thickness greater than zero but less than about 10^{-8} m;

introducing a composite gas mixture (G_1—G_3) which comprises a boron containing gas and a first oxygen containing gas of proportions differing from stoichiometric proportions for production of substantially pure boron oxide by a predetermined difference Δ in the range, greater than -3 to -0.3, or 0.06 to 6, where Δ expresses the difference in moles by which the amount of oxygen in the reaction chamber differs from the amount of oxygen necessary to react stoichiometrically with two moles of boron in the reaction chamber:

forming a boron source layer on said silicon body by reacting said composite gas mixture in the presence of said silicon body:

maintaining throughout the two preceding steps a total gas pressure around said silicon body of less than 10 Torr (1.3 kPa); and

heating thereafter said silicon body and boron source layer, first in a non-oxidizing ambient so as to promote formation of a boron-silicon compound in intimate contact with said silicon body, then followed by a drive period in an inert ambient wherein boron is incorporated in said silicon body to a desired depth, thereafter followed by exposure to a second oxygen containing gas to re-oxidize any remaining boron-silicon compound.

This combination of process steps minimizes the dopant source thickness variations and further minimizes the effect of those remaining thickness variations on the resultant resistivity obtained even though relatively close spacing and many large diameter silicon wafers are processed in the reaction chamber at the same time.

Brief description of the drawings

Fig. 1 shows in schematic form apparatus suitable for the practice of the invented method;

Fig. 2 shows experimental results for dopant source layer film thickness formed according to the method of this invention on different silicon wafers as a function of their position within the wafer load batch, for different values of the ratio of reactants at constant BCl_3 input rate;

Fig. 3 shows the dopant source layer film thickness as a function of wafer position within the wafer load batch for different boron source gas flow rates and different total system pressure;

Fig. 4 shows the dopant source layer film thickness ratio as a function of the departure of the boron source gas and oxidant gas from B_2O_3 stoichiometry;

Fig. 5 shows the coefficient of uniformity of resistivity from wafer to wafer within a wafer load batch as a function of the number of wafers in centrally selected groups from a 100 wafer load and for several values of boron source gas flow rates and total system pressure.

Detailed description of preferred embodiment

An apparatus 9 shown schematically in Fig. 1 is typically used in the practice of this invention, wherein silicon wafers 10—12 having been installed in wafer holder 13 and are placed in reaction tube 14 located within heating means 15. Reaction tube 14 is closed in a substantially gastight manner by end cap 20 which is connected to an exhaust pump, and end cap 16 containing vacuum type access door 17 and pressure

sensor 18 and mass flow control 19 to which in turn are connected several sources 21—23 of high purity gases G_1—G_3.

The following is an example of the practice of a preferred embodiment of the method of this invention, utilizing the apparatus illustrated in Fig. 1.

1. Preparation and initial oxidization

Silicon wafers to be processed are cleaned, loaded into a wafer holder and inserted in the reaction zone of a high temperature (e.g. 800°C) furnace in a dry protective atmosphere by methods well known per se in the art. Fifty to one hundred four inch (10.2 cm) wafers with wafer to wafer spacing at 1—5 mm, typically 3 mm, are typically used. One or more dummy (scrap) wafers may be placed at each end of the load. The reaction chamber is evacuated to pressure of less than 10 Torr (1.3 kPa), preferably less than 1 Torr (0.13 kPa), and in most cases typically in the range 0.05—0.15 Torr (0.67—20 Pa).

Hydrogen and oxygen are admitted to grow an initial oxide film of thickness D_o less than 10^{-8} m (100 Angstrom units), typically less than 0.5×10^{-8} m (50 Angstrom units). This oxide forms a protective layer which seals the silicon surface to prevent subsequent pitting or etch damage during subsequent stages of the process. While this procedure is convenient other methods well known per se in the art may be used.

2. Deposition

BCl_3, H_2 and O_2 are admitted to the reaction chamber at flow rates adjusted to maintain total pressure below 1 Torr (0.13 kPa), to give a desired SiO_2/B_2O_3 deposition rate, and to give a desired mole fraction Δ of oxidant gas to boron. Typical conditions are, BCl_3 flow of 3—15 cm^3/minute, total pressure of 0.05—0.5 Torr (6.7—66.5 Pa), deposition time 30 minutes and mole difference Δ between greater than −3 and +6 but not equal to zero. After the desired boron source layer thickness D_s is achieved, gas supplies are shut off and the chamber evacuated.

3. Heat cycle

The wafers are allowed to "soak" in the evacuated reaction chamber at, typically 800°C for a predetermined time, typically 15 minutes, to promote the formation of SiB_x. They are then heated to the "drive" temperature, typically 900°C, in an inert ambient where they remain for a time necessary to achieve the desired junction depth, typically 30 minutes in these experiments. The temperature is then reduced to 700—800°C typically, and H_2 and O_2 admitted for typically 30 minutes to re-oxidize the SiB_x formed earlier. The re-oxidation step is necessary to convert the SiB_x back to an oxide so that it can be readily removed without having to etch the silicon. This avoids interference with subsequent processing steps. The reoxidation may be performed in the same or a different furnace.

An alternative heat cycle is to omit the soak step and proceed directly to the drive step, in which case the re-oxidation step may be shortened or eliminated. However, it is expected that doping uniformity will be degraded.

The times and temperatures given in the above exemplary method are illustrative of convenient values. Other combinations of temperature and time may be selected by methods well known per se in the art to give equivalent results. Further, in the examples presented, the soak step is conveniently carried out in vacuum. Any non-oxidizing ambient will give equivalent results.

It was discovered that the thickness and uniformity of the boron source layer depended critically upon the relative proportions of the boron source gas and the oxidant gas, which in most cases was H_2O or its equivalent in the form of independently injected hydrogen and oxygen. Mole differences Δ and γ are defined by the following equation as a measure of the amount (in moles) by which the water vapor oxidant, or the excess oxygen, respectively, differ from the stoichiometric ratio necessary to produce B_2O_3 in the presence of silicon.

$$2BCl_3+(3+\Delta)H_2O+\gamma O_2 \xrightarrow{Si} SiO_2/B_2O_3+6HCl$$

It was discovered that with both Δ and γ equal zero; that is, only sufficient oxidant for the stoichiometric reaction of BCl_3 to form B_2O_3, that little or no boron source layer or significant additional SiO_2 film was formed on the wafers, during the run times of intreest (typically 30 minutes), and pressures and flow rates used. As excess oxidant over the stoichiometric ratio was supplied, that is Δ greater than 0 or γ greater than 0 or both, then film formation occurred but with uniformity along the wafer load significantly dependent upon the amount of excess oxidant. Film formation also occurred as the composite gas mixture was made rich in BCl_3 compared to the stoichiometric ratio, e.g. Δ less than zero but greater than −3, and γ equal to zero. (For Δ equals −3 and γ equals 0, no oxidant is present and no B_2O_3 is expected.) At high flow rates and pressures some film formation occurred at stoichiometry ($\Delta=\gamma=0$), but uniformity was poorer.

Fig. 2 shows the film thickness formed on the silicon wafers measured in Angstroms (10^{-10} m) as a function of wafer position along the wafer holder for different amounts of excess oxidant, lines 30—33 of Fig. 2 corresponding to values of Δ=6, 3.1, 1.6, and 0.79 respectively. It can be seen that more uniform deposition is obtained at small values of excess mole difference Δ, for Δ greater than zero.

Fig. 3 shows the effects of varying the flow rate and pressure of reactants on the uniformity. In practice,

flow rate was adjusted and resulting total system pressure P measured at gauge 18 of Fig. 1. Since the system is being continuously evacuated by the pump, reducing the gas input flow rate also results in a drop in system pressure. Flow meters were calibrated to read in cubic centimeters per minute of gas at atmospheric pressure and room temperature (approx. 20°C). Line 40 corresponds to a flow rate of 14.7 cm^3 per minute of BCl_3 and P=0.145 Torr (19.2 Pa), and line 41 corresponds to 7.3 cm^3 per minute and P=0.095 Torr (12.6 Pa). In both cases the hydrogen and oxygen flow rates were adjusted to be in the molar ratio 2:1 and of magnitude necessary to give Δ=0.2 mole excess H_2O. An additional run carried out at a flow rate of 4.8 cm^3 per minute of BCl_3, and P=0.075 Torr (10 Pa), and otherwise identical conditions, produced no measurable film.

Based on these and other experiments, a more genrealized relationship was discovered between the uniformity of the boron source layer deposited in this manner and the departure of the reactant mixture from the ratios necessary for the stoichiometric production of B_2O_3. These relationships are illustrated in Fig. 4 which presents the film thickness ratio, that is, the ratio of film thicknesses measured on wafers taken respectively from the source and pump end of the wafer holder (see Fig. 1) versus the amount by which the reactant ratios differ from B_2O_3 stoichiometry, for three different total system pressures. It was found that the film thickness ratio improved (decreased) as Δ approached zero, i.e. stoichiometry (Fig. 4, lines 60—61). However, for values of a close to zero, that is approximately in the range −0.03 to +0.06 (Fig. 4, regions 62—63), little or no film was obtained for most of the times, temperatures, flow rates, and pressures utilized. This is an unanticipated result. For values of Δ on either side of the "anomolous deposition" zone 62—63, the film thickness ratio was found to be a slowly varying function of the BCl_3 (or H_2O) concentration, particularly for negative values of Δ. This slowly varying relationship is a desirable result. No pitting or etching of the Si was observed even though the atmosphere is non-oxidizing for a less than zero.

Curve 60 shown in Fig. 4 represents conditions for approximately constant oxidant flow rate and curve 61 for approximately constant boron source flow rate. Utilizing different flow rates or reaction chamber pressures produces a family of curves 64—65 and 66—67, displaced approximately vertically up and down from curve 60—61, up corresponding to higher flow rates and pressures and down to lower flow rates and pressures, other things being substantially equal.

Operation at total system pressures P below 10 Torr (1.3 kPa), preferably below 1 Torr (0.13 Pa), is an important aspect of this process in that low pressures contribute to boron source deposition uniformity by increasing the mean free path of constituent atoms or molecules, and by reducing deposition rates. The flow rate is also reduced so that smaller quantities of reactant gas are consumed, a desirable economy. Note however, that low pressure operation is insufficient by itself to achieve the desired results since the proper range of Δ must also be selected.

The resistivity variations are best described by means of three coefficient of uniformity C_w, C_l, C_r, all defined by the same general equation as follows:

$$C=(2\sigma/\bar{R}_s)\times 100 \quad \text{(percent)}$$

where

σ=standard deviation of sheet resistance.

$\bar{R}_s$=average value of sheet resistance measured in ohms per square, and

where C corresponds to one of three experimentally determined values expressing the uniformity within a wafer (C_w), from wafer to wafer in a load or batch (C_l), or from run to run (C_r), corresponding to the locations where σ and $\bar{R}_s$ are measured.

Fig. 5 shows the coefficient of uniformity C_l from wafer to wafer in a load as a function of variously sized *center groups* of wafers from the load, for two different pressures and flow rates (P=0.145 Torr/19.3 Pa and 14.7 cm^3 per minute of BCl_3, line 50, P=0.095 Torr/12.6 Pa and 7.3 cm^3 per minute of BCl_3, line 51), both carried out at Δ equal to 0.2. In these runs, the coefficient of uniformity within a wafer C_w was found to be better than 1.8%. Comparing this value with line 51, Fig. 5, one can see that for the central 50 wafers or less of the 100 wafer batch that C_l and was also approximately 1.8%, identical to C_w which is a desirable result.

Approximately 90% of the 100 wafer load has C_l less than 3% and 98% less than 4% (line 51, Fig. 5). No dummy wafers were used in this test, thus when the first and last wafer are included in the measured sample (i.e. abscissa points 99—100), the value of C_l jumps from 4 to 8%. The first and last wafers of a batch normally show greater non-uniformity of doping than all others in the batch, independent of batch size, because they have the greatest perturbing effect on gas flow. These wafers may be replaced by dummy wafers, or additional dummy wafers may be added to the load. Thus, by utilizing an appropriate number of dummy wafers, coefficients of uniformity better than 3% can be expected across an entire load of 100 or more four inch (10.2 cm) wafers. Higher flow rates and pressures (line 50 of Fig. 5) degrade the uniformity of resistivity along the load.

In other tests, batches of 150 two inch (5.1 cm) wafers have been processed using 4 inch (10.2 cm) dummy wafers and C_l less than 2% obtained for all 150 wafers. Use of dummy wafers having a diameter larger than the wafers of the production batch was found to improve uniformity along the batch.

Run-to-run uniformity C_r was determined from a series of seven runs with fifty 3 inch (7.6 cm) wafers per run in which deposition, soak, drive and reoxidation temeratures and times were respectively: 920°C,

30 minutes; 920°C, 20 minutes; 955°C, 30 minutes; and 700°C, 30 minutes, and $\Delta=0.2$ was used. For these runs, wafer uniformity C_w was 1.3%, load uniformity C_l was 2.6%, and run-to-run uniformity C_r was 2.3%. Thus, the repeatibility (measured by C_r) was comparable to the uniformity (measured by C_w and C_l). These results compare favorably to prior art values reported in the technical literature for C_w to 1—4%, C_l of 3—10% and C_r of 4—20% most of which were obtained using relatively small numbers of wafers per batch (less than 10 to 40), relatively small diameters (1.5—3 inches, 3.8—7.6 cm), a variety of doping techniques such as boron nitride source wafers, spin-on doped glasses and various gas sources, and a variety of wafer to wafer spacings, mostly unspecified. Prior art method tests in the inventors' laboratory on loads of fifty 3 inch (7.6 cm) diameter wafers at 5 mm spacing gave values for C_w of 2.0—3.3%, C_l of 4.2—6.4% and C_r of 8.4%. When the same methods were applied to four inch wafers much poorer values were obtained. Thus, the results obtained using the invented method are better and apply to larger numbers of larger wafers, these achievements being significant improvements over the prior art.

The following general rule has been formulated for choosing the optimum flow rate and pressure of reactants, which is, utilize the minimum overall flow and pressure of reactants (boron source gas plus oxidants) to give just sufficient boron doped film (boron source layer) to act as a non-depleting diffusion source. Optimum values of flow rate and pressure can be determined by experiment for any given reaction chamber geometry, pump capacity, wafer load configuration, source gas formulation, oxidant formulation and temperature. Application of this rule leads to the most uniform source layer film thickness across the wafer load and correspondingly the lowest coefficient of uniformity of load resistance. It has been calculated that the minimum boron source layer film thickness to act as a non-depleting diffusion source must be of the order of a few hundred Angstroms (10^{-10} m), e.g. less than 500 Angstroms (5×10^{-8} m) equivalent of B_2O_3, which corresponds to a few tens of Angstroms (10^{-10} m) of SiB_x during the diffusion drive step. At the same time, the reactant ratios must be adjusted to operate in the regions of favorable film thickness ratio defined in Fig. 4.

For the conditions utilized, it is estimated that only between 10 and 20 percent of the boron potentially available in the reactor reaches the wafers. Some will react on the chamber walls and the rest is exhausted with the waste gases in various forms. More silicon can be placed in the reaction chamber without substantially increasing the depletion effects provided the reactant concentrations are maintained in the appropriate range as determined from the flow rates, temperatures, and system pressures illustrated herein. Thus, the process is amenable to being scaled to wafer loads in excess of 100 wafers and diameters larger than four inches (10.2 cm) and is limited fundamentally, it is believed, only by the length or volume of the uniform temperature reaction zone obtainable with the given furnace.

Thus it is apparent that there has been provided in accordance wuth the invention, means for uniform and reproducible boron doping of silicon, which may be accomplished at low pressure, which may be accomplished with smaller source and reactant gas consumption, which may be accomplished while preventing undesirable etching of the silicon surface, which provides for controlled oxidation of the silicon, and which provides for the formation, utilization, and subsequent removal of boron-silicon intermediate layers as an aid in obtaining improved uniformity and reproducibility of doping without disruption of subsequent process steps.

While the invention has been described in terms of BCl_3 as a boron source gas and hydrogen and oxygen mixtures as oxidants, and various exemplary procedures and apparatus, it will be obvious to those skilled in the art that the inventive method is useful with other boron source compounds and oxidants and with other reactor geometries, heating methods, structures, and procedures which may differ in detail but preserve the central relationships among process materials and steps.

Claims

1. A method for substantially uniformly and reproducibly boron doping a silicon body (10, 11, 12) within a reaction chamber (14) characterised by the steps of:

forming a protective layer of silicon oxide on said silicon body, wherein said layer of silicon oxide has a thickness greater than zero but less than about 10^{-8} m;

introducing a composite gas mixture (G_1—G_3) which comprises a boron containing gas and a first oxygen containing gas of proportions differing from stoichiometric proportions for production of substantially pure boron oxide by a predetermined difference Δ in the range, greater than -3 to -0.03, or 0.06 to 6, where Δ expresses the difference in moles by which the amount of oxygen in the reaction chamber differs from the amount of oxygen necessary to react stoichiometrically with two moles of boron in the reaction chamber;

forming a boron source layer on said silicon body by reacting said composite gas mixture in the presence of said silicon body;

maintaining throughout the two preceding steps a total gas pressure around said silicon body of less than 10 Torr (1.3 kPa); and

heating thereafter said silicon body and boron source layer, first in a non-oxidizing ambient so as to promote formation of a boron-silicon compound in intimate contact with said silicon body, then followed by a drive period in an inert ambient wherein boron is incorporated in said silicon body to a desired depth,

30 minutes; 920°C, 20 minutes; 955°C, 30 minutes; and 700°C, 30 minutes, and Δ=0.2 was used. For these runs, wafer uniformity C_w was 1.3%, load uniformity C_l was 2.6%, and run-to-run uniformity C_r was 2.3%. Thus, the repeatibility (measured by C_r) was comparable to the uniformity (measured by C_w and C_l). These results compare favorably to prior art values reported in the technical literature for C_w to 1—4%, C_l of 3—10% and C_r of 4—20% most of which were obtained using relatively small numbers of wafers per batch (less than 10 to 40), relatively small diameters (1.5—3 inches, 3.8—7.6 cm), a variety of doping techniques such as boron nitride source wafers, spin-on doped glasses and various gas sources, and a variety of wafer to wafer spacings, mostly unspecified. Prior art method tests in the inventors' laboratory on loads of fifty 3 inch (7.6 cm) diameter wafers at 5 mm spacing gave values for C_w of 2.0—3.3%, C_l of 4.2—6.4% and C_r of 8.4%. When the same methods were applied to four inch wafers much poorer values were obtained. Thus, the results obtained using the invented method are better and apply to larger numbers of larger wafers, these achievements being significant improvements over the prior art.

The following general rule has been formulated for choosing the optimum flow rate and pressure of reactants, which is, utilize the minimum overall flow and pressure of reactants (boron source gas plus oxidants) to give just sufficient boron doped film (boron source layer) to act as a non-depleting diffusion source. Optimum values of flow rate and pressure can be determined by experiment for any given reaction chamber geometry, pump capacity, wafer load configuration, source gas formulation, oxidant formulation and temperature. Application of this rule leads to the most uniform source layer film thickness across the wafer load and correspondingly the lowest coefficient of uniformity of load resistance. It has been calculated that the minimum boron source layer film thickness to act as a non-depleting diffusion source must be of the order of a few hundred Angstroms (10^{-10} m), e.g. less than 500 Angstroms (5×10^{-8} m) equivalent of B_2O_3, which corresponds to a few tens of Angstroms (10^{-10} m) of SiB_x during the diffusion drive step. At the same time, the reactant ratios must be adjusted to operate in the regions of favorable film thickness ratio defined in Fig. 4.

For the conditions utilized, it is estimated that only between 10 and 20 percent of the boron potentially available in the reactor reaches the wafers. Some will react on the chamber walls and the rest is exhausted with the waste gases in various forms. More silicon can be placed in the reaction chamber without substantially increasing the depletion effects provided the reactant concentrations are maintained in the appropriate range as determined from the flow rates, temperatures, and system pressures illustrated herein. Thus, the process is amenable to being scaled to wafer loads in excess of 100 wafers and diameters larger than four inches (10.2 cm) and is limited fundamentally, it is believed, only by the length or volume of the uniform temperature reaction zone obtainable with the given furnace.

Thus it is apparent that there has been provided in accordance wuth the invention, means for uniform and reproducible boron doping of silicon, which may be accomplished at low pressure, which may be accomplished with smaller source and reactant gas consumption, which may be accomplished while preventing undesirable etching of the silicon surface, which provides for controlled oxidation of the silicon, and which provides for the formation, utilization, and subsequent removal of boron-silicon intermediate layers as an aid in obtaining improved uniformity and reproducibility of doping without disruption of subsequent process steps.

While the invention has been described in terms of BCl_3 as a boron source gas and hydrogen and oxygen mixtures as oxidants, and various exemplary procedures and apparatus, it will be obvious to those skilled in the art that the inventive method is useful with other boron source compounds and oxidants and with other reactor geometries, heating methods, structures, and procedures which may differ in detail but preserve the central relationships among process materials and steps.

Claims

1. A method for substantially uniformly and reproducibly boron doping a silicon body (10, 11, 12) within a reaction chamber (14) characterised by the steps of:

forming a protective layer of silicon oxide on said silicon body, wherein said layer of silicon oxide has a thickness greater than zero but less than about 10^{-8} m;

introducing a composite gas mixture (G_1—G_3) which comprises a boron containing gas and a first oxygen containing gas of proportions differing from stoichiometric proportions for production of substantially pure boron oxide by a predetermined difference Δ in the range, greater than -3 to -0.03, or 0.06 to 6, where Δ expresses the difference in moles by which the amount of oxygen in the reaction chamber differs from the amount of oxygen necessary to react stoichiometrically with two moles of boron in the reaction chamber;

forming a boron source layer on said silicon body by reacting said composite gas mixture in the presence of said silicon body;

maintaining throughout the two preceding steps a total gas pressure around said silicon body of less than 10 Torr (1.3 kPa); and

heating thereafter said silicon body and boron source layer, first in a non-oxidizing ambient so as to promote formation of a boron-silicon compound in intimate contact with said silicon body, then followed by a drive period in an inert ambient wherein boron is incorporated in said silicon body to a desired depth,

* C L M S *

thereafter followed by exposure to a second oxygen containing gas to re-oxidize any remaining boron-silicon compound.

2. The method of claim 1 wherein said boron source layer has a thickness of the order of a few times 10^{-8} m equivalent of B_2O_3.

3. The method of claim 1 wherein said first oxygen containing gas contains hydrogen and oxygen.

4. The method of claim 1 wherein said second oxygen containing gas contains hydrogen and oxygen.

5. The method of claim 1 wherein said boron-silicon compound has a thickness corresponding to a few times 10^{-9} m of SiB_x during said drive period.

6. The method of claim 1 wherein said pressure of said composite gas mixture within the said reaction chamber is less than 1 Torr (0.13 kPa).

Patentansprüche

1. Verfahren zur überwiegend gleichförmigen und reproduzierbaren Bordotierung eines Siliciumkörpers (10, 11, 12) innerhalb einer Reaktionskammer (14), gekennzeichnet durch die Stufen:

Ausbilden einer Schutzschicht aus Siliciumoxid auf dem Siliciumkörper, wobei die Schicht aus Siliciumoxid eine Dicke von größer als 0, jedoch weniger als etwa 10^{-8} m besitzt;

Einführen einer zusammengesetzten Gasmischung (G_1—G_3), umfassend ein borhaltiges Gas und ein erstes sauerstoffhaltiges Gas in Anteilen, die sich von den stöchiometrischen Anteilen zur Erzeugung von überwiegend reinem Boroxid durch eine vorbestimmte Differenz Δ im Bereich von größer als −3 bis −0,03 oder 0,06 bis 6 unterscheiden, wobei Δ die Differenz in Molen angibt, durch die sich die Sauerstoffmenge in der Reaktionskammer von der Sauerstoffmenge, die zur stöchiometrischen Umsetzung mit zwei Molen Bor in der Reaktionskammer erforderlich ist, unterscheidet;

Ausbilden einer Borquellenschicht auf dem Siliciumkörper durch Umsetzen der zusammensetzten Gasmischung in Gegenwart des Siliciumkörpers;

Aufrechterhalten während der gesamten zwei vorangehenden Stufen eines Gesamtgasdruckes um den Siliciumkörper herum von weniger als 10 Torr (1,3 kPa); und

danach Erhitzen des Siliciumkörpers und der Borquellenschicht zuerst in einer nicht-oxidierenden Umgebung, um so die Bildung einer Bor-Silicium-Verbindung in innigem Kontakt mit dem Siliciumkörper zu fördern, worauf ein Steuerungszeitraum in einer inerten Umgebung folgt, in dem Bor in den Siliciumkörper bis zu einer erwünschten Tiefe eingelagert wird, wonach die Aussetzung an ein zweites sauerstoffhaltiges Gas erfolgt, um jegliche verbleibende Bor-Silicium-Verbindung zu reoxidieren.

2. Verfahren nach Anspruch 1, wobei die Borquellenschicht eine Dicke in der Größenordnung von einigen 10^{-8} m, äquivalent zu B_2O_3, hat.

3. Verfahren nach Anspruch 1, wobei das erste sauerstoffhaltige Gas Wasserstoff und Sauerstoff enthält.

4. Verfahren nach Anspruch 1, wobei das zweite sauerstoffhaltige Gas Wasserstoff und Sauerstoff enthält.

5. Verfahren nach Anspruch 1, wobei die Bor-Silicium-Verbindung eine Dicke entsprechend einigen 10^{-9} m an SiB_x während des Steuerungszeitraums besitzt.

6. Verfahren nach Anspruch 1, wobei der Druck der zusammensetzten Gasmischung innerhalb der Reaktionskammer weniger als 1 Torr (0,13 kPa) beträgt.

Revendications

1. Procédé pour doper au bore de façon essentiellement uniforme et reproductible un corps de silicium (10, 11, 12) à l'intérieur d'une chambre de réaction (14), caractérisé en ce qu'il consiste à:

former une couche protectrice d'oxyde de silicium sur le corps de silicium, la couche d'oxyde de silicium ayant une épaisseur supérieure à zéro mais inférieure à environ 10^{-8} m;

introduire un mélange de gaz composed (G_1—G_3) qui comprend un gaz contenant du bore et un premier gaz contenant de l'oxygène de proportions différant des proportions stoechiométriques pour la production d'un oxyde de bore essentiellement pur d'une différence prédéterminée Δ dans l'intervalle, supérieur à −3 à −0,03, ou 0,06 à 6, où Δ exprime la différence en moles dont la quantité d'oxygène contenue dans la chambre de réaction diffère de la quantité d'oxygène nécessaire pour réagir de façon stoechiométrique avec deux moles de bore dans la chambre de réaction;

former une couche-source de bore sur le corps de silicium en faisant réagir le mélange de gaz composé en présence du corps de silicium;

maintenir d'un bout à l'autre des deux opérations précédentes une pression totale de gaz autour du corps de silicium inférieure à 10 Torr (1,3 kPa); et à

chauffer ensuite le corps de silicium et la couche-source de bore, d'abord dans un milieu non oxydant de manière à favoriser la formation d'un composé de bore-silicium en contact étroit avec le corps de silicium, opération suivie par une période d'entraînement dans un milieu inerte où du bore est incorporé dans le corps de silicium jusqu'à une profondeur voulue, opération suivie ensuite par une exposition à un second gaz contenant de l'oxygène pour réoxyder tout composé de bore-silicium restant.

* C L M S *

2. Procédé selon la revendication 1, dans lequel la couchesource de bore a une épaisseur de l'ordre de quelques fois 10^{-8} m équivalentes de B_2O_3.

3. Procédé selon la revendication 1, dans lequel le premier gaz contenant de l'oxygène contient de l'hydrogène et de l'oxygène.

4. Procédé selon la revendication 1, dans lequel le second gaz contenant de l'oxygène contient de l'hydrogène et de l'oxygène.

5. Procédé selon la revendication 1, dans lequel le composé de bore-silicium a une épaisseur correspondant à quelques fois 10^{-9} m de SiB_x pendant la période d'entraînement.

6. Procédé selon la revendication 1, dans lequel la pression du mélange de gaz composé dans la chambre de réaction est inférieure à 1 Torr (0,13 kPa).

* C L M S *