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Effective impurity gettering by phosphorus- and boron-diffused polysilicon passivating contacts for silicon solar cells

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ABSTRACT

This paper presents direct experimental evidence for the strong impurity gettering effects associated with the formation of both phosphorus and boron doped polysilicon/oxide passivating contacts for silicon solar cells, doped via thermal diffusion from $POCl_3$ or BBr_3 sources. Ion-implanted iron is used as a marker to quantify the gettering effectiveness via carrier lifetime measurements. The process conditions for fabricating optimum polysilicon passivating contacts are found to remove more than 99.9% of the iron from the silicon wafer bulk. The gettering effects of $POCl_3$ and BBr_3 diffused polysilicon/oxide contacts mainly arise from the dopant diffusions, as opposed to gettering by structural defects in the polysilicon films. The thin oxide interlayer hinders the gettering effectiveness at low diffusion temperatures, although its blocking effect becomes small at the moderate temperatures used to fabricate optimum polysilicon contacts. The gettering effectiveness increases with increasing diffusion temperature. The gettering of iron from the silicon wafer bulk to the surface layers is found to have a negligible impact on their ability to suppress recombination at the interface with the silicon wafer. Therefore, the formation of polysilicon/oxide passivating contacts, via thermal diffusion from $POCl_3$ and BBr_3 sources, not only achieves high quality surface and contact passivation but also has the net additional benefit of achieving very effective gettering of unwanted impurities in the silicon wafer bulk.

1. Introduction

Passivating contacts for silicon solar cells reduce carrier recombination at the metal-silicon interface, leading to improved device efficiencies. Recently, doped polysilicon passivating contacts, formed by a layer of phosphorus- or boron-doped polycrystalline silicon film (commonly referred to as polysilicon, or poly-Si), together with an ultra-thin dielectric interlayer, have enabled significant gains in cell efficiencies. Examples include the world-records for both-side-contacted 25.7% single-crystalline [1] and 21.9% multicrystalline silicon (mc-Si) [2] solar cells, as well as a 25% interdigitated back contact (IBC) cell [3]. Given their compatibility with high temperature processes, polysilicon/oxide passivated contacts can be incorporated into current mass production of solar cells. Nevertheless, industrial silicon wafers have varying levels of purity and crystallinity, and they are subjected to different environments in terms of contamination control.

Impurities such as transition metals are commonly found in silicon wafers for solar cells, creating recombination centres in the silicon wafer bulk and therefore lowering device efficiencies. Phosphorus (P) diffusions are commonly used to achieve effective impurity gettering in silicon solar cell fabrication (see, for example, [4–8]). The gettering effects of boron (B) diffusions, on the other hand, rely on the specific process conditions [9–11]. Given the prominent role that impurity gettering has played in the development of silicon PV technology, and the potential for doped polysilicon/oxide contacts to replace P- and B-doped silicon layers for junction formation purpose, their potential impurity gettering effects need to be investigated and understood.

Gettering of silicon wafers by backside undoped (i.e. intrinsic) polysilicon films has been widely known and used in microelectronics for decades [12–16], and is attributed to a combination of impurity segregation and relaxation mechanisms [17]. Depending on the impurity solubility and diffusivity in silicon oxide, certain process conditions also result in backside polysilicon gettering in the presence of an oxide interlayer [18]. Recently, Krügener et al. reported minority carrier lifetime improvements upon the formation of phosphorus-doped polysilicon/oxide passivating contact structures by ex-situ doping of

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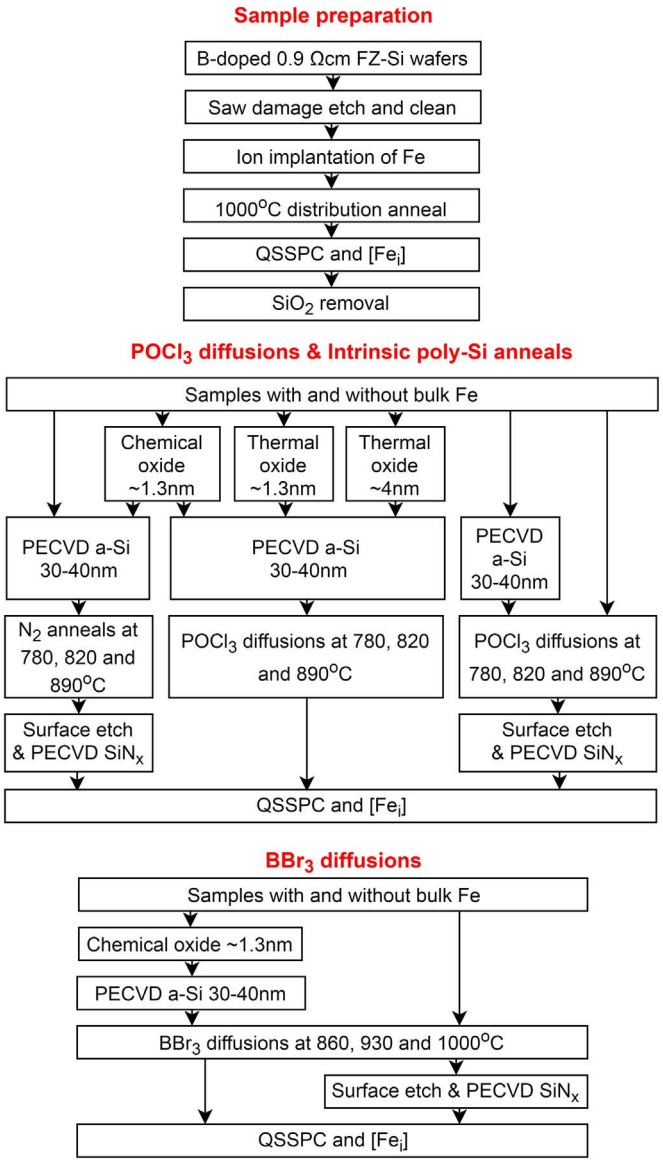

Fig. 1. A flowchart for the experimental procedures.

low-pressure chemical vapour deposited (LPCVD) polysilicon layers by ion implantation and subsequent annealing [3]. However, Krügener *et al.* did not find significant gettering during the fabrication of boron-doped polysilicon/oxide contacts by LPCVD and ion implantation.

This work aims to quantify the possible gettering effects of phosphorus and boron diffusion-doped polysilicon/oxide passivating contacts, via directly monitoring the changes in impurity concentration in the silicon wafer bulk. Iron (Fe) is used as a marker to quantify the gettering effectiveness, due to its pervasiveness in solar-grade silicon and its easy, accurate quantification techniques [15]. The polysilicon/oxide layers are doped by thermal diffusion using $POCl_3$ or BBr_3 sources. The intrinsic polysilicon films are formed by plasma-enhanced chemical vapour deposited (PECVD) amorphous silicon (a-Si) films, which partially recrystallise during the thermal diffusion step [19,20]. Details of the fabrication technique and optimisation processes for the doped polysilicon/oxide contacts used in this study were previously published in Refs [21–23].

2. Experimental methods

A flowchart outlining the experimental procedures is shown in Fig. 1. Details are described below.

High quality float-zone silicon (FZ-Si) wafers with precise amounts of intentional iron contamination were used in this work. The boron-doped p-type silicon wafers had a resistivity of 0.9 Ωcm and a thickness of 180 ± 5 μm after saw damage etch. The silicon wafers were implanted with ^{56}Fe using a relatively low ion implantation energy of 70 keV. The implantation dose was $1.8\times10^{11} cm^{-2}$, which corresponds to a volumetric Fe concentration of $10^{13} cm^{-3}$ for the 180-μm thick wafers. The implanted wafers were then annealed at 1000 °C in dry oxygen for a total of 2 h to uniformly distribute Fe throughout the wafer thickness.

The implantation energy and doses used here, combined with an 1000 °C post-implantation anneal, are expected to result in negligible residual damage in silicon wafers [24]. The solubility of Fe in silicon at 1000 °C is $4 \times 10^{14} cm^{-3}$ [25], which is well above the implanted Fe concentration of $10^{13} cm^{-3}$, meaning that the implanted Fe remain dissolved in silicon, i.e. as interstitial Fe (Fe_i) in the silicon wafer bulk. The amount of Fe precipitation during the 10 °C/min cool-down to 800 °C is negligible, as was previously found for Fe-implanted FZ-Si samples [26], and is also confirmed via lifetime-based measurements of the interstitial Fe concentrations ([Fe_i]) using the FeB pair-breaking technique [27,28]. The bulk Fe_i concentrations were found to be $(1 \pm 0.1) \times 10^{13} cm^{-3}$. After lifetime measurements, the thermally grown silicon oxide layers were removed in dilute hydrofluoric acid (HF).

The Fe-implanted wafers with the same initial Fe_i concentration of $10^{13} cm^{-3}$, together with a control group of non-implanted FZ-Si wafers of the same resistivity and thickness, were subjected to the fabrication of doped polysilicon/oxide contacts on both sides of the wafers (symmetric structure). In order to study the gettering effects, variations in the fabrications steps were experimented, as shown in Fig. 1. These include, varying the interlayer oxide properties (chemical oxide, thermal oxide of different thicknesses, and no oxide), and replacing the dopant diffusions with nitrogen anneals. The same phosphorus and boron diffusions were also performed on silicon wafers without the polysilicon/oxide layers, i.e. the conventional $POCl_3$ and BBr_3 diffusions for forming heavily doped silicon surface layers were included. Each process step is described as follows.

Thin chemical silicon oxide layers were grown by immersing silicon wafers in a 60 wt% nitric acid bath at a temperature of ~90 °C for 30 min. Thermal oxide layers were grown by annealing silicon wafers in dry oxygen at 600 °C and 850 °C respectively for 5 min. Previous ellipsometry measurements show that the oxide thicknesses are ~1.3 nm for the chemical and 600 °C thermal oxide layers, and ~4 nm for the 850 °C oxide [19,21–23].

Intrinsic a-Si layers of 30–40 nm were deposited by PECVD, at a reactor set temperature of 500 °C and an on-sample temperature of ~250 °C.

Phosphorus or boron diffusion doping was achieved by using $POCl_3$ or BBr_3 as diffusion sources in quartz tube furnaces. Phosphorus diffusions were carried out at 780 °C, 820 °C and 890 °C for the same total time of 40 min. Boron diffusions were at 860 °C, 930 °C and 1000 °C for 80 min. The loading and unloading temperature was 700 °C, and the ramp-up and cool-down rate was 10 °C/min. No forming gas anneal was conducted after the diffusion steps. A subset of the samples underwent nitrogen anneals for the same temperature profiles as $POCl_3$ diffusions. The high temperature processes also enable the partial recrystallisation