Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

Self-aligned carrier-selective PEDOT:PSS contacts on optically highly transparent boron-emitters

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A B S T R A C T

As the efficiency of silicon solar cells increases continuously, recombination at the metal contacts becomes more and more limiting, unless the contacts are passivated. Passivating contact layers on the front side, however, usually lead to parasitic absorption. To prevent this we develop a new self-aligned deposition process to implement a passivating layer only under the metal contacts. As passivating layer for the contacts on an optically highly transparent boron emitter we use PEDOT:PSS, which can be electro-polymerized at an anodic surface in an aqueous electrolyte. This electro-deposition technique is used to deposit PEDOT:PSS in the openings of the patterned dielectric passivation layers on the boron emitter of an n-type silicon solar cell. We demonstrate that the electrical properties of the electro-deposited PEDOT:PSS layer are suitable for a passivating contact layer and that the Fermi-level is de-pinned at the interface with silicon.

1. Introduction

The implementation of carrier-selective passivated contacts is of paramount importance for reaching top efficiencies with crystalline silicon solar cells. Solar cells with carrier-selective contacts on both sides can be manufactured with significantly less processing steps than interdigitated back contact (IBC) solar cells. Full area carrier-selective contact layers like amorphous silicon [1], TopCon [2] or poly silicon [3] however, cause significant parasitic absorption when applied on the front side. For this reason a well passivated optically highly transparent selective boron emitter on the front side with regular metal contacts may still outperform passivated contacts on the front side. The pros and cons of a selective boron emitter versus a full area carrier selective contact system on the front side become apparent when looking at the best results achieved with both concepts. The best silicon hetero-junction solar cell with contacts on the front was manufactured by Kaneka. Adachi et al. reported 2015 an efficiency of 25.1% [4]. Because of the excellent contact passivation with amorphous silicon they reached an open circuit voltage of 738 mV. Considering the parasitic absorption by the TCO layer and the amorphous silicon layers on the front side the short circuit current density of 40.8 mA/cm^2 was outstanding. The best solar cell with metal contacts on a boron emitter on the front side was manufactured at Fraunhofer ISE. Glunz et al. also reported an efficiency of 25.1% in 2015 [5]. Fraunhofer ISE's solar cell reached an open circuit voltage of 718 mV partially limited by recombination at the metal contacts. The lack in open circuit voltage,

however, was fully compensated by the high short circuit current density of 42.07 mA/cm^2 enabled by the excellent optical transparency of the passivated boron emitter.

Implementing a passivating contact layer only under the metal contacts on a boron emitter would allow combining the advantages from both approaches. Targeting an industrial implementation of such a front side, we should ideally abstain from the use of masking and alignment steps. Otherwise the concept may lose its advantages concerning a much simpler manufacturing compared to the IBC solar cell design.

This motivated us to start the development of a self-aligned structuring or deposition process for carrier selective contacts.

2. Approach

The simplest path to implement passivated contacts in self-aligned process seems to be an electro-chemical deposition of the passivating contact layer into the grid-shaped openings of the dielectric passivation layers on the front side and subsequent plating of the metal contacts. The envisioned solar cell structure is schematically shown in Fig. 1. Like for regular plated metal contacts, the dielectric passivation layers may be patterned via photolithography or industrially more feasible with a laser followed by a damage etch. For the electro-chemical deposition the metalized rear-side of the solar cell is electrically contacted while the front side is in contact with an electrolyte bath that contains a precursor of the material, which is to be deposited. As the dielectric
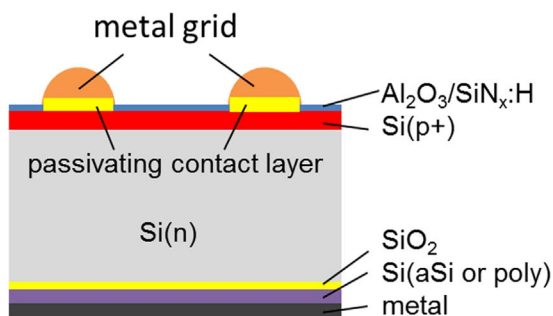

Fig. 1. Envisioned solar cell structure featuring a highly transparent passivated boron emitter and a passivating contact layer under the metallization on the front side. The rear side features full area passivating contact layers, e.g. made of amorphous silicon or a silicon dioxide tunneling barrier with a silicon contact layer on top.

layers are insulating, the material will only be deposited in the openings where the electrolyte is in contact with the silicon. A survey of possible materials which can be electrochemically deposited and are supposedly carrier selective led us to poly(3, 4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS).

The highly doped conductive polymer blend PEDOT:PSS is widely used in organic photovoltaics as hole contact. It is well known to passivate silicon surfaces [6,7] and electrically contact the valence band of silicon [8]. It was already demonstrated that PEDOT:PSS applied on full area from ready-made dispersions can serve as a heterojunction emitter of n-type silicon solar cells [9–11] as well as a back-surface-field of p-type silicon solar cells [12].

PEDOT can also be electro-polymerized in aqueous solution containing EDOT as a precursor [13]. As EDOT is hardly soluble in water a surfactant has to be added to the solution. Interestingly, PSS also is one suitable anionic surfactant to dissolve EDOT. Also other surfactants e.g. sodium dodecyl sulphate (SDS) are suitable in principle. It is reasonable to assume that the anionic surfactant in the solution is co-deposited at the anode where EDOT is then oxidized and subsequently polymerized. In this way a blended film of PEDOT and the surfactant (PEDOT:surfactant) is deposited.

Initially it was not clear if a deposition of PEDOT:surfactant is possible on silicon. To our knowledge only deposition on noble metals [14] and TCO [15] were reported in literature. For silicon it was not clear if the anodic potential would not cause the formation of an insulating SiO_2-layer on the surface instead of EDOT being oxidized.

3. Experimental

We investigated electro-deposition of PEDOT from aqueous solutions containing EDOT and three different surfactants: PSS, SDS and NaPSS. As conductive salt we used $LiClO_4$. We bubbled nitrogen into deionized water for 30 min to reduce the amount of dissolved oxygen, then added 5 mM EDOT, 70 mM of the respective surfactant and 100 mM $LiClO_4$. Finally the solution was put into an ultrasonic bath for 30 min at 30 °C. We first tested full area deposition on the surfaces of round n- and p-type 4 in. wafers, that were cleaned in HNO_3 and HF, stored for several days before the electro-deposition, so that a native SiO_2 grew on the surface, and finally were broken into quarters. We covered a small area at the corner of the wafer quarter with a PEDOT:PSS film of a commercially available micro emulsion (Heraeus, CLEVIOS PH1000). The corners were contacted with a clamp to apply the anodic potential, but were not immersed it into the electrolyte. The PEDOT:PSS film at the corner establishes good electrical contact between the clamp and the wafer. As cathode we placed a platinum mesh in the electrolyte. We varied the current density between 6 μA/cm^2 and 60 μA/cm^2. After deposition we rinsed the samples with deionized water and dried them on a hot plate at 150 °C for 5 min.

We characterized the morphology of the deposited films with scanning electron microscopy (SEM). With Kelvin probe (KP) we measured the work function. For calibration we measured the work function of bare n-type and p-type wafer surfaces, which resulted in the same reading. Hence, we assumed that the work function of a bare silicon surface is pinned to the band middle at 4.55 eV and referenced the work function shifts measured on samples with electro-deposited films to the value of the bare silicon surface. The built-in potential we measured on n-type silicon wafers with the respective electro-deposited films using surface photovoltage (SPV) measurements [16]. We measured the contact resistance between the deposited films and silicon by measuring the resistance through a p-type wafer with the electro-deposited films on both sides. We pressed silver plates of defined area on both sides of the sample and measured the resistance between the silver plates with a multimeter. The sheet resistance we measured on films electro-deposited on n-type wafers, so that the wafer conductivity does not contribute. We used a Jandel four-point probe head and a precision source meter.

For demonstrating the self-aligned local deposition we patterned the SiN_x/Al_2O_3 passivation layers on a 300 Ω boron emitter of small 2 cm × 2 cm n-type solar cell with photo-lithography. The rear side of the solar cells featured a passivated amorphous silicon contact with full area Ti/Pd/Ag metallization. For the electro-deposition we held the solar cell rear side with vacuum though a metal tube over the electrolyte bath, so that only the front side was wetted with the electrolyte. The metal tube also served as the electrical contact to the rear side. Even though the solar cell is under reverse bias at the electro-deposition, the ambient light in our experimental environment generated enough photo current, which can pass the pn-junction in reverse direction.

With modulated photoluminescence we quantitatively measured the minority carrier lifetime [17] before and after electro-deposition averaged over the solar cell surface.

4. Results and discussion

For the range of investigated current densities we obtained homogeneous deposition of a blue film on n- and p-type silicon with PSS and SDS as surfactant. A picture of the sample after deposition of PEDOT:PSS is shown in Fig. 2a. Fig. 2b shows an SEM image of the deposited film. The film is very smooth considering the thickness of 100–120 nm. The deposition with NaPSS showed poor reproducibility and the obtained films had a laterally inhomogeneous color. For PSS and SDS we calculated from the film thickness a Faraday efficiency of about 50% considering only PEDOT deposition. If we assume that also some surfactant is incorporated into the film the Faraday efficiency is even lower, as only one electron per monomer unit is required for the deposition of PSS instead of two electrons per monomer unit of PEDOT. For SDS the difference is even larger as only one electron per molecule is required. This shows that side reactions happen during the deposition process, possibly also the oxidation of silicon.

Kelvin probe measurements resulted in a work function of 5.01 eV for films with PSS, 5.02 eV for films with SDS and 4.87 eV for films with NaPSS. The films with PSS and SDS are perfectly suitable to contact the valence band of silicon. The work function of films with NaPSS is slightly too low. The results also indicate that the doping level of films deposited with PSS and SDS is higher than for films deposited with NaPSS. The crucial question is though, whether the work function is maintained at the interface between the film and the silicon wafer, i.e. whether the Fermi-level at the interface is de-pinned. This is characterized with SPV measurements, which allow determining the built-in potential. For PSS we obtained a built-in potential of 800 mV. For SDS we obtained about 30 mV less. The error is in the range of 100 mV, considering that we did not correct the results for the Dember voltage, because of strong undetermined parasitic absorption within the electro-deposited films. Still the results are very promising and clearly show a