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Modeling of the boron emitter formation process from BCl₃ diffusion for N-type silicon solar cells processing

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Abstract. This work is devoted to the study of boron doping diffusion process for n-type silicon solar cells applications. Deposition temperature is an important parameter in the diffusion process. In this paper we investigate its influence using an industrial scale furnace [1] (LYDOPTM Boron), which is developed by Semco Engineering. We especially used a numerical model (Sentaurus) in order to further understand the boron diffusion mechanism mainly with respect of the diffusion temperature. The model calibration is based on boron concentration profiles obtained by SIMS (Secondary Ion Mass Spectrometry) analysis. We observed that the boron profiles could be correctly simulated by a single fitting parameter. This parameter, noted k_{Boron} which is connected to the chemical reaction kinetics developed at the interface between the boron silicon glass (BSG) and the silicon substrate.

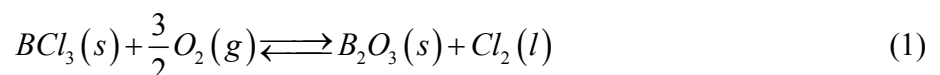
Introduction

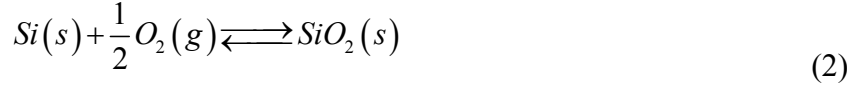
Boron doping is used in silicon solar cells applications usually as BSF for p-type silicon [2]. It also can be used for p+ emitter formation in n-type structure [3]. Indeed, it is established that using n-type silicon present several benefits with respect to p-type silicon. For instance, a higher tolerance to common metal impurities, which induces higher lifetime values and efficiencies, was already demonstrated [3]. Recently, it has reported that boron doping process using BCl₃ as a doping source can be accomplished with the LYDOPTM system technology [1]. It is clearly shown that the boron emitter sheet resistance is mainly adjusted by the diffusion and drive-in process steps conditions. In the industrial point of view, the reduction of development time process to reach a sheet resistance target is needed in terms of development cost reduction. The purpose of this work is to propose a numerical method allowing to define the process conditions for a given sheet resistance.

Process description

The boron diffusion process was performed at low pressure (200-600 mbar) and high temperature in the 900-960°C range. BCl₃ gas decomposition is achieved by introducing O₂ into the reactor. This decomposition is described by the following chemical reactions steps:

i) Deposition step

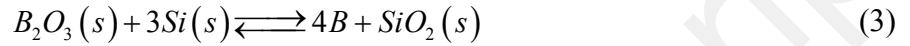




The mixture of B₂O₃ and SiO₂ layers is called BSG (Boron Silicon Glass) which is deposited at the substrate surface plays the role of boron doping source

2) Drive-in step:

The B₂O₃ layer is subsequently reduced in contact with the silicon wafer surface to generate the boron doping element and silicon dioxide:



Besides, residual chlorine species generated from BCl₃ oxidation (reaction 1) could react with metal contaminants producing volatile metal chlorides, which are evacuated from the tube.

Boron emitter characterization is performed by sheet resistance (4 point-probe measurements) and SIMS profiles. Then, the BSG layer is etched off by HF treatment (3 min in 10%HF). Knowing that an additional in-situ drive-in step under O₂ is necessary in order to improve the etched off treatment.

Simulation description

A non-equilibrium point defect diffusion model (pair diffusion) has been used throughout the study [5] and is briefly presented in the following. The boron diffusion is explained by the common oxidation enhanced diffusion mechanism (OED) described by the following reactions



where I, V, (BI) and Bs are the interstitial, the vacancy, interstitial and substitutional boron, respectively. The first reaction (4), in the forward direction, is the kick-out mechanism (KO). The second is the Frank-Turnbull mechanism (FT), and (6) is the bulk recombination, where < 0 > denotes the silicon lattice site. The charged species are taken into account in (4-5-6), which are for boron Bs⁻, (BI)⁺, (BI)⁻, and for point-defects I⁰, I⁺, V⁰, V⁺⁺, V⁻, V⁻. The electrons and holes are also included in (1- 3) in order to keep the electroneutrality of each of these reactions. All the charged species are considered under equilibrium with the neutral ones [4].

During surface oxidation, Si interstitials are injected into the bulk leaving the substitutional complex formation (BS - Si). Once formed, this complex can diffuse and then dissociate into substitutional boron and interstitial silicon. We used the Sentaurus process because this point-defect diffusion model is well introduced. However, B₂O₃ component is not implemented in the standard process simulator, which is commonly devoted to semiconductor device. In this case, we proposed to introduce a new element composed by SiO₂ and B which acts as a BSG-like diffusion source. The drive-in reaction (3) is taken into account by an interface parameter, k_{Boron} related to the boron flux throughout B₂O₃/Si interface

Results

The sheet resistance distribution on wafers of all diffusions experiment is quite uniform (<4%) and the corresponding average values are shown in Table 1. Sheet resistance decreases from 100Ω/sq to 48Ω/sq when the temperature is increased from 900°C to 960°C. This wide range confirms that the temperature diffusion is a suitable parameter to adjust sheet resistance emitter.

Table 1 : Average measurements datas of sheet resistance and carrier lifetime for BCl₃ diffusion process.

Diffusion	Temperature (°C)	Sheet resistance (Ω.cm ²)
1	900	100,8
2	925	74,4
3	940	59,8
4	960	48,8

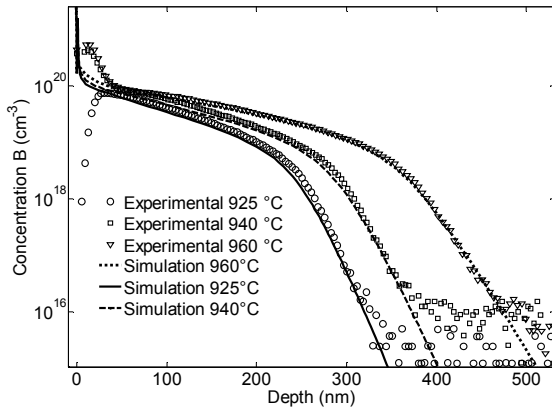


Figure 1 : SIMS and simulation boron profiles for 3 diffusion temperatures

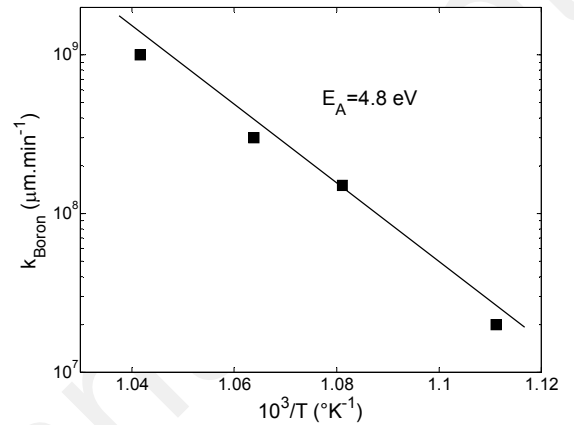


Figure 2 : k_{Boron} parameter as function of 10³/kT

On figure 1, we have reported model and experimental SIMS boron profiles as a function of the diffusion temperature. The simulated boron concentration profiles agree with the SIMS measurements. Indeed, as shown in figure 4, the k_{Boron} parameter variation with diffusion temperature is well described by an Arrhenius plot with a calculated activation energy, E_A = 4,8 eV.

$$k_{Boron} \propto A \times e^{-\frac{E_a}{kT}} \quad (5)$$

Several kinetic phenomena are accountable for this activation energy: B₂O₃ decomposition and SiO₂ formation by oxidation reaction with O₂. De Frésart *et al* studied B₂O₃ decomposition by Si and reported that energy activation of this reduction was E_A = 4.5 ± 1 eV including B₂O₃ decomposition and SiO₂ formation [5] [6]. The similar temperature dependence between B₂O₃ reduction and k_{Boron} parameter suggest that our equivalent model is a good approximation of diffusion process. And the k_{Boron} parameter is a suitable magnitude to incorporate the various chemical reactions at B₂O₃/Si interface

However, the interface reaction is also modulated by others process parameters. In the next work, our model will be calibrated as a function of O₂ flow rate and pressure.

Conclusion

We developed a numerical model of boron doping process using BCl₃ as a doping source in a low-pressure diffusion furnace (LYDOP™ Boron) from Semco Engineering. An equivalent model has been proposed in order to take into account the B₂O₃ layer during boron diffusion. The k_{Boron} parameter was introduced to fit experimental data as function of the diffusion temperature. The latter is thermally activated as shown by an Arrhenius plot. The energy activation is found to be E_A = 4.8 eV. Similar activation energy, reported by Frésard [6], suggests that k_{Boron} parameter is related to the decomposition reaction of B₂O₃.

Summary

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