INFLUENCE OF BORON DIFFUSION ON THE SI SURFACE PASSIVATION

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ABSTRACT: The formation of p^+ emitters using boron diffusions is gaining momentum in research for the ultimate use in commercial solar cell fabrication. However, the effect of boron diffusions on the interface defect properties is little known. In this work, varying surface charge densities are applied to diffused and undiffused surfaces in order to create an accumulation layer to allow direct comparison of surface conditions of diffused and undiffused silicon, as interface states will dominate under these conditions.
Keywords: silicon, SiO_2, boron, charge

1 INTRODUCTION

A disadvantage of the use of Czockralski (Cz) silicon in mono-crystalline solar cells is limited by the unavoidable occurrence of boron-oxygen pairs in boron doped wafers. These boron-oxygen pairs cause recombination of minority carriers and therefore limit the lifetime and efficiency of the cell [1]. One way to avoid this problem is to use n-type silicon (typically phosphorus doped), in which these recombination causing pairs do not occur despite the presence of oxygen [2].

However the use of n-type silicon wafers necessitates p-type boron diffused emitters. Such emitters are much less well characterized than phosphorus doped emitters. so in order examine further the use of n-type silicon as a bulk, characterization of p-type emitters such as boron is necessary. In this paper boron emitters are investigated in some detail using a method where-by charge is applied to the silicon surface in order to push the surface into accumulation.

It has been found that boron diffusions increase the defect density at the $Si\text{-}SiO_2$ interface above a certain substrate doping level [3]. However, it is difficult to obtain data that can be used to examine this hypothesis due to the fact that diffused surfaces are more difficult to analyze than a lowly or moderately doped surface.

Under deep accumulation conditions the surface minority carrier concentration saturates and becomes only weakly dependant on surface charge density, and nearly independent of substrate doping (particularly in accumulation). This implies that measurement of the emitter saturation current density J_{oe} at high surface charge densities, particularly in accumulation, can be used to detect any differences in interface defect properties, provided that differences in recombination in the emitter itself can be accounted for. This method has also been applied to phosphorus emitters in another paper presented at this conference entitled "Influence of Phosphorus Diffusion on the $Si\text{-}SiO_2$ Interface" [4].

2 EXPERIMENTAL

2.1 Sample Preparation

Samples used for lifetime-voltage measurements were p type, float-zoned, <100>, >100Ω/cm, 500µm thick Si wafers. After etching in acid solution and a standard RCA cleaning, samples received a passivating oxide of around 90 nm that was thermally grown at 1000°C in dry oxygen with an in-situ anneal in nitrogen, followed by annealing in forming gas (FGA, 5% H_2 in 95% Ar) at 400 °C for 30 min.

All boron emitters were made using a liquid boron tribromide source in a diffusion furnace at a temperature of 900°C to obtain a sheet resistance of around 200 Ω/ , with variability across a sample at 5%. This method of diffusions has been used and characterized for buried contact solar cells at the University of New South Wales [5].

A thin layer of aluminium (approx 5 nm thick) was evaporated onto both surfaces of the sample, so that there was at least 5 mm overhang over the photo-conducting coil of the lifetime tester during measurement. This thickness was carefully chosen to allow uniform conductance across the surface, and a reasonable amount of light through to allow lifetime measurements. See conference paper entitled "Accurate Measurement of Extremely low Surface Recombination Velocities" for further details on this method [6]. In brief, this method allows simultaneous measurement of Joe and effective lifetime with the use of a photoconductive coil as charge is applied and the surface is pushed into accumulation. All measurements were taken at a carrier density of 4×10^{15} cm^{-3}.

2.2 Leakage current

Attempts to create an inversion layer on the surface of boron diffused samples, through the application of positive voltage, resulted in high leakage currents of up to 50 mA. Attempts to eliminate this leakage current were made by the addition of an LPCVD nitride (50 nm) but the effect could not be eliminated. It was found that the application of a positive voltage caused an electrical breakdown of the insulating layer/layers. The effect can best be seen in Fig 1. Therefore thus far surfaces have only been examined while in accumulation, in which circumstance the leakage current remains negligible for approximately 50% of samples if clean processing practices are observed. In order to get 100% yield of samples with negligible leakage current under

accumulation conditions, the use of the addition of LPCVD nitride (50 nm) deposited at 775°C at 0.5 torr, in combination with a thermally grown oxide (50 nm) was found successful. J_{oe} determined from oxide only and oxide/nitride stacks are both presented in this paper.

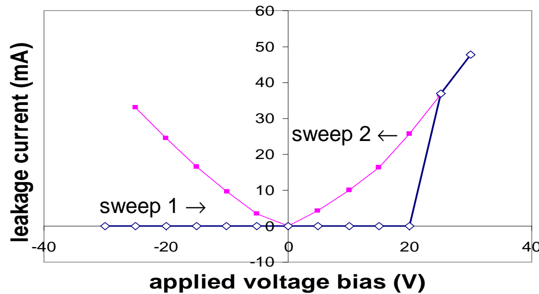

Fig 1: Measured leakage current through sample prepared as above. Sweep 1: the voltage was first swept in the negative direction and then swept through to positive values. Sweep 2 followed from positive to negative with permanent breakdown evident.

3 RESULTS AND DISCUSSION

3.1 Examination of <100> high resistivity lightly boron diffused sample

The lifetime and Joe of a boron diffused sample with a silicon oxide layer were observed as a function of applied voltage bias as can be shown in Fig 2 for a injection carrier density of 4×10^{15} cm^{-3}. It can be observed that J_{oe} decreases as the sample approaches accumulation conditions, and then stabilizes as surface recombination is saturated.

S_{eff} was then calculated from J_{oe} to have a value of 2.0 cm/s by the following equation.

$$S_{eff} = J_{oe}(p_o+n)/(q.n_i^2) \qquad (1)$$

Where S_{eff} is the effective surface recombination velocity, J_{oe} is the emitter saturation current density, p_o is the hole concentration in thermal equilibrium, n is the photogenerated minority carrier density, q is the charge of an electron, and n_i is the intrinsic carrier concentration.

Due to minority carriers saturating at the surface, it is not necessary to know the exact surface concentration to determine an estimate of the surface recombination velocity (SRV), which eliminates the recombination due to the emitter that is included in a value of S_{eff}. Using PC1D (semiconductor modelling software), inputted with a spreading sheet resistance profile taken from a similarly diffused sample, and bandgap narrowing of 0.0025 eV as proposed by King [7], the surface concentrations were estimated for majority carriers, $Na_{maj}=1\times10^{20}$ cm^{-3} and minority carriers, $Nd_{min}=1\times10^{12}$ cm^{-3}.

Using this value for electron concentration at the surface, a surface recombination velocity (SRV) of around 790 cm/s was determined. This value was estimated from measurements with the sample in accumulation. With no charge applied, the value of SRV should be lower, since the range of defect energy levels for which defects contribute significantly to recombination increases with increasing (effective) doping. However the difference in the range of recombination-active energy levels is small for heavily doped surfaces, and so it can be assumed that when no charge is applied to the surface, the SRV will be similar to that determined while in accumulation due to the Shockley Read Hall relationship, whereby the surface in still under low injection conditions given that there is a significantly larger number of acceptor atoms than minority carriers.

With the model we also estimated that 4.5 fA/cm2 of the J_{oe} for this sample could be accounted for by recombination in the emitter. Subtracting this from our measured value of 6.2 fA/cm^2, we found that saturation current density due to the surface alone could be estimated to be 1.7 fA/cm2. An undiffused sample processed together with our boron diffused sample except for the diffusion, showed a J_{oe} of 0.72 fA/cm^2. Subtracting this value from the surface current density of 1.7 fA/cm^2 we find that 1.0 fA/cm^2 of the Joe is due to boron atoms at the surface. Therefore, we can see the boron adds significant defects to a $Si\text{-}SiO_2$ interface.

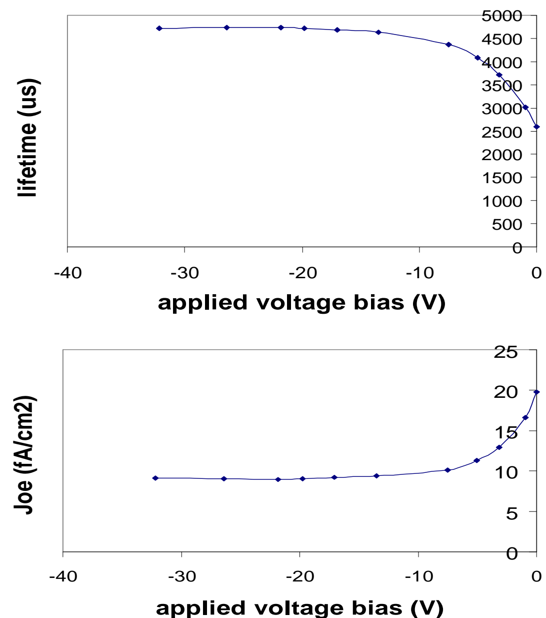

Fig2: Lifetime (upper) and Joe per side (lower) as a function of applied voltage. Injection carrier density 4×10^{15} cm^{-3}.

It should be noted that King found SRV for a range of boron diffused surfaces to be 1640 cm/s, specifically the surface concentration range of 2×10^{17} to 2×10^{19} cm^{-3}. Our sample was estimated to have a surface concentration between 2×10^{18} and 4×10^{18} cm^{-3}. Within this range of concentrations he foudn phosphorus doped surfaces to have an SRV between 300 and 500 cm/s [8]. Our results seem to uphold his conclusion that boron does create more surface defects than phosphorus. Kings method directly evaluated SRV through knowledge of surface concentration and wafer thickness.

3.2 Other surfaces

Joe values of a variety of other surfaces were obtained in accumulation with the same method. Surfaces investigated include boron diffused, phosphorus diffused

and undiffused; surfaces with a thermal oxide only and with a Si_3N_4-SiO_2 stack; and (100) and (111) oriented surfaces.

Best J_{oe} can be seen in Table 1. We have also included worse J_{oe} in Table 2. to give an indication of the range of samples we successfully evaluated without problems caused by significant leakage currents.

Once again, it can be seen that a boron diffusion does induce defects at the Si-SiO_2 interface as expected, with a emitter saturation current density almost ten times higher at 6.12 fA/cm^2, than for that of an undiffused sample from the same processing batch. For <111> silicon the boron diffused sample demonstrates the highest J_{oe}, indicating that surface orientation is the dominating cause of defects under these circumstances.

Table 1: Best Joe per side (fA/cm^2) attained for varying surface conditions under accumulation. First number in boron columns is initial Joe per side without charge applied.

Surface	<100> undiff	<111> undiff	<100> boron	<111> boron
SiO/Si	0.72	6.4	22→6.1	91→23
SiN/SiO/Si	1.9	7.3	25→3.9	210→54

Table 2: Worst Joe per side (fA/cm^2) attained under accumulation. These results are taken from over 30 samples that did not demonstrate significant leakage current. First number in boron columns is initial Joe per side for same sample without charge applied.

Surface	<100> undiff	<111> undiff	<100> boron	<111> boron
SiO/Si	2.9	7.3	20→9.1	91→24
SiN/SiO/Si	3	20	74→15	200→60

It is also noted that a <100> boron diffused surface with an oxide nitride stack can demonstrate a lower Joe per side in accumulation than an oxide only interface. One theory to explain this could be that the strain the nitride places on the surface actually compensates for the strain of the boron diffusion. Further experimental work needs to be done to explore this properly.

3.3 Further discussion and conclusion

It seems that boron diffusions do induce significant degradation of the Si-SiO_2 interface, as seen by an increase in Joe for diffused samples, which is always greater than would be expected merely due to the recombination in the emitter. This degradation is most pronounced for <111> with samples with an oxide/nitride stack, while less pronounced for <100>, in particular <100> samples with an oxide nitride stack.

Taking the best achieved Joe of a boron emitter pushed into accumulation at 6.2 fA/cm^2 and using a short circuit current value of 40 mA/cm^2, as seen by Glunz etal for an n-type Cz silicon bulk [9], an open circuit voltage limit of 760mV is imposed for a boron diffused surface. Although this means an even higher Voc is possible for a phosphorus emitter, when it is combined with a boron doped Cz bulk, the increase in ideality factor would drive down fill factor and thus the efficiency of the cell [10].

These experiments demonstrate that boron is viable as an emitter. Even though it generates more surface defects than a phosphorus diffusion it does not impose a serious limit on cell efficiency when combined with the improved bulk life-time of an n-type Cz bulk.

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