DIFFUSION STAINING TECHNIQUES

By

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ABSTRACT

Cross-section staining of p-type diffusions was investigated. The method employed a stain formulation of Diffusion depths of 1.9 microns were delineated and photographed using a scanning electron microscope.

INTRODUCTION

There are several methods of determining the diffusion depth of dopants into silicon. The groove-and-stain method provides a quick, rough estimate of the diffusion depth, but lacks accuracy due to the error associated with it. This error results from the three measurements that must be made in order to take one reading (see Figure 1) :

1) M, the distance from top to bottom of the diffusion trench,
2) N, the distance from the bottom of the diffusion to the opposite edge of the trench,
3) D, the grinding wheel diameter.

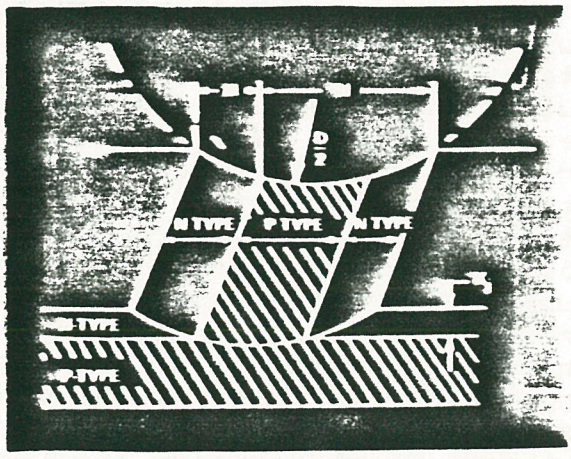

Figure 1

All of these measurements are made by the "best guess" of the operator and are not really accurate. If it is necessary to know the exact depth of the dopant into the wafer, another method must be used. This new method was chosen to be the cross-section stain. The accuracy is greatly improved by this

method since only one measurement is made and it is made with a scanning electron microscope (SEM).

Cross-section staining can be broken down into three techniques (1) :

1) Electrochemical displacement plating

This method creates a visible discoloration of p-n junctions after electrochemical plating takes place. The p and n regions provide differing electrochemical potentials which facilitate adequate decoration. The problem with this method is that the time it takes to set up the electrochemical cells and power supply is long.

2) Oxidation-reduction reactions in silicon

Highly oxidized areas will also be visible under the microscope. If the stain formulation is such that it is a good oxidizer, the doped areas will be decorated enough to be measured under a microscope. But, when the geometries get very small, it is difficult to see the difference between the n and p regions since their masses differ only by a few parts per million. Using an SEM won't help much either because there are no physical edges at the p-n junction.

3) Differential etch rates

Once understood, the method of differential etching provides the sharpest and most reliable images. Here, the stain used is really a removal etchant. The etchant attacks the doped region at a greater rate than the bulk silicon because the dopant-silicon bonding energy is lower. In the case of an n-type wafer doped with boron, the etching ion attaches itself to the boron much more rapidly which facilitates the removal of silicon in the doped area. Care must be taken so that overetching does not occur otherwise upper layers will collapse onto the desired diffusion region. Once the region has been properly stained, the SEM delineates the diffusion by highlighting the edge created at the p-n junction. This edge effect causes an increase in secondary electron emission which provides the contrast needed for a good SEM image.

The chemical reactions that take place in a removal etch are as follows (1) :

Oxidation $\quad Si + (O) \longrightarrow SiO_2$

Complexation $\quad SiO_2 + 6HF \longrightarrow SiF_6^- + 2H_2O + 2H^+$

The differential etch rate method was chosen for research because of its high potential for the RIT integrated circuit fabrication lab.

EXPERIMENTAL

Three n-type, 3 - 8 cm, <100> wafers were coated with Allied Chemical Boron B-150 spin-on dopant. The chosen spin speed and spin time (3000 rpm for 20 seconds) resulted in a thickness of about 5000 Å according to the B-150 data sheets. A 35 minute diffusion was performed at 1150°C in air ambient. Since the presence of the oxide formed from the B-150 during diffusion will be necessary to serve as the upper barrier for the diffusion depth measurement, it was not stripped.

The above process parameters were fed into the SUPREM II process modelling program in order to obtain an estimate of the diffusion depth.

One wafer was used specifically for groove-and-stain measurements. Several attempts were made in which the grooving time was varied. The stain formulation was one part HF, two parts HNO_3, and twelve parts acetic acid. Light was also used during the staining process.

Two diffusion stain formulations were chosen for the sake of comparison. Stain A was made up of four parts HF, four parts HNO_3, and two parts water. Stain B was made up of three parts HF, five parts HNO_3, and three parts acetic acid.

Stain	%HF	$\%HNO_3$	Motoring Agent
A	40	40	20% Water
B	27	46	27% Acetic

The nitric acid serves as the oxidizing agent and the hydrofluoric acid serves as the complexing agent for both stain formulations. The two major differences between stains A and B are the concentrations of the constituents and the type of motoring agent used.

One wafer was cross-sectioned into sixteen samples suitable for SEM use. Eight of the samples were used for Stain A and the remaining eight were used for Stain B. Each sample was immersed into a plastic beaker containing the correct stain. Samples 1 - 8 had stain times of 1, 3, 5, 7, 10, 15, 20, and 30 seconds respectively for both stain formulations. The five-second and twenty-second stained samples were mounted at an angle on the stud so that an edge-view could be obtained in the SEM. Once the image was established, a photo was taken at a magnification of 2000.

RESULTS

There were discrepancies between the three methods used to find the diffusion depth. Table 1 shows each staining method and the resulting diffusion depth obtained :

Table 1

Method	Depth (microns)
SUPREM II	3.5
Groove/Stain	0.4
Stain A	1.9
Stain B	3.0

SUPREM II did not seem to be very reliable concerning this process because there were some values called for that could not be calculated at the RIT facility. Assumed values were used in hopes that they were chosen correctly, but the 3.5 micron value is most likely incorrect.

The groove-and-stain method was also highly inaccurate. The decorated areas had extremely ragged edges which made it very difficult to make accurate measurements.

Stain A yielded the most accurate and the most precise results. The concentration of HF was sufficient to keep SiO from forming and to ensure proper delineation for the SEM. Repeatable results were observed with this stain and the diffused area can be seen easily (see Figure 2).

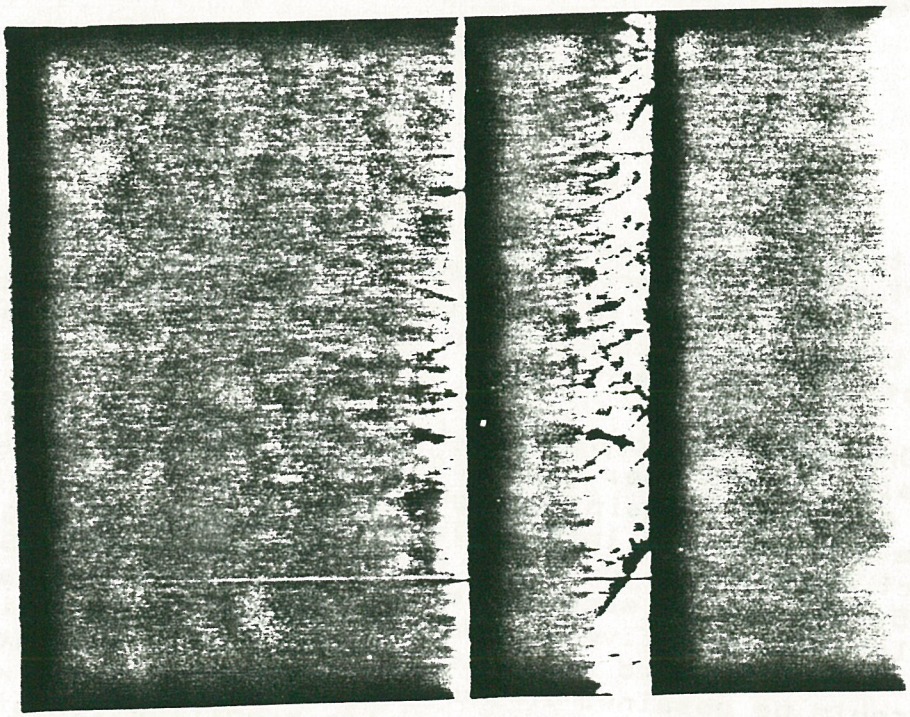

Figure 2

Stain B showed signs of over-oxidation. This was evidenced by the fact that the diffused regions were etched minimally and the remaining surfaces were overly decorated. There are two factors that could have caused this. The first was due to a dilution effect resulting from the large amount of oxide on top of the diffusion region. This extra oxide consumed the HF from the stain local to the diffusion which decreased the silicon removal rate. The second factor was due to SiO formation around the diffused area (1). Since there was too much oxygen in the vicinity, the yield from the reaction forming SiO was greater than the silicon-removal yield. The result is a false delineation over non-diffused silicon due to the SiO spreading.

SUMMARY

The 3:5:3 mixture of HF, HNO_3, and acetic acid showed signs of over-oxidation which resulted in inaccurate diffusion depth measurements. The 4:4:2 mixture of HF, HNO , and water was found to produce high-quality stained images in the SEM for stain times of around five seconds. This process could be used to help standardize the groove-and-stain method, to calibrate new and existing equipment, or to tabulate values that would be fed into SUPREM II.

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