

Deconfounding the Effects of Cu and Cr on Perceived Fe Contamination in Si Using an SPV Technique

Steven V. Nagel
Microelectronic Engineering
Rochester Institute of Technology
Rochester, NY 14623

Abstract— The effects of iron, copper, and chrome on minority carrier diffusion length measurements in p-type, boron doped, silicon were investigated using a surface photovoltage (SPV) technique. Attempts were made to reproduce previous results for iron and chrome, metals which form complexes with boron. Also an attempt was made to study the effect that copper contamination would have upon the SPV results. It was found that the iron results were reproducible, FeB could be photodissociated, and that the chrome contaminated wafers were not effected by the photodissociation, CrB pairs were not broken. The copper contaminated wafers were found to be effected by the photodissociation step, which significantly reduced the measured diffusion lengths.

1. INTRODUCTION

The need for smaller and/or more efficient semiconductor devices has led to an increased effort to reduce, or in some cases even eliminate, impurities in silicon substrates. Perhaps the most important set of these impurities are the fast diffusing metallics that have energy trap levels in silicon near midgap. These metallics effectively reduce carrier lifetimes and may also adversely effect the integrity of gate oxides¹. These facts create a need for an analytical technique that is very sensitive, requires little sample preparation, and has a quick turn around time. A technique was developed using surface photovoltage (SPV) minority carrier diffusion lengths in order to measure iron, perhaps the most common of these impurities. This technique is based upon the fact that in p-type, boron doped, silicon; iron complexes with boron. When the substrate is illuminated, or heated and quick quenched, these pairs are disassociated. This is often termed the activation step. The unpaired iron is a more efficient trap and the minority carrier lifetime is therefore reduced. Due to the measurable differences in diffusion lengths before and after activation, an iron concentration can be determined.

Other metals are known to have trapping properties that may also be effected during the activation step. The most completely studied of these metals is chrome². Chrome also complexes with boron, and when disassociated becomes a less efficient trap. The clouding of perceived iron levels due to chrome can be minimized by using the photodissociation method instead of the heating and quick quenching method. This is due to the fact that the CrB pairs do not photodissociate as readily as the FeB pairs. Copper is another metallic contaminant that may effect SPV results. After a high temperature process (above 900°C) and a slow cool, copper tends to precipitate at the silicon surface. At the silicon-silicon dioxide interface, the copper does not influence the diffusion length measurements. After the photoactivation step, however, the copper reduces the diffusion length.

2. EXPERIMENTAL

P-type, boron doped, 150 mm, <100> silicon wafers that had a resistivity between 8 and 12 Ohm-cm; were oxidized in wet ambient at 950°C to grow a target oxide thickness of 500 angstroms. The diffusion lengths of the wafers were then measured to assure that the oxidation process did not lead to high initial metallic impurity levels, which would contribute to noise in the experiment. These wafers were then implanted with iron, copper and chrome at various doses and combinations of elements. The energies of the implants were adjusted so that the peak metal concentration was located at the silicon-silicon dioxide interface. The wafers were then annealed at 950°C for 45 minutes in nitrogen. Twenty-four hours after the anneal, the diffusion lengths were then measured using the SPV technique. A photodissociation step was performed next and the diffusion length was remeasured. After waiting 24 hours for the FeB pairs to reform, the measurement, activation, and remeasurement process was repeated.

3. RESULTS AND DISCUSSION

The initial minority carrier diffusion lengths, after oxidation and prior to implantation, are given in Table I. The legend names in this document, M*D*, stand for the order in which the iron measurements were taken (M) and the diffusion length before and after activation (D1 and D2). Measurement one (M1D1 and M1D2) were prior to implantation, all others are after implantation and anneal.

Table I: Initial screening for [Fe], post oxidation.

Wafer #	M1D1 (um)	M1D2 (um)	Initial [Fe] (cm ⁻³)
SPV-132 01	419	319	4.34E+10
SPV-132 02	426	360	2.32E+10
SPV-132 03	430	365	2.20E+10
SPV-132 04	429	363	2.26E+10
SPV-132 05	428	362	2.28E+10
SPV-132 06	430	366	2.16E+10
SPV-132 07	431	364	2.27E+10
SPV-132 08	431	366	2.19E+10
SPV-132 09	430	362	2.33E+10
SPV-132 10	429	362	2.31E+10
SPV-132 11	428	359	2.42E+10
SPV-132 12	429	362	2.31E+10
SPV-132 13	431	363	2.32E+10
SPV-132 14	434	365	2.31E+10
SPV-132 15	435	365	2.33E+10
SPV-132 16	433	364	2.32E+10
SPV-132 17	428	361	2.33E+10
SPV-132 18	428	360	2.37E+10

All of the wafers used for the experiment had a background iron concentration of less than 5.0E+10 atoms/cm³. This concentration was calculated using Equation 1 which defines the relationship between the change in diffusion lengths and iron concentration³.

Equation 1: Calculation of [Fe] using SPV diffusion lengths before and after activation.

$$Fe (cm^{-3}) = 1.05 \times 10^{16} (L_1^{-2} - L_2^{-2})$$

A. Iron Analysis

Diffusion lengths of the wafers implanted with iron decreased dramatically. This was expected because the FeB complex is a fairly effective trap. When the wafers were exposed to light during the activation step, the pairs

disassociated and the diffusion lengths dropped further because the interstitial Fe trap is more effective than the FeB pair. After the 24 hour recombination period, the diffusion lengths fully recovered and after photodissociation returned to the same level as observed in Figure 1.

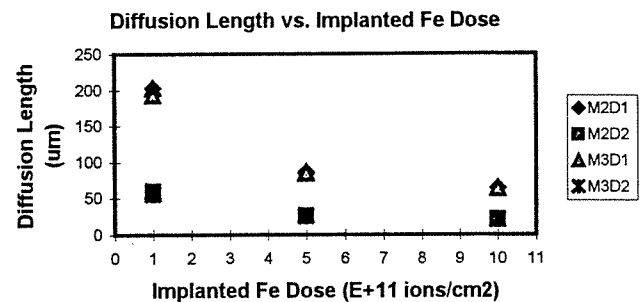


Figure 1: Diffusion lengths of Fe implanted wafers before and after activation, prior to and proceeding a 24 hour recombination period.

The corresponding diffusion lengths and iron concentrations are given in Table II.

Table II: Fe dose and resulting [Fe] calculated.

Fe Dose (cm ⁻²)	M2D1 (um)	M2D2 (um)	M3D1 (um)	M3D2 (um)	[Fe] (cm ⁻³)
1E+11	202	58.8	202	58.9	2.77E+12
5E+11	85.8	25.7	85.8	25.6	1.46E+13
1E+12	63.6	20.8	63.3	20.6	2.21E+13
1E+11	194	55.8	193	55.8	3.09E+12
5E+11	84.2	25.3	84.0	25.2	1.50E+13
1E+12	63.3	20.6	63.0	20.5	2.23E+13

These values for the observed iron concentrations are slightly higher than would be expected at these doses by approximately a factor of two. The wafers used were approximately 675um thick so the resulting concentration should have been 1.48E+12 cm⁻³ for the lowest implanted dose. The calculated [Fe] of 3E+12 cm⁻³ indicates that the implant dose was actually 1.87E+11 cm⁻² opposed to the targeted dose of 1E+11 cm⁻².

B. Chrome Analysis

The diffusion lengths of the Cr implanted wafers were reduced after photodissociation. The diffusion lengths for each chrome dose are summarized in Table III.

Table III: Diffusion lengths of chrome implanted wafers before and after photodisassociation.

Cr Dose (cm ⁻²)	M2D1 (um)	M2D2 (um)	M3D1 (um)	M3D2 (um)	[Fe] (cm ⁻³)
1E+11	403	281	402	281	6.80E+10
5E+11	396	257	394	257	9.13E+10
1E+12	396	253	392	252	9.70E+10
1E+11	407	278	405	279	7.09E+10
5E+11	401	249	398	250	1.02E+11
1E+12	404	268	400	267	8.17E+10

The amount of chrome implanted into the wafer does not track with the perceived iron concentration. If the CrB pairs were disassociating, the diffusion length should have increased with chrome dose. Also, by comparing M2D1 to M3D1 in Table III, it can be seen that the diffusion lengths fully recovered after the twenty four hour recombination period. Which is not long enough for CrB pairs to reform². Therefore the "iron" that is calculated using the SPV method is believed to be iron that was contributed by the implantation process.

C. Copper Analysis

During the SPV testing sequence, wafers implanted with copper reacted very differently than either chrome or iron implanted wafers as can be seen in Figure 2.

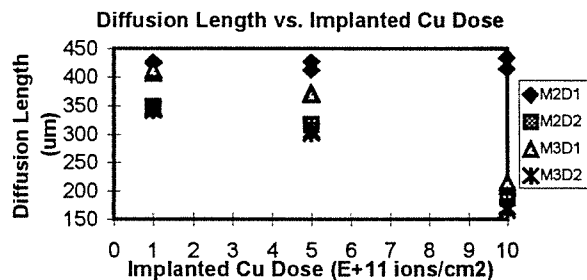


Figure 2: Diffusion lengths of Cu implanted wafers before and after activation.

The copper does not effect the initial diffusion length (See Table IV or Figure 2) which indicates that either the copper in it's current form is not a very effective trap or is located at the surface where it would not be seen using SPV. However the ability to see an effect of copper after photodisassociation indicates that the iron must already be in the bulk. That is because it is highly unlikely that a light pulse would inject copper atoms from the surface into the bulk.

Table IV: Summary of copper implanted wafer diffusion lengths.

Cu Dose (cm ⁻²)	M1D1 (um)	M1D2 (um)	M2D1 (um)	M2D2 (um)	M3D1 (um)	M3D2 (um)
1E+11	431	363	424	344	406	341
5E+11	434	365	426	316	372	301
1E+12	435	365	433	187	208	165
1E+11	433	364	426	348	412	345
5E+11	428	361	412	317	370	306
1E+12	428	360	414	192	215	171

Diffusion lengths of the copper implanted wafers did not fully recover after the recombination period. The level to which the diffusion length drops after photodisassociation is dependent upon the copper implant dose. The level to which the diffusion length recovers is attributed to iron because it's not dependent upon the copper dose. This data is summarized in Table V.

Table V: Summary of copper effect on perceived [Fe].

Cu Dose (cm ⁻²)	Initially Perceived [Fe] (cm ⁻³)	Cu Induced [Fe] Error (cm ⁻³)	Actual [Fe] (cm ⁻³)
1E+11	3.03E+10	5.29E+09	2.50E+10
5E+11	4.73E+10	1.80E+10	2.93E+10
1E+12	2.44E+11	1.87E+11	5.76E+10
1E+11	2.88E+10	4.00E+09	2.48E+10
5E+11	4.26E+10	1.48E+10	2.78E+10
1E+12	2.24E+11	1.66E+11	5.77E+10

To achieve a better understanding of the surface to bulk concentration variations, the standard plot used to extract diffusion length by SPV was expanded to include more measurements at varying wavelengths. Shown in Figure 3 is one such plot for the wafer with the highest copper implant dose.

Figure 3 shows that there is a slight increase in copper concentration near the surface (indicated by the slight curving near the zero point). However this is not enough to significantly effect the resulting diffusion length that is inferred from the plot.

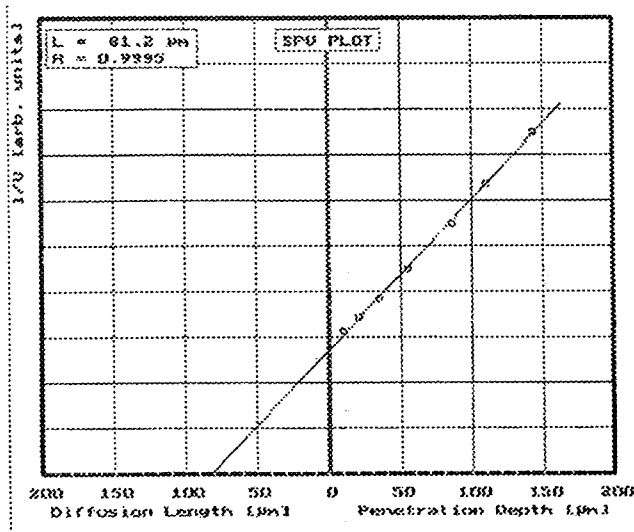


Figure 3: Intensity divided by SPV vs. inverse absorption at varying intensities.

Taking all of this information into account, it appears that copper, already present in the bulk of the silicon, is being somehow altered during the photodissociation step to form a much more effective trap. It is possible, however, that more than one trap is formed during this activation since the diffusion lengths measured do not fit the same type of equation as iron to arrive at a contaminant concentration. Another measurement technique, such as deep level transient spectroscopy (DLTS), will need to be used to determine exactly what trap or traps are formed.

4. CONCLUSIONS

Surface photovoltage is a fast and reliable way to determine iron contamination levels in p-type silicon. Chrome levels appear to have little effect upon diffusion length measurements and do not cloud iron results when a photodissociation step is performed to break FeB pairs. Copper concentration has an effect upon the perceived iron concentration in a sample and has the ability to lead to erroneously high results. A second measurement made after a 24 hour iron and boron recombination period, leads to a more exact iron measurement.

REFERENCES

- [1] W. Henley, L. Jastrzebski, and N. Haddad, "Effects of Iron Contamination on Thin Oxide Breakdown and Reliability Characteristics," Proceedings of the 1993 IEEE International Reliability Symposium, 1993.
- [2] K. Mishra, "Identification of Cr in p-type Silicon Using the Minority Carrier Lifetime Measurement by the Surface Photovoltage Method," Appl. Phys. Lett., 68 (23), 3 June 1996.
- [3] L. Jastrzebski, W. Henley and C. Nuese, "Surface Photovoltage Monitoring of Heavy Metal Contamination in IC Manufacturing," Solid State Technology, December 1992.

ACKNOWLEDGEMENTS

The author acknowledges the Integrated Sensor Solution and Analytical Technology Divisions of the Eastman Kodak Company for their financial support of this project and Dean Seidler and Albert Filo of Eastman Kodak for their guidance in this work.

Steven V. Nagel, originally from Candor, NY, received a B.S. degree in Microelectronic Engineering from the Rochester Institute of Technology in 2000. He attained co-op work experience in the Image Sensor Solution division of Eastman Kodak in the dielectric films and DI water areas. He is joining Microchip Technologies as a process engineer starting in June 2000.