Correlation Study between Doping Techniques towards Diffusion Rate and Oxidation Rate

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Abstract- **This paper is to investigate correlation between doping technique towards diffusion rate and oxide growth rate. There are two types of doping technique that has been investigated such as Solid Source, SS and Spin on Dopant, SOD. Four inches wafers were used to investigate the effects of doping technique towards diffusion rate and oxidation rate. The resistivity of silicon substrate is measured by using 4-point probe while the oxide thickness is measured by an Ellipsometer. From this experiment, it can be concluded that diffusion rate of Solid Source is about 86% better than Spin on Dopand. While the oxide growth of Solid Source, SS is 3.6% better than Spin on Dopant.**

Keywords– *Solid Source (SS), Spin on Dopant (SOD), concentration, resistivity, diffusion, oxide thickness*

1.0 INTRODUCTION

Oxide layer is most important part in device fabrication. This is because it will affect the device characteristic and it performances. Characteristic of the device is determine by it electrical properties such as concentration and conductivity. By using best doping technique, specific type of dopant and by applying annealing process, the characteristic of the device can be optimize. Doping is a process of adding various atoms into a silicon substrate to alter its resistivity and type. There are many methods of doping techniques such as ion implantation, diffusion, solid source, SS and spin on dopant, SOD. In this experiment, SS and SOD are used as the doping technique. This is due to the capability that UiTM have to fabricate the MOS capacitor.

The different between spin on dopant and solid source is the types of dopant that being used. Liquid dopant is used in spin on dopant whereas solid dopant is used in solid source. For both liquid and solid dopant, it is divided into two types which are N-type which referred to Phosphorus and P-type that referred to Boron. Phosphorus is a chemical element that has a symbol P and atomic number 15 [1]. It has 5 valence electron (pentavalence) and also known as donor atom. The majority carrier for Phosphorus is electron. Boron is a chemical element with atomic number 5 and the chemical symbol is B [2]. Boron has 3 valence electron (trivalence) known as acceptor atom and its majority carrier is holes.

Spin on dopant is preferred method for application of thin, uniform film to flat substrate [3]. An excess amount of liquid dopant is dropped into the silicon substrate. The substrate is then rotated at high speed by using spin coater in order to spread the liquid dopant by centrifugal force [4]. Normally the spin speed is between 1500 to 6000 rpm and the spin time is from 10 sec to several min [4]. The substrate that has been coat with liquid dopant is diffused. During the diffusion process, atom at the surface of the silicon substrate that has high concentration is diffused to the silicon substrate that has low concentration [5].

Solid source doping process is the process where solid source is place in parallel with the silicon substrate. During the diffusion process, solid source material is converted into vapor form. Vapors from the heated solid source are transported to the wafer, where they react with silicon and release the dopant, which then diffuse into the silicon substrate [5]. Equation (1) shows the reaction process.

$$2Sb_2O_3 + 3\,Si \longrightarrow 3SiO_2 + 4Sb \qquad (1)$$

There are two advantages of using solid source which are uniformity and ability to use hydrogen injection to reduce defects at the silicon wafer surface [6].

By using different doping process, it will produce different diffusion and concentration rate in the silicon substrate. Typically the diffusion process can be divided into two stages called pre-deposition and drive-in [5]. In pre-deposition process, the desired amount of dopant is introduced to the silicon substrate, whereas the dopants that were introduced during pre-deposition step are allowed to diffuse downward [6].

Annealing process is applied in the fabrication order to investigate the effect of temperature towards carrier concentration and the oxide growth. There are several parameters that can vary in during annealing process such as time and temperature. As temperature or time increase, the diffusion and oxidation rate also increase.

Thermal oxidation is the process that employs oxidants to oxidize silicon surface to silicon dioxide at elevated temperature. Silicon dioxide is an excellent insulator where it resistivity is larger than 10^{16} Ωcm. it also can be performed by using chemical vapor deposition but thermal oxidation provides the best quality in terms of purity, density and insulation. It must be conducted at relatively high temperature which is greater than 800°C [6]. There are two types of oxidation process which are dry and wet oxidation. The type of oxidation used in device fabrication in industry is depends on its application. Wet oxidation give higher oxidation rate compared to the dry oxidation but it produce low oxide thickness quality. Equation (2) and (3) shows the chemical equation during the dry and wet oxidation respectively.

$$Si_{(solid)} + O_{2\,(gas)} \longrightarrow SiO_{2\,(solid)} \quad (2)$$

$$Si_{(solid)} + 2H_2O_{(liquid)} \longrightarrow SiO_{2\,(solid)} + 2H_{2\,(gas)} \quad (3)$$

The main objectives of this research are to determine the effect of doping techniques towards diffusion and oxidation rate, to measure the concentration and oxide thickness when use different types of dopant, and to investigate the effect of temperature towards diffusion and oxidation rate. MOS capacitor is used as a test structure of the experiment. The MOS capacitor is a sandwich of metal plate with insulator at middle. In Semiconductor technology, the substrate of the MOS capacitor is semiconductor material which is silicon.

2.0 FABRICATION

The fabrication has three major process which are doping, diffusion and wet oxidation process. Fig. 1 shows the flow chart of the process to fabricate the MOS capacitor.

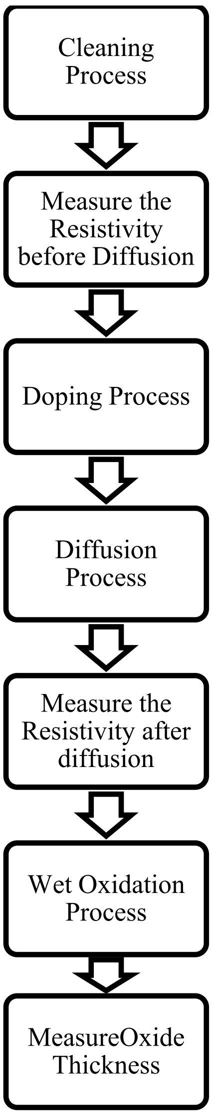

Fig. 1. Process sequence to fabricate MOS capacitor

The Buffered Oxide Etch, BOE is used to clean the silicon substrate. Before the doping process occurs, the resistivity of substrate is measured by using four point probes. Then two different doping processes are performed which are SS and SOD. Both SS and SOD has been explained in 2.1 and 2.2 respectively.

Next, the quartz boat with the silicon substrate is put onto the diffusion furnace for the drive-in process. During the diffusion (drive-in) process, three different temperatures is set in order to get the different diffusion rate. The baseline for this process is 60 minutes. Then the resistivity after diffusion is measured.

The final process is the wet oxidation process. During this process, the quartz boat which contained of doped silicon substrate is loaded onto the oxidation furnace. The temperature and time is set to 1000°C and 30 minutes respectively. Finally, the oxide layer (thin film) is measured by using Ellipsometer.

2.1 Solid Source, SS

Solid source with concentration of $9x10^{20}$ cm^{-3} and bare silicon substrate are loaded in parallel and facing each other inside the quartz boat. The same type of dopant and silicon substrate is used in the process in order to get highly doped of dopant. For example, N-type of dopant is parallel to N-type silicon substrate and vice versa.

Fig. 2. Solid Source

2.2 Spin on Dopant, SOD

During SOD process, N-type liquid dopant is dispensed onto N-type silicon substrate whereas P-type liquid dopant is dispensed onto P-type silicon substrate. The liquid dopant concentration used is about $2x10^{20}$ cm^{-3}. The liquid is spread across the silicon substrate. High rotational speed (2000 rpm) with duration 20 sec is applied to the silicon substrate. Centripetal acceleration will cause most of the dopant to spread to, and eventually off, the edge of the substrate, leaving a thin film of the dopant on the surface [4]. The heavily doped of dopant is produced. The silicon substrate that has been coat with dopant is loaded onto the quartz boat.

Fig. 3. Spin Coater and P-type Liquid Dopant

3.0 Results And Discussions

3.1 Effect on Dose Concentration

The experimental results of the concentration that affect by temperature and types of dopant are presented graphically in Fig. 4 and 5. Its shows that, as temperature increased, the concentration also increased.

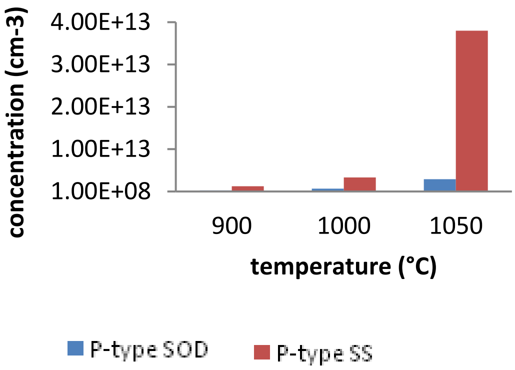

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Fig. 4. Concentration against temperature for P-type

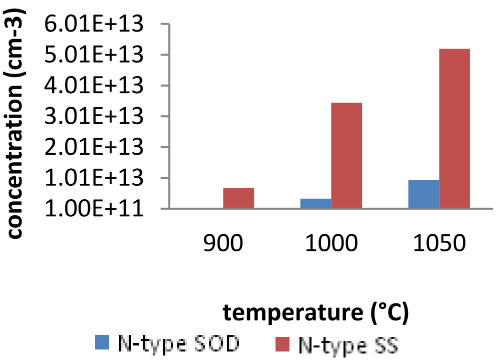

Fig. 5. Concentration against temperature for N-type

Temperature has a most profound on the influence on the coefficients and diffusion rate [8]. The relationship between diffusion coefficient and temperature is shown in equation (4). Where D is indicative of the rate at which atoms diffuse [9].

$$D = D_0 + \exp(-\frac{Qd}{RT}) \qquad (4)$$

From equation 4, it shows that when temperature is increased, the rate of atom that diffuses onto the silicon substrate also increased. The effect of these phenomena is increased on the carrier concentration. There are three region involve in the variation of temperature and carrier concentration which are Freeze-out region, extrinsic region and intrinsic region [10].

The graphs also show that N-type dopant has higher concentration compared to P-type dopant. An electron has light mass compared to hole where it has a mass that is approximately 1/1836 that of the photon. Impact from that, it can easily diffuse into the silicon substrate. So, many electrons can diffuse and it diffuses deeper. Therefore, high dose concentration is produced.

The graphs also show that, SS give higher concentration compared to SOD. In SS, when temperature increased, atom at the surface of SS will vibrate and produced high surface reaction. Next, these atoms are diffuse from the SS surface which has higher concentration to the silicon substrate which has low concentration. Diffusion process is more easy and faster by using SS. Thus the concentration and diffusion rate is increased. However, in SOD atom of liquid dopant contains of contamination so it takes time for nitrogen to eliminate the contamination. Besides that, atoms on the surface of silicon substrate need to evaporate before it can be diffuse into the silicon substrate. These phenomena will reduce the concentration and diffusion rate.

3.2 Effect on Oxide Thickness

Carrier concentration is one of the factors that affect the oxidation rate. Fig. 6 and 7 shows that, as the concentration increased the oxide thickness also increased.

For phosphorus oxidation rate, the surface reaction becomes important [11]. Surface reaction (diffusion) involved the motion of atom, molecules and atomic clusters at solid material surface [9]. The rate of the motion atom is also called as jump rate. Equation (5) shows that temperature is one factor that affects the jump rate, Γ.

$$\Gamma = \nu e^{-E_{diff}/kBT} \qquad (5)$$

The relationship between E_{diff} and k_BT called as thermodynamic factor. These jump atoms (phosphorus) tend to pile up at the silicon surface. The concentration of dopant (atom) is higher at the silicon surface. These atoms are then diffused onto the silicon substrate which has low concentration. The equation shows that as the temperature increased, the jump rate of atom also increased. So high carrier concentration is then produced in the silicon substrate. This will increase the oxidation rate.

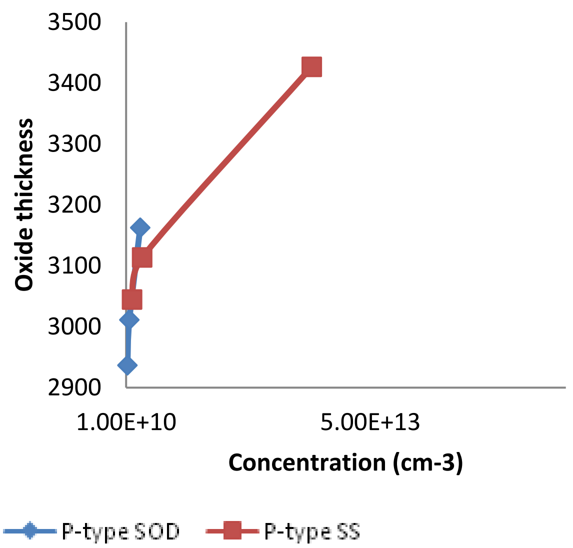

Fig. 6. Oxide thickness of P-type material

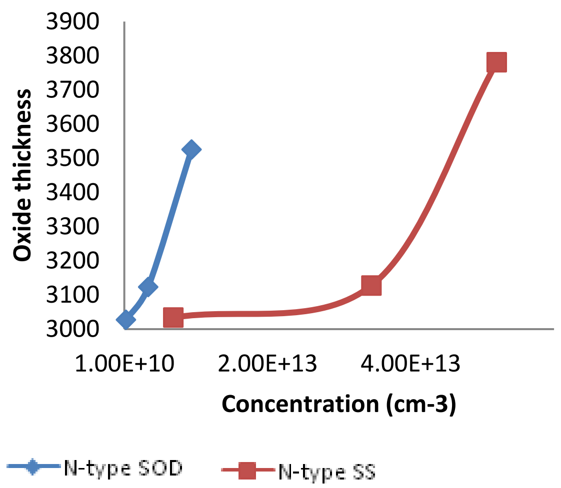

Fig. 7. Oxide thickness of N-type material

For the P-type dopant (Boron), the oxidation process is diffusion control predominant. When the boron is segregates into the oxide, the bond structure in the silica become weak. As the boron concentration increased the bond structure in the silica become weakens [11]. The weakens bond structure allows both oxygen,O_2 and water,H_2O molecules to enter the silicon dioxide,SiO_2 more easily and also diffuse through it rapidly, thereby leading to enhance oxide growth [12].

As have been discussing in section 3.1, type of dopant is one of the factor that affect the carrier concentration and Phosphorus give higher carrier concentration compared to the Boron. The resultant is, the oxide growth of Phosphorus is higher than Boron.

3.3 Effect of Residue

All measured data has been tabulated in table 1 and table 2. Fig. 8 and 9 graphically shows that resistivity of SS is lower compared to SOD. There are several advantages that can make SS have higher dopant concentration that diffuse in the silicon substrate and also make the oxide thickness become thicker. First advantage is its ability to use hydrogen injection to reduce or eliminate defect at the silicon wafer surface [5]. Besides that, because of the distance between SS is close proximity to the silicon substrate during the diffusion process it can eliminate the depletion effect. Since there is small impurities interfere in the reaction, the concentration and the oxide thickness become larger. N-type SS has better diffusion and oxidation rate compared to P-type SS. The reason that N-type SS gives higher diffusion and oxidation rate compared to P-type SS has been discussed in 3.1 and 3.2 respectively.

Fig. 10 shows that P-type SS has higher percentage of resistivity compared to N-type SS. So it is proven that the concentration and conductivity of P-type is less due to higher resistivity. Furthermore, fig. 11 shows that the percentage of oxide thickness of SS in both P-type and N-type is in positive. These positive percentages refer to the thicker oxide thickness growth in the SS compared to SOD.

Table 1
Resistivity of P-Type Dopant

TEMPERATURE	resistivity of SOD	resistivity of SS
900°C	54949.53	1934.65
1000°C	3961.05	382.96
1050°C	1403.48	257.80

Table 2
Resistivity of N-Type Dopant

TEMPERATURE	resistivity of SOD	resistivity of SS
900°C	16132.08	3542.71
1000°C	6420.52	1310.15
1050°C	1527.34	115.9

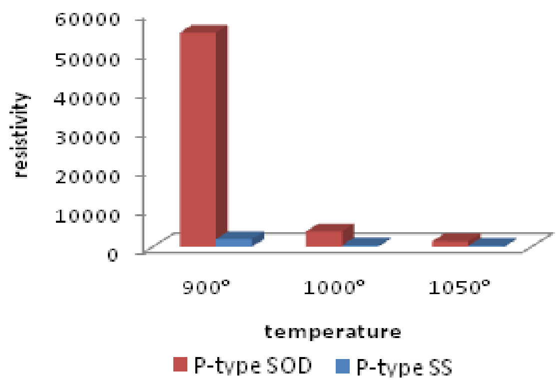

Fig. 8. Resistivity of P-type by using SS and SOD

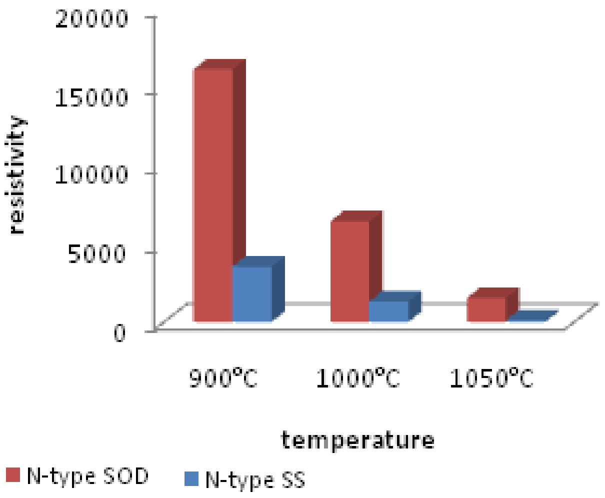

Fig. 9. Resistivity of N-type by using SS and SOD

In SOD, there is more impurities (native oxide) interfere because the spin coat process is done at not totally clean room. The effect is less dopant concentration diffuse in the silicon substrate. Furthermore, the oxide thickness becomes thin. There are several parameter involve in SOD which are solution viscosity, solid concentration, angular speed and spin time [4]. It has a difficulty to determine the suitable speed and spin time that can produce thicker oxide thickness.

Besides that, SOD involves a large number of variables that tends to cancel and average out during the spin process and it is best to allow sufficient time for this to occur [4]. Because of these reasons, the oxide thickness that growth on top of the silicon substrate by using SOD is thinner compared to SS. The reason that P-type SOD gives lower diffusion and oxidation rate compared to N-type SOD has been discussed in 3.1 and 3.2 respectively.

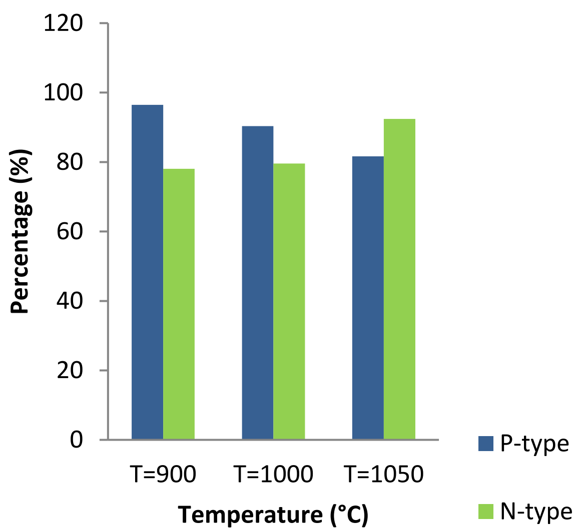

Fig. 10. Percentage of resistivity

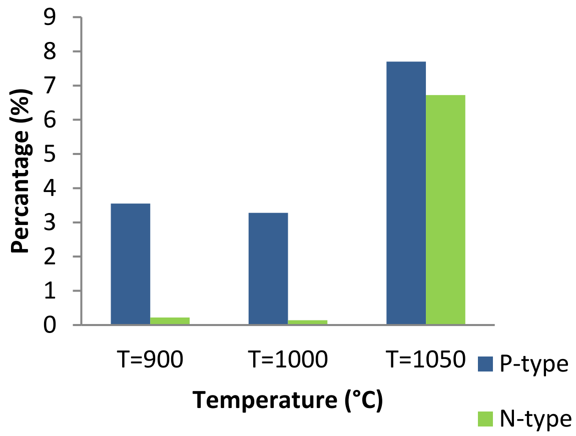

Fig. 11. Percentage of oxide thickness

4.0 Conclusions

Based on discussion, it can be concluded that the diffusion and oxidation rate is affected by the doping technique. There are two types of doping technique used which are Solid Source, SS and Spin on Dopant, SOD. Solid Source, SS give higher diffusion and oxidation rate compared to Spin on Dopant, SOD. This is because, by using Solid Source it can used hydrogen injection to reduce the contamination inside the silicon substrate.

Extrinsic semiconductor is divided into two which are P-type and N-type. N-type dopant produces better diffusion rate because it has higher carrier concentration. Besides that, thicker oxide layer are growth on top of it silicon substrate. In the other hands it produces higher oxidation rate due to lightly weight of electron compared to hole.

Furthermore, carrier concentration and temperature also affect the diffusion and oxidation rate. As the temperature increased, carrier concentration also increased. As the result, it increased the oxidation rate during the oxidation process.

For the future development, diffusion and oxidation rate can be investigated by using different doping and annealing technique. Ion implantation can be use as the doping technique. Since annealing is one of the factor that effect both diffusion and oxidation rate, so the process of annealing can be applied during oxidation process. Time and temperature can be use as parameter that varies during this process. For recommendation, dry oxidation can replace wet oxidation in the oxidation process because it will produce better quality of oxide thickness. Quality of oxide thickness play important role in the device fabrication because it will affect the device performance.

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