PROCESS MODELING OF SOLID SOURCE
PHOSPHORUS DIFFUSIONS USING SUPREM-III

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Abstract

Carborundum PH-1025 Solid Planar Diffusion Sources were used to perform a statistically designed diffusion matrix. The data taken from this matrix included junction depth, sheet resistance and transferred glass thickness. Modifications to the existing SUPREM-III diffusion model failed to produce good correlation between SUPREM-III and the experimental data.

Introduction

The diffusion of phosphorus in silicon at high concentrations is not accurately modeled by the Gaussian and Complementary Error functions. This is due to the presence of such phenomena as concentration dependant diffusivity and electric field enhancement of diffusion. The phosphorus diffusion profile is composed of two regions (high concentration and tail) separated by a kink. The diffusion of phosphorus in these two regions is governed by different diffusivity expressions. Figure 1 shows a typical profile (1).
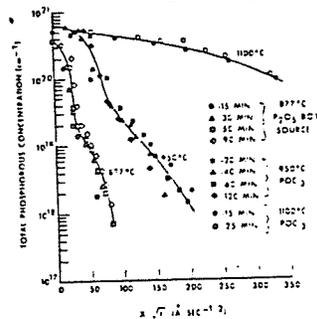

Fig. 1. Total phosphorus concentration vs. reduced distance for three diffusion temperatures.

Figure 1

The SUPREM-III diffusion model is based on the models proposed by R.B.Fair and J.C.C.Tsai (1). Their study determined the existence of three intrinsic diffusivities which govern the concentration profile. In the high concentration region the diffusion of phosphorus occurs by the interaction of P with neutral and doubly charged vacancies. The total diffusivity in this region is given by

Eq.#1 $Dt = h(Dix + Di2-(n/ni)**2)$

where Dix is the intrinsic diffusivity of the phosphorus neutral vacancy pair, Di2- is the intrinsic diffusivity of the phosphorus

double negative charged vacancy pairs and h is the electric field enhancement term.

In the tail region of the phosphorus profile, the concentration has dropped below that of the intrinsic carrier concentration so the diffusivity remains constant. Here the interactions with neutral and singly negatively charged vacancies dominates. The value for the diffusivity in the tail region is given by the following expression

Eq.#2 Dtail = Dix + Di-

where Dix is the (P/Vx) intrinsic diffusivity and Di- is the (P/V-) intrinsic diffusivity.

An accurate model must handle all of these factors correctly. According to the results of this study, the standard SUPREM-III diffusion model does not accomplish this for solid source diffusions. This model underestimates the amount of dopant introduced into the wafer. The result of this is an underestimation of junction depths and overestimation of sheet resistance. See the Appendix for graphs comparing the experimental data to SUPREM-III predictions for the same process.

Modifications to the SUPREM-III diffusion model were performed in an attempt to correct this problem. The parameters altered were the surface concentration and the diffusivities. Other parameters could be altered but with little justification from a physical standpoint. Earlier work by Paul Whalen showed the surface concentration to be around 5e20 /cm3. Simulations were also run using the option of solid solubility to determine the surface concentration. The possibility for oxidation enhanced diffusivity provided the justification for altering the diffusivities. It was assumed that the vacancy diffusion model physics of SUPREM-III are correct. It was also assumed that the differences between the SUPREM-III results and the process results are the result of the different chemistry between the gaseous source case that SUPREM-III was based on and the solid source chemistry used in this experiment.

The discrepancy may be caused by the surface reaction that releases the P into the silicon. The following is a brief process description. The Carborundum PH-1025 SPDS is a wafer of material that will fit into a standard diffusion boat along with the device wafers to be doped. The source wafer consists of silicon pyrophosphate (SiP2O7) in an inert ceramic binder. At diffusion temperatures the siliconpyrophosphate decomposes into P2O5 glass which is a vapor and SiO2 which is left behind on the source.

#3 SiP2O7 --> P2O5 + SiO2
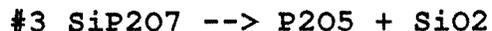
The P2O5 diffuses along a concentration gradient from the source to the device wafer and is deposited . The P2O5 then

diffuses to the wafer surface where it decomposes to release the phosphorus into the wafer. It is proposed the reaction proceeds according to the following equation

$$\#4 \quad 2P_2O_5 + 5Si \longrightarrow 5SiO_2 + 4P \ .$$

If this equation is true, the underestimations of SUPREM-III may be due to a neglecting of oxidation enhanced diffusion. The ability of SUPREM-III to model oxidation enhanced diffusion during pre-deposition was not determined in this study.

Experiment:

RS1 was used to design a two factor, three level, full factorial experimental matrix. The two factors were the diffusion soak temperature and the time at this temperature. The three responses measured were the junction depth, sheet resistance and the transferred glass thickness. Table 1 is the experimental values specified by RS1.

Table 1: RS1 Experimental Matrix

Run #	Soak Time	Soak Temp
1	10	1025
2	40	975
3	40	1025
*4	40	1000
5	10	975
6	25	1000
7	25	975
8	25	1000
9	10	1000
10	25	1025

* actual soak time was 35 minutes

The diffusion process was as follows. The source and device wafers were loaded into a standard diffusion boat. The boat was then loaded into a standard diffusion tube at 800 degrees C with nitrogen flowing. This nitrogen flow was present to prevent contaminants from entering the tube and to provide a motionless ambient in which the P2O5 glass can diffuse to the device wafer. Once the boat had been loaded into the tube the temperature was allowed to stabilize for 20 minutes after which time the ramp to the desired diffusion temperature began. The ramp rate used was 5 C/min. Once at the desired soak temperature, the wafers remained there for the desired soak time. The temperature was then ramped back down to 800 C at 5 C/min at which time the wafers were removed. Activation runs, both initial and daily, were run according to the specifications supplied by Carborundum. The sources were stored overnight in the diffusion tube at 475 C with a small flow of nitrogen present to prevent contamination or oxidation of the sources.

The process results of interest were the junction depth , sheet rho and transferred glass thickness. The glass thickness was measured using the ellipsometer to ensure that the run was successful. Comparing the measured glass thickness to the data supplied by Carborundum allowed for a disaster check of the process. Once the glass thickness had been verified it was stripped using buffered HF. The sheet resistance measurements were taken using the four point probe. The junction depths were measured using groove and stain techniques. The groove and stain process had to be carefully controlled to achieve repeatable results. All the wafers were grooved within a short period of time using the same groove time , stain time and stain illumination. The sheet resistance and junction depth data were plotted to allow for graphical as well as numerical comparison with the results of the SUPREM-III simulations.

DISCUSSION

Graphs 1 & 2 in the Appendix show the performance of the process across the matrix. The junction depth curves for different temperatures share the same slope with vertical displacement between the curves. The sheet resistance curves show vertical displacement between curves as well as increasing slopes with increasing temperature. This would indicate a faster incorporation of dopant into the silicon at higher temperatures which is as expected.

The solid solubility option did not produce values that matched the results of the experimental diffusions Graphs 1a & 1b. Unfortunately, increases in the surface concentration parameter did not remedy the situation. Modifications to the diffusivities brought the model closer but the model was still not accurate at all points (graphs 2a & 2b). Without actual doping profiles by SIMS analysis it will be highly unlikely that SUPREM-III will be fit to the RIT solid source diffusion process. In addition to needing the junction depth and sheet resistance the depth of the high concentration region, the depth and concentration at which the kink occurs as well as the concentration in the tail region are also needed. Without such data it will be difficult to determine which parameter needs to be modified and when. It may be possible to create separate parameter sets for each diffusion temperature but this would not result in a true model. Another possibility is that there may be some physical process (i.e. oxidation enhanced diffusion) in effect that is not being modeled by SUPREM-III. If this is the case then the SUPREM-III model may not match the process no matter what modifications are made.

CONCLUSION

Without more knowledge about the profiles to be modeled,modifications to SUPREM-III will result in a haphazard set of model parameters at best. Even with the profiles known

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the possible effect of oxidation enhanced diffusion might not be modelable by SUPREM-III. Modifications to SUPREM-III using only surface concentration, junction depth and sheet resistance can not be expected to yield a reliable and accurate model for the solid source diffusion process.

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