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Selective emitter formation by laser doping of spin-on sources

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ABSTRACT

Formation of selective emitter (SE) structures with a controlled dopant profile by laser (KrF Excimer laser at 248 nm) annealing of spin-on dopant sources is presented. Different barrier layers (BL) like spin-on glass (SoG), PECVD deposited SiN and SiO_x were used as semi-transparent barrier layers for the dopant diffusion. The presence of BL at the interface between silicon substrate and the layer of dopant source controls the dopant profile of shallow emitter (ShE) during thermal diffusion, so that the etch back step could be avoided. This method allows the realization of shallow and selective emitters using a single layer of dopant source. The dopant concentration and depth with respect to the laser parameters and barrier thickness were analyzed using secondary ion mass spectrometry. It was found that the doping profile of phosphorous was precisely controlled in the shallow region upto 200 nm with a suitable emitter sheet resistance. Also, the SiN and SoG layers acted as effective phosphorous diffusion barriers for both shallow and selective emitters. On the other hand, the SiO_x barrier layers, relatively lower thickness, resulted in the best electrical results at comparably lower laser fluences. In addition, laser induced damage in the silicon crystal at moderate laser fluences is nominal, and is found to be considerable at higher energies due to the enhanced energy absorption of silicon. Periodic structures were observed on the surface of laser treated silicon at the moderate laser fluences. The results were presented in detail in terms of physical behavior of the dopant diffusion with respect to laser fluence in the presence of barrier layer.

1. Introduction

Emitter engineering has a significant role in enhancing the solar cell efficiency and cost effectiveness in terms of process steps [1]. A uniform and low sheet-resistance emitter (n^{++}) is used in the conventional crystalline silicon solar cell device. The presence of n^{++} layer enables a good metal contact to the emitter, but the blue response of the device is usually poor. This is because of inhomogeneity of the dopant and thereby lattice distortion, which could be expected at such high carrier densities. This leads to enhanced defect-assisted recombination. Moreover, the chemical concentration might be higher than the electrically active concentration because of a few inactive dopant atoms [2]. The heavily doped phosphorus in the emitter region results in an enhanced carrier recombination (Auger) and hence short lifetime of the charge carriers, leading to ineffective surface passivation and thus a lower operating voltage of the solar cell device. A higher voltage and a better Ohmic contact are therefore contradictory requirements to be enabled. Therefore, a homogeneous emitter involves a compromise between the two aspects to get the better performance of the solar cell device.

Extensive work is under progress to find out a solution for the doping level and a good Ohmic contact by means of selective doping of the emitter, which is called as 'selective emitter' (SE) approach that combines both features. The SE approach decouples the trade-off that allows heavy doping underneath the contacts and a low doping in the photoactive region. The heavy doping at the metal/silicon interface reduces the series resistance, and the low doping in the photoactive area enhances the carrier collection and hence the blue response. Several ways have been reported to realize the selective emitter employing different steps, like deposition of a barrier for phosphorous diffusion, and then the local removal of the diffusion barrier by screen printed etching paste followed by $POCl_3$ diffusion for high-doping [3–6]. Usually, the selectively patterned emitter doping profile is obtained using expensive photolithographic or screen printed alignment techniques and multiple high temperature diffusion steps [7], etch back emitter etc. [8]. It is also possible to make SE from doped dielectric layer, which serves as a dopant source for the laser doping and rest of the layer remains with the dopant. However, the doped layer might not be the ideal choice for the emitter passivation and leads to the concept of

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double layer [9]. Alternatively, reduction of the dopant source strength or controlled diffusion through a barrier layer avoids dead layer formation.

In the present work, it is aimed to develop the selective emitter structure using minimum processing steps in comparison to the multistep processes. An attempt has been made to realize the selective emitter structure and homogeneous shallow emitter using a single dopant layer employing an intermediate semitransparent diffusion barrier layer (BL). The process involves selective laser doping of phosphorous from a spin-on dopant layer followed by a single thermal diffusion step. The doping profile of shallow emitter was controlled by the thickness of BL. The controlled emitter doping is advantageous to avoid etch back step. In other words, with this approach, peak surface doping or dead layer formation could be avoided in the photoactive area despite the doping efficiency depends on the thickness and permeability of the barrier layer, and heavy doping could be achieved by laser irradiation in the region where the metal contacts are to be deposited. Additionally, the barrier layer acts as an antireflection coating to the laser radiation, which enables to achieve high doping efficiency at relatively lower laser power and hence reduced laser induced damages. The attempts made in this study and the results obtained are herein discussed in detail.

2. Experimental

The substrates used in this study are <1 0 0> oriented p-type crystalline silicon wafers of a thickness of 250 μm with resistivity in the range, 10–30 Ω cm. Spin-on-dopant (SoD) source, P509, procured from Filmtronics (USA), was spun onto the barrier layer coated substrates. Different dielectric layers such as Spin-on-Glass (SoG – Filmtronics) derived layers deposited by Spin-on, and SiN and SiO_x deposited by PECVD were tested as semitransparent layers for the P-diffusion. The SiN_x films were deposited using SiH_4 and NH_3 gases at 400 °C, while the SiO_x films were grown by dissociating SiH_4 and N_2O gases at 350 °C.

The dielectric barrier layer of the interest was deposited on silicon wafers using a suitable method as explained above. Then the dopant source layer was spin-coated using SoD solution of P509 (2×10^{21} P/cm^3) followed by curing at 250 °C for 10 min to remove the solvent slowly. A KrF laser of 248 nm with a pulse width of 50 ns was used for the laser selective doping and the doping was carried out at different laser fluences ranging from 0 to 8 J/cm^2. The spot size used in this study is of the order of 5 mm × 5 mm in order to make it feasible to measure the sheet resistance using four probe method, and the repetition rate is 1 Hz. The surface morphology was analyzed using atomic force microscope. Finally, shallow emitter was formed by classical thermal annealing at 900 °C for 30 min. Similar process flow was applied for all the structures with different kinds of barrier layers studied in the present investigation. The process flow of realizing selective emitter structures using barrier layer is schematically represented in Fig. 1. The shallow and selective emitters were characterized by four-point probe and secondary ion mass spectrometry (SIMS) measurements to know the electrical sheet resistance and dopant profile, respectively.

3. Results and discussion

Different barrier layers like SoG, SiN and SiO_x were used to examine their suitability to control the diffusion of phosphorous in silicon to form shallow emitter and selective emitter from a single layer of dopant source. The attempts made in this study are presented in the following steps.

3.1. Doping through SoG and SiN barrier layers

In this case, PECVD deposited SiN (80 nm) and Spin-on deposited glass films (80 nm) were used as semi-transparent barrier layers to control diffusion of the dopant. At the wavelength of KrF laser (248 nm), the surface reflectance of P509/c-Si structure (without barrier layer) is found to be ∼70%, which reduced to 51 and 33%, respectively when SiN and SoG barrier layer present at the interface of P509 and silicon substrate. This implies that the amount of laser power density to be absorbed by silicon is more in the presence of barrier layers and hence targeted SR could be achieved at the lower laser fluences. The variation of sheet resistance of thermal diffused shallow emitter and laser doped (LD) lines is shown in Fig. 2. The shallow emitter was made at the annealing temperature of 900 °C for 30 min.

The SR of shallow emitter (ShE) (the data presented at the laser fluence of 0 J/cm^2) is very high of the order of 425 and 572 Ω/□, respectively for SiN and SoG as barrier films on silicon. This indicates that the SiN and SoG are effective barrier layers against phosphorus for thermal diffusion at 900 °C for 30 min. It is therefore possible to form a homogeneous emitter by this method that can be easily passivated. However, such high sheet resistances also indicate the ultra-shallowness of the junction, which leads to a poor open circuit voltage. In the case of selective emitter, the figure represents that the SR reduces as the power is increased. The minimum SR of 351 and 412 Ω/□ were achieved for SiN and SoG, respectively at a laser fluence of 2.8 J/cm^2. The SR enhanced at higher energies (>2.8 J/cm^2), which could be due to the ablation of the emitter, formation of crystalline disorder during recrystallization [10], doping inhomogeneity, incorporation of oxygen [11]. It can be seen that the achieved SRs of the emitter are different for SiN and SoG barriers. In general, the dopant profile in the emitter depends on several factors such as diffusion coefficient of barrier layer for the dopant atoms and its thickness [12], precursor layer ablation etc. [13]. Therefore, a strong dependency of emitter SR on the barrier type was observed in spite of high SR of ShE and SE. However, there are reports in the literature that ShE and SE have been formed using P-doped layer of SiN. The selective emitter made using such doped dielectric layer (SiN:P) of 75 nm resulted in a low SR of ∼30 Ω/□ at a laser (515 nm) power of ∼2.9 W [14]. Analogous to the explanation given by Grove et al. [12], it can be assumed that the segregation coefficient of P in SiN and SoG layers might be >1. Hence the impurities

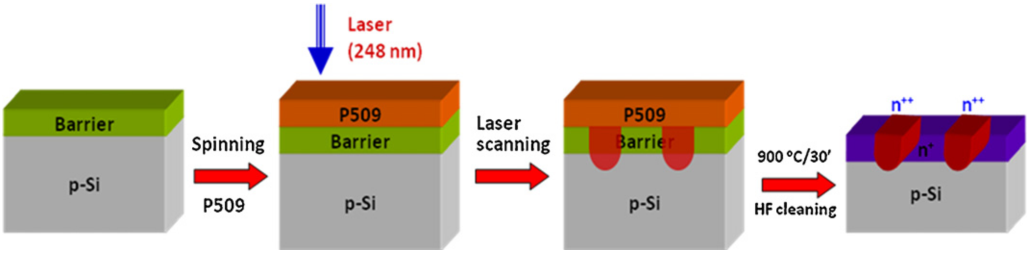

Fig. 1. Schematic representation of the process flow to realize the selective (doping) emitter on p-type silicon substrates using different barrier layers like SoG, and PECVD deposited SiN and SiO_x.