Influence of surface near doping concentration on contact formation of silver thick film contacts

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ABSTRACT

We investigate the properties of silver thick film contacts on phosphorus doped alkaline textured silicon surfaces with varying surface doping levels. Using scanning electron microscopy, we find that the surface near doping concentration influences the formation of silver crystallites especially those that are in direct contact with both the silicon surface and the contact finger. The observed correlation between direct silver crystallite imprint coverage and specific contact resistance allows for extracting the specific contact resistance of individual crystallites to be approximately 3.3 $\mu\Omega\,cm^2$, which agrees well with theoretical predictions. Furthermore we present a new approach that allows for a quantitative separation of direct and indirect current conduction channels. For our experimental conditions, the assumption of current conduction exclusively by transport through silver crystallites adequately describes the experimental data. Finally we fabricate bifacial n-type solar cells with peak efficiencies of 19.9%.

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1. Introduction

Screen printed silver based thick film metallization is the most widespread technique for contacting phosphorus-doped surfaces of industrial silicon solar cells. Even though screen printed metallization has been used for many years in the photovoltaic industry, neither the mechanism of current conduction nor contact formation between the silver finger and the doped silicon is understood completely. Concerning current conduction various models exist, of which the following two are currently proposed to be the most relevant. One model assumes direct current flow from the doped region via silver crystallites into the bulk finger [1,2], whereas the second model suggests a multi-step tunneling process through an insulating glass layer that separates the silicon surface from the bulk contact finger [3,4]. According to this model small silver colloids embedded in the glass film mediate current conduction through this glassy layer.

As far as contact formation is concerned, most research has traditionally been focused on the influence of paste composition and sintering parameters on the microstructure of the contacts [5–8]. Recently, the interaction of the phosphorus-doped areas and the metallization has moved into the center of attention. Several authors [9–11] published that a decrease in inactive phosphorus concentration leads to an increase in specific contact resistance, which is also true for other deposition techniques such as aerosol printing [12]. By comparison little research has been performed on contact formation on textured surfaces for phosphorus doping levels below $10^{20}\,cm^{-3}$, since historically it has been difficult to achieve suitable specific contact resistances [9]. According to Kulushich et al. [11] contact formation in the absence of inactive phosphorus does not allow for a contact resistance that is suitable for solar cell application, since no crystallites form at the silicon surface. In contrast Schubert [9] reported crystallite formation on planar surfaces without inactive phosphorus and recently crystallite formation has been reported on textured silicon surfaces "without P doping" [10], but in this case it is unclear to which extend the contact resistance is affected.

This paper extends the current understanding of contact formation by systematically varying the surface near doping over a large range with small changes in the depth of the doping profile. The contacts are characterized by monitoring contact resistance by transfer length method (TLM) measurements as well as microscopic properties by scanning electron microscopy (SEM). Correlation with measurements of the dark saturation current density enables an evaluation of the trade-off between resistive and recombinational losses with regard to device performance. In summary this paper contributes to a comprehensive understanding of how microstructural changes influence macroscopic properties of solar cells.

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2. Experiment

As a substrate material for the characterization of the contacts we use phosphorus doped 156×156 mm² Czochralski (Cz) grown silicon wafers with a base resistivity of $3\,\Omega$ cm. After an alkaline texturing process the wafers are subjected to a $POCl_3$ based diffusion process in a tube furnace, that allows for a controlled manipulation of the doping concentration by using two deposition phases [13]. The first deposition phase determines the depth of the doping profile, while a variation of the $POCl_3$ concentration in the process atmosphere during the second deposition phase changes the surface near doping concentration. In this paper we vary the surface near doping concentration from well below the solid solubility of phosphorus in silicon to above solid solubility ($3 \cdot 10^{20}$ atoms/cm³), where SiP precipitates formation is expected [14]. Please note that the solubility limit is the same for all doping profiles, since the temperature profiles are identical for all diffusion processes applied in this paper. After the diffusion process inductive measurements yield the sheet resistance. The phosphosilicate glass (PSG) layer resulting from the diffusion process is removed in diluted hydrofluoric acid. In order to simulate a conventional solar cell process, the surface is subsequently passivated by a SiN_x layer deposited by plasma enhanced chemical vapor deposition. The contact grid is screen printed onto the SiN_x layer. We use a commercially available screen printing paste (Sol9610A by Heraeus Precious Metals GmbH & Co. KG), which is fired in an inline conveyor belt furnace for contact formation. All samples are fired at the same set point peak firing temperature and belt speed. Contact properties are observed by TLM measurements on 4 positions per wafer as well as scanning electron microscopy (SEM) after wet chemical removal of i) the bulk silver finger in HNO_3 solution (69%) for 10 min at 90 °C and ii) the glassy layer in diluted hydrofluoric acid (5%) for 1 min at room temperature. Electrochemical capacitance voltage (ECV) measurements extract the active doping concentration of the phosphorus doped area in the center position of planar saw damage etched 156×156 mm² wafers. In order to illustrate the trade-off between low contact resistance and low carrier recombination, we fabricate symmetrical carrier lifetime samples on 125×125 mm² float zone (FZ) p-type silicon wafers with a base resistivity of $1\,\Omega$ cm. Alkaline texturing, diffusion, passivation and firing are performed in parallel with the Cz–Si samples for characterizing contact formation. Quasi steady state photoconductance (QSSPC) measurements yield an upper limit of the recombination parameter J_0 in low injection conditions [15]. We vary the surface doping concentration by varying the $N_2–POCl_3$ gas flow Q_{POCl_3} during the second deposition phase, while leaving the $N_2–POCl_3$ gas flow during the first deposition phase constant [13].

For the fabrication of solar cells we use 156×156 mm² pseudosquare n-type Cz Si wafers with a base resistivity of $\sim 3\,\Omega$ cm. Alkaline texturing and cleaning is followed by deposition of a borosilicate glass (BSG) layer covered by a SiO_x capping layer by atmospheric pressure chemical vapor deposition (APCVD). This deposition is performed on one side of the wafers in one deposition process using an inline tool by SCHMID Group. Then wafers are subjected to a $POCl_3$ based co-diffusion process in an industrial tube furnace. A hydrofluoric acid (HF) based solution then removes the resulting PSG layer as well as the BSG and SiO_x capping layer. Now the boron emitter is passivated by a stack consisting of a 4 nm thick Al_2O_3 layer covered by a 70 nm thick layer of SiN_x and the phosphorus BSF by a SiO_xN_y/SiN_x stack [16,17]. The Al_2O_3 layer is deposited by atomic layer deposition using an inline tool, the additional layers by plasma enhanced chemical vapor deposition (PECVD). For the metallization advanced printing processes are utilized. The paste on the phosphorus doped BSF is applied using double printing. For the metallization of the boron emitter a paste

containing silver and aluminum is double printed in order to form the fingers grid. The busbars on the boron emitter are printed using a non-contacting Ag-paste. After contact formation in a belt furnace a laser edge isolation is performed (Figs. 1 and 2).

3. Results and discussion

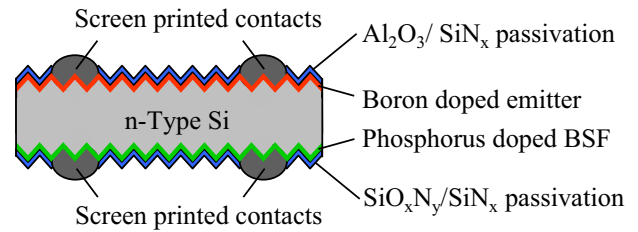Fig. 3 presents selected ECV measurements of the surface near doping concentration.

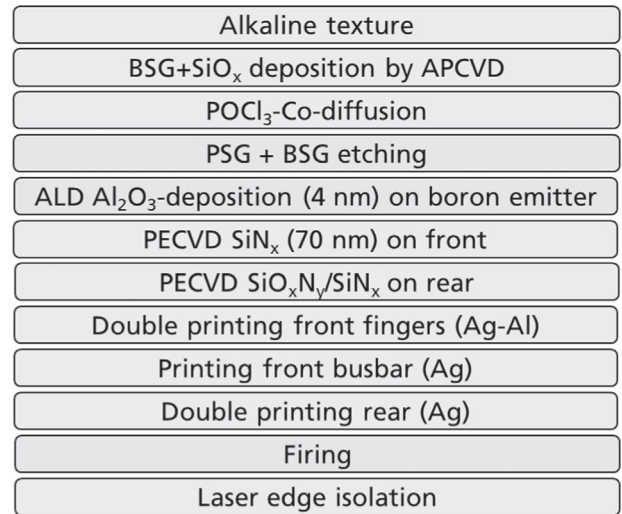**Fig. 1.** Cross section of bifacial n-type solar cell (CoBiN).

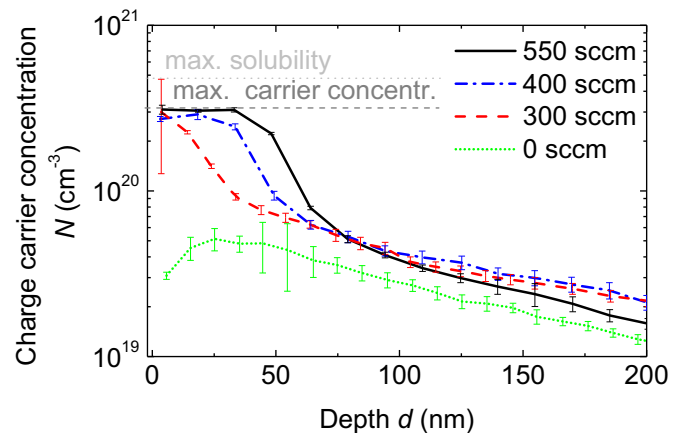**Fig. 2.** Solar cell process for co-diffused bifacial solar cell based on n-type Cz–Si substrates (CoBiN).

Fig. 3. Surface near charge carrier concentration determined by ECV denominated by their $N_2–POCl_3$ gas flow Q_{POCl_3} during the second deposition phase measured on planar reference samples. Maximum solubility of phosphorus in silicon and maximum carrier concentration are determined according to Solmi et al. [14].