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A New Method for Making Shallow p-type Junctions

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Abstract -- In this paper we will present a new method for making shallow p-type junctions in silicon by molecular ion implantation. Unlike current molecular ion implantation methods which use boron and fluorine molecules, this new method uses an element which is completely miscible in silicon. Note that fluorine is an element that saturates at a very low concentration in silicon. The compounds used in this new method are boron silicides and boron germanium molecules. These compounds have several distinct advantages including the facts that the co-element silicon (or germanium) has a very high saturation value in the silicon matrix, the co-element is massive and therefore creates more damage during implantation, and the co-element has a larger projected range than the boron. Note that the Rp for fluorine is shallower than that of Boron for a BF_2 implant. Recent experiments indicate that BSi ion beams can be generated in a sputter ion source with efficiencies of 0.5% with respect to the generated Si beam. A plan to develop a new ion source that is compatible with current ion implantation systems will be presented.

I. Introduction

As the overall dimensions of semiconductor devices are miniaturized and made ever smaller, the formation of very shallowly doped regions, e.g. those less than a tenth-micron in depth, becomes a major limiting factor in the fabrication process for all miniature devices, including but not limited to MOSFET and CMOS devices.

The method used to make these vital CMOS and MOSFET transistors involves the formation of both n-type and p-type doped regions where n-type doped regions can be formed by the ion implantation of n-type elements in Group V A of the Periodic Table, and p-type doped regions can be formed by the ion implantation of elements in Group III A of the Periodic Table.

Technical difficulties currently hamper the formation of shallowly doped regions. In most semiconductor fabrication processes, the dopant boron is used to form p-type regions, and boron has a very low atomic number (Z=5). Traditional ion implantation techniques pose several problems in implanting low Z dopants. During the ion implantation process, a low Z dopant such as boron tends to channel through the crystalline structure of the substrate and forms a very undesirable, deep implantation profile tail where the concentration and depth of the dopant easily extends beyond the desired junction depth. This inability to control the junction depth seriously degrades device performance. Thus, it is difficult to use conventional implantation technologies to implant a low atomic dopant to form shallowly doped regions for VLSI circuits or ULSI circuits. Although there are techniques that are currently available to minimize the channeling effect, these techniques require additional processing steps and thus result in higher manufacturing costs. An existing method for implantation of boron ions is to use ultra low energy ion implantation techniques, but these techniques pose other problems. One problem is that it is difficult to manufacture ultra low energy ion implantation equipment, i.e. equipment generating energy less than 5 keV. Another problem is that using low energy ion implantation (energy less than 5 keV) can result in sputtering and Transient Enhanced Diffusion (TED).

There are several possible p-type dopants including B, Al, Ga, In, and Tl. It is required that the dopant have enough solubility to create a substitutional site in the substrate. Only boron has a solid solubility limit which is sufficient to obtain the doping levels needed for ULSI semiconductors. Boron is the only choice. When the concentration of a dopant exceeds the solid solubility limit in a substrate it dramatically effects the annealing behavior of the implant. A much longer annealing cycle is needed to recrystalize the amorphous region and the residual damage is very hard to anneal[1].

Several techniques are currently used to overcome the technical difficulties associated with ion implantation of low z dopants and low energy ion implantation. In one case, the shallow p-region is formed using a heavier ion compound, i.e. BF_2. Due to the higher mass of the compound, the constituent atoms of the BF_2 ion provide a shallower penetration depth for a given ion energy, thus enabling the formation of shallower p-type regions. The BF_2 ions provide another key advantage in that they reduce the channeling effect and thus the associated problems. This improvement is accomplished by the increased crystalline structural damage caused by the heavier fluorine atoms of the ion compound. Furthermore, since fluorine is neither a p-type nor an n-type dopant, the fluorine atoms that are introduced from the BF_2

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ions do not directly contribute to the electrical performance of the semiconductor device.

However, the introduction of fluorine generates a new set of problems[2]. Due to their low solubility in silicon, the fluorine atoms tend to migrate, particularly if the substrate is heated. After a BF_2 ion implantation process, any subsequent process which requires elevation of temperature will tend to cause the implanted fluorine to migrate to the silicon surface, i.e. silicon-oxide interface. In some cases, this migration cause the fluorine to coalesce and form a gap or bubbles at the interface which in turn causes contact problems such as poor contact reliability, high contact resistance, and unstable electrical performance.

For all the above reasons, BF_2 ion implantation is not a desirable solution for the fabrication of shallowly doped regions. Therefore, there is a profound need in the art of semiconductor device fabrication, particularly for devices requiring shallowly doped regions, for a fabrication process that will resolve these difficulties and limitations.

Boron-hydrogen clusters have also been suggested as a possible method for introducing boron into a silicon substrate[3]. This method does not have enough mass to produce fully amorphized layers at a depth greater than the Rp of the implant. The use of BSi or BGe solves this difficulty.

II. Summary of the Process

The object of the present process is to provide a fabrication process for forming shallowly doped regions in semiconductor devices. This process provides a method for introducing a dopant in the fabrication of semiconductor devices where a doped region is formed that has a well-defined, reproducible shallow-depth and an uniform diffusion profile. This method provides a method for introducing a dopant in the fabrication of semiconductor devices where the contacts to the substrate surfaces of the resultant semiconductor devices have low contact resistance. This new method also has the advantage that it provides a method for introducing a dopant in the fabrication of semiconductor devices having shallow-depth regions which minimizes channeling effects in the implantation process.

Briefly, the new method for manufacturing shallowly doped semiconductor devices is as follows: (a) a substrate where the substrate material is represented by the symbol Es (element of the substrate); and (b) implanting the substrate with an ion compound represented by the symbol $E_{1x}E_{dy}$, where E_1 represents an element having high solubility in the substrate material with minimal detrimental chemical or electrical effects and can be the same element as the substrate element, E_d (dopant element) represents an element which is an electron acceptor or donor having high solubility limit in the substrate material, and x and y indicate the number of respective E_1 and E_d atoms in the ion compound. For example, in implementing the method, a silicon substrate is implanted with Si_2B ion compounds to create a shallowly p-doped region. In another implementation, a silicon substrate is implanted with Ge_xE_{dy} ion compounds. In yet another implementation, a germanium substrate is implanted with Si_xE_{dy} or Ge_xE_{dy} ion compound.

In another embodiment, the ion compound implanted is represented by the symbol $E_{1x}E_{2y}E_{dz}$ where E_1 and E_2 represent two elements having high solubility in the substrate material with minimal detrimental chemical, electrical, or physical effects, and one of the elements can be the same element as that of the substrate material, E_d represents an element which is an electron acceptor or donor in the substrate, and x, y, and z indicate the number of respective E_1, E_2, and E_d atoms in the ion compound. For example, a silicon substrate is implanted with $Si_xGe_yE_{dz}$ion compound.

Note that it is within the scope of the present method to use ion compounds comprised of E_nE_d elements where En represents two or more elements in various atomic ratios and Ed represents the doping element.

The present method can also be applied to a previously doped region to alter the doping in that region. For example, the present method can be applied to a previously n-doped region where a p-type dopant ion compound of the present invention is implemented to change the total active dopant of the n-doped region, and vice versa.

The method can also be used in conjunction with preamorphized substrate materials such as Si or Ge implanted silicon substrates.

Note that the use of the term "ion compound" in this specification refers to both positively and negatively charged ion compounds which may have one or more charges and various extra hydrogen atoms attached to the ion compound.

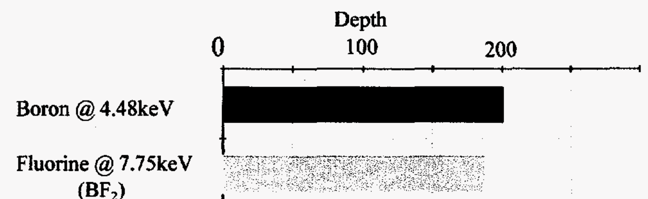

Fig 1 TRIM[4] Rp for BF2 @ 20keV

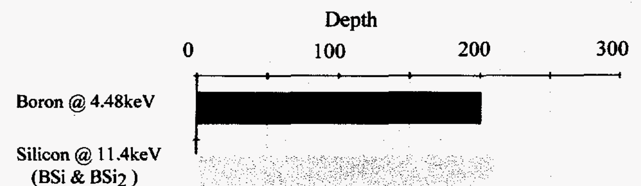

Fig 2 TRIM[4] Rp for BSi @15.9keV BSi2 @ 27.25keV

Species	KV	Element	Ratio	Energy	Projected Range
BF2	20	B	11/49	4.48	201
		F	19/49	7.75	187
BSi2	27.25	B	11/67	4.47	201
		Si	28/67	11.4	209
BSi	15.9	B	11/39	4.48	201
		Si	28/39	11.4	209
BGe2	65	B	11/59	4.48	201
		Ge	74/159	30.25	280
BGe	35	B	11/85	4.48	201
		Ge	74/85	30.9	285

Table 1. Projected Range Table for 5 keV equivalent boron

III. Benefits of the New Process over BF_2 Implants

One of the current methods for making shallow p-type junctions in silicon is to use BF_2 ions. This method has several problems including the following: (a) the solubility of fluorine in silicon is low, (b) fluorine is not a dopant in silicon, (c) fluorine precipitates and forms bubbles, (d) all of the fluorine must be removed before residual defects can be annealed out of the silicon. Finally, the projected range for fluorine (using a BF_2 molecule) is less than that for the boron. In the case of both silicon (BSi and BSi_2) and for germanium (BGe and BGe_2) the boron projected range is less than that of the other element in the molecule. Thus the amorphous zone created by the implant will be substantially deeper than the boron. See Fig 1 and Table 1.

IV. Current Research

A. Molecular Ion Implantation

A General Ionex Model 860 Cesium Sputtering ion source was used to generate molecular BSi ions. The sputtering target for the source was made by cold pressing SiB_6 powder with copper filings. The BSi^- beam current was 10% the intensity of the Si^- generated by this source configuration. The ions were extracted from the source at 20keV and analyzed in a 15 degree magnet. A slice of <100> Silicon was placed in the Faraday Cup with a zero degree tilt and implanted at room temperature

A SIMS analysis was performed at SEMATECH on the implanted silicon on a Cameca IMS4f. 10B and 11B were monitored as positive secondary ions under O2+ bombardment at an impact energy of 3 keV. Secondary ions were collected from the center 10% of a 170 um x 170 um rastered area. The atomic concentrations of 10B and 11B were calculated using a relative sensitivity factor (RSF) determined from implanted standard. Stylus profilometry was used to determine the depth scale for the profiles. Note that the profile shows evidence of channeling during the implant process. This is probably due to the zero degree tilt used during the implantation step. The dose of each species and the junction depth (Xj) are listed in Table 2.

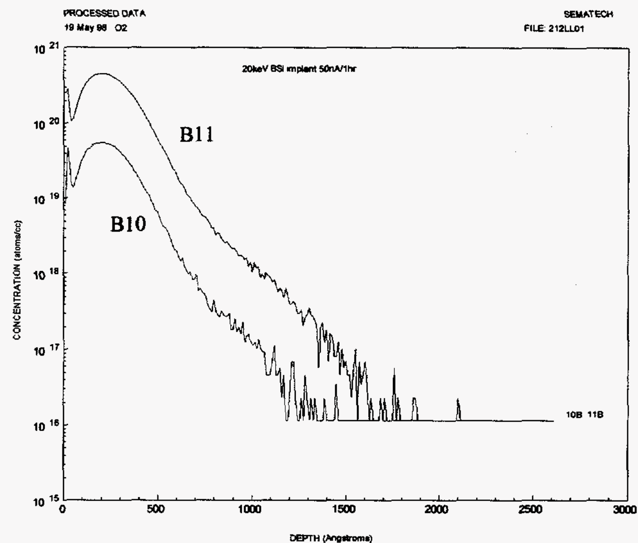

Fig. 3 20 keV BSi^- Implant profiles

Species	Dose (atoms/cm2)	Xj* (nm)
10B	1.58e14	104
11B	1.36e15	143

Table 2. Dose and Junction Depth

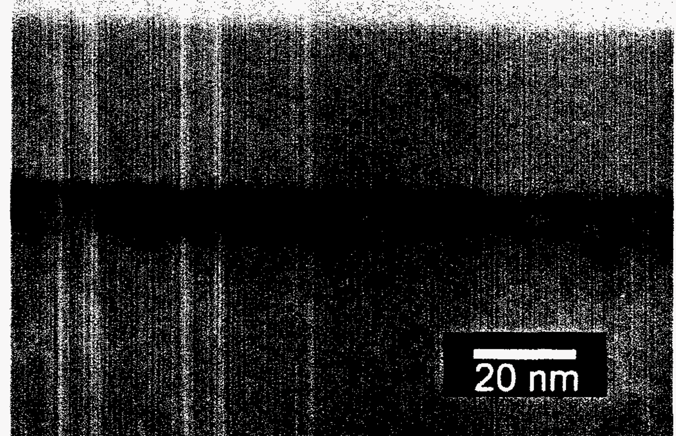

Fig 4. TEM Micrograph of BSi implant

Note that the TEM Micrograph of the unannealed sample shows an amorphous layer from the surface to near the BSi Rp and a damage layer in the region close to the channelling tail in the SIMS profile. By using conventional techniques we believe that we can elminate these channeling effects.

B. Varian Associates

Varian Associates has begun an internal program to develop a production-worthy BSi_x ion source capable of high

beam currents. The first phase of this project is the design and assembly of a proof-of-concept ion source. The ion species output and general performance of this source will be evaluated on a test stand. If these results look promising, the Phase 1 design will be modified to produce a prototype source for use in ion implanters. This prototype source would be installed on a Varian implanter and enable the BSix shallow junction process to be studied with silicon wafers. Finally, if Phase 2 is successful and the technology appears to meet the needs of the marketplace, then a commercial product will be developed.

C. SIMS analysis of SiB_4

In an experiment designed to determine if BSi molecules made better positive or negative ions a SIMS analysis was performed on the SiB_4 powder. The powders were pressed into In foil. A minimum amount of powder was loaded so that charging would not be a problem during sputtering. The powders were sputtered with approximately 200nA of 8 keV O2+ (incidence angle about 40 deg) and 60nA of 14.5 keV Cs+ (angle about 25 deg). Analysis areas were chosen such that several small particles of the powders would be overscanned by the primary ion beams (about 170 um x 170 um). Secondary ions were collected from the center 20% of the sputtered area. Medium mass resolution was used to reduce isobaric interferences. The O_2 bombardment showed a region around m/z 39 in the positive ion mass spectrum with a significant interference of SiB^+ from $39K^+$. This interference was not present in the negative ion mass spectrum under Cs+ bombardment. Figure 4 shows the results of the O_2 bombardment. Note that the BSi yield is considerably less than the Boron yield. Figure 5 shows the results of the Cs+ bombardment. Note that the BSi^- yield is greater than the boron yield.

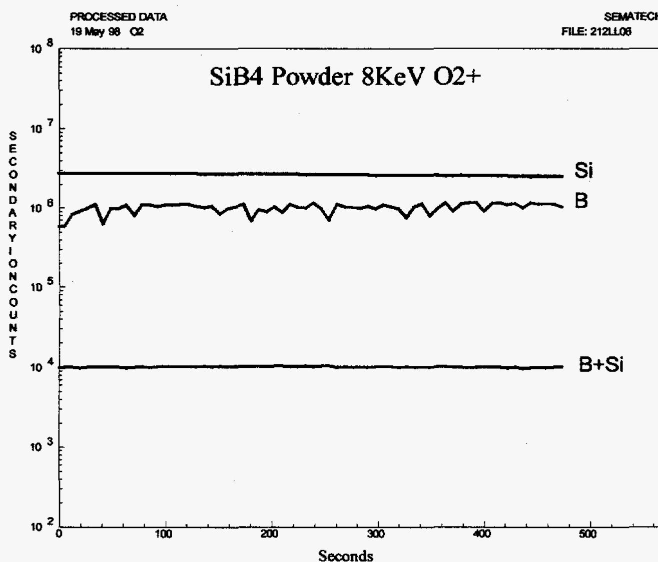

Fig 4. Oxygen Bombardment of SiB_4 powder

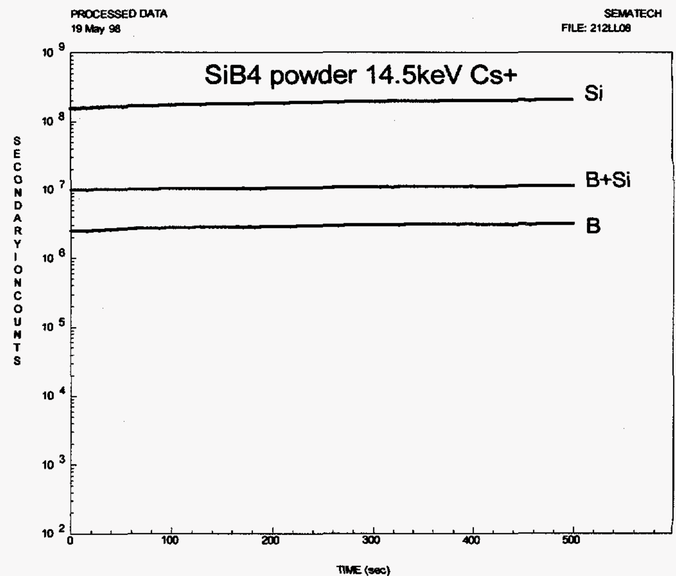

Figure 5. Cs+ Bombardment of SiB_4 Powder

V. SUMMARY

We have presented a new method for the formation of shallow p-type junctions using molecular ion implantation. We have demonstrated this method by the implantation of 20 keV BSi^- into silicon. Considerable work needs to be performed to further demonstrate the application of this new method to the fabrication of sub micron ULSI semiconductors.

ACKNOWLEDGMENT

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