KELVIN PROBE FORCE MICROSCOPY (KPFM): INVESTIGATION OF LOCAL BORON DOPED EMITTER REGIONS FORMED BY INKJET BORON INKS FOR INDUSTRIALLY FEASIBLE IBC SOLAR CELLS

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ABSTRACT: Solar cell concepts like the IBC concept based on locally doped areas promise a high efficiency of more than 24%. This, however, imposes two major challenges: the capability to create these locally doped regions and – which is often forgotten – the capability to check the actual electronic quality of these sometimes microscopic regions (doping level etc.). In order to keep manufacturing costs small, the approach of local doping by ink jetting boron-containing inks is chosen for this contribution. Though liquid deposited doping sources exhibit inhomogeneous properties by itself, the spatial resolved quality control is of utmost importance. Therefore, Kelvin probe force microscopy (KPFM) is applied to map the surface potential and thus the local doping level. Using this technique, some special features of ink jetted boron-containing inks and driven-in emitters like edge sharpness, dopant distribution among other topics are discussed.
Keywords: Boron, Doping, n-Type, Inkjet, Characterization, KPFM, SKPM

1 INTRODUCTION

In silicon a p^+-type (emitter) layer is most commonly formed by a BBr_3 based diffusion. In the case of IBC (interdigitated back contact) silicon solar cells local p^+ emitter regions alternate with n-type base regions at the solar cells' rear side. Unfortunately a BBr_3 based tube furnace diffusion affects all surfaces of the Si wafer, and therefore creating a local emitter needs several structuring and masking steps. An alternative, less labour intensive approach is to form a local emitter by applying a boron-containing ink (e.g. in stripes) locally structuring a silicon substrate by a one-step inkjet process followed by a subsequent high temperature drive-in step. The lateral distribution of boron in the Si substrate especially along the edge of an ink stripe and in non-covered adjacent areas in between two stripes caused by out-gassing or finite boron sources is of high relevance for IBC Si solar cells. If the metallization of one polarity comes to lie across an unintentionally formed lateral pn-junction, the resulting short circuit leads to a reduced efficiency on the solar cell level. Therefore, the actual local doping level at the edge of boron doped stripes represented by a change in the surface potential is investigated by spatially resolved Kelvin probe force microscopy (KPFM) measurements [1-4].

2 EXPERIMENTAL SET-UP

2.1 Sample preparation

The samples are prepared according to the process flow diagram shown in Fig. 1. The 3 × 3 cm² samples were made from n-type FZ silicon wafers with a bulk resistivity of 7 Ωcm (printed with boron ink, chemically polished). The wafer was covered by a set of boron-containing ink stripes printed with different inkjet parameters. The drive-in step leads to an emitter sheet resistance of approximately 70 Ohm/sq (full area measurement, before oxidation) and a depth of approximately 500 nm (@$1\cdot10^{17}$/cm³ dopants). Before removing the residue of the boron ink in a 5% HF solution optical microscopy images were taken in order to correlate the KPFM measurements to microscopy images. For this purpose a pattern of dots was engraved by laser on the samples prior to HF etching of the BSG. To avoid (surface) charge effects the wafer is grounded via a GaSn contact field during the KPFM measurement.

As will be discussed later, a well-defined pn-junction is required as reference. Therefore, a reference wafer (1 Ωcm, mechanically polished) featuring a sharp pn-junction achieved by photolithographical masking and a standard boron-oxide-layer and subsequent drive-in step was processed in order to quantify the spatial resolution of the KPFM technique and to complete the investigation.

In addition, it was found to be favourable to clean the surface properly in order to avoid surface artefacts as well as to deposit a thin thermal oxide passivating the surface of the wafer in order to suppress a collapse of the Fermi-level splitting at the surface.

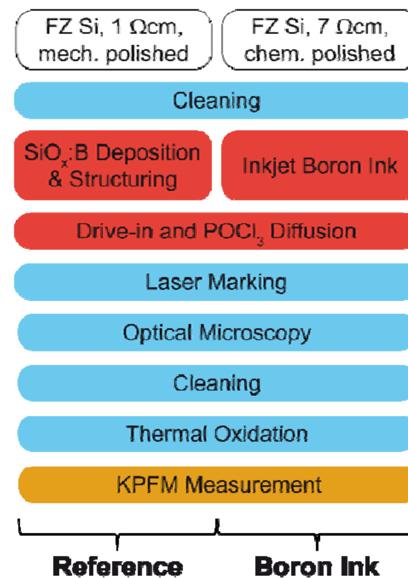

Figure 1: Sample preparation for the reference and the boron-containing ink process.

2.2 KPFM measurement

KPFM is a modification of atomic force microscopy (AFM). This method allows to evaluate the lateral 2D Fermi-level at sub-micrometer resolution on a given Si

substrate [4]. However, since KPFM is a surface sensitive measurement the surface topology has to be taken into account, as well as surface charge effects, capacitance effects of the tip/cantilever geometry and the collapse of the Fermi-level splitting due to surface band bending or surface defect states.

The surface topology of each line is measured prior to each KPFM line scan. Afterwards the Kelvin probe measurement is performed at constant sample-tip distance z. In general – neglecting the other effects mentioned – by applying an electric field, the electric force between the tip on the cantilever and the sample surface is given by [2]:

$$F = \frac{1}{2}\frac{\partial C}{\partial z}\Big[\Big\{\big(V_{ext} - V_{cpd}\big)^2 + \frac{1}{2}{V_{ac}}^2\Big\} + \big\{2(V_{ext} - V_{cpd})V_{ac}sin(\omega t)\big\} - \Big\{\frac{1}{2}V_{ac}^2\cos(2\omega t)\Big\}\Big] \quad (1)$$

V_{ext} represents a constant applied voltage between tip and sample while V_{ac} is modulated by $sin(\omega t)$. V_{cpd} is the potential (difference) being the quantity to be measured. C denotes the tip-sample capacitance.

For investigating the surface potential, the most important of the three terms in (1) is the second one. It depends on the potential difference between tip and sample multiplied by the applied AC voltage. For the measurement of the potential difference V_{cpd}, the second term is zeroed by adjusting V_{ext} so that $V_{ext} = V_{cpd}$. Therefore, V_{ext} is the quantity to be measured.

Kelvin probe measurement is performed with an *Asylum research MFP-3D* AFM in ambient air. The resonance frequency of the cantilever is around 72 kHz, the tip radius is approximately 28 nm. The resolution of the surface and potential mappings is set to 35 nm, the distance between tip and sample during the potential measurement is set to the lowest value possible (usually 40 – 50 nm below the average distance in AC-mode, which is conducted in 5% repulsive mode). The sample is illuminated and as close as possible to thermal equilibrium conditions to avoid thermal drift. Scan rates differ from 0.1 to 1 Hz. Topography images are flattened in 1st order, the potential data is extracted unmanipulated.

3 RESULTS

The samples are inspected by optical microscopy to identify suitable measurement sites for KPFM. Fig. 2 shows a typical edge of the used ink on the Si substrate.

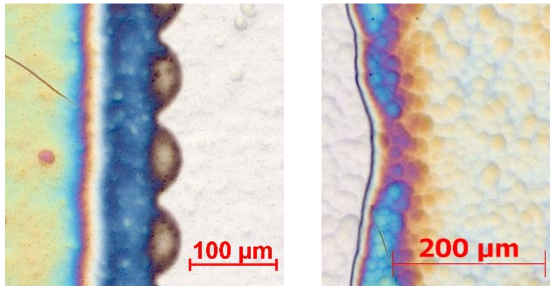

Figure 2: Typical edges of ink jetted boron-containing ink stripes (left: irregular edge, right: regular edge), the colour change caused by interferometry indicates the thickness of the boron-containing ink. The thickness of the brown area is around 30 nm, blue is at 100 - 200 nm, purple is between 200 - 300 nm and yellow/green is around 400 nm.

In contrast to boron diffusion sources deposited via gas phase reactions (e.g. doped glass), the liquid ink is affected by its surface tension as well as by the wettability and morphology of the substrate. As can be seen by the colour change in Fig. 2, the used boron-containing ink tends to contract due to its surface tension and drying before the high temperature drive-in step. Therefore, it cannot be ruled out that the diffusion profile depth underneath the edge region differs from the thicker core region.

Additionally, it can be seen that the stripes printed by depositing overlapping ink drops can result in symmetrically arranged semicircles at the edge.

To clarify whether the signal in the KPFM potential is smeared out by limits of the method itself or whether the signal is displaced, not sharp or changed in any way by the surface conditions caused by the deposition with the inkjet process and/or drying of the boron containing ink, the afore-mentioned reference sample with a sharp edge is investigated. Figure 3 shows its AFM topography (top graph) as well as the corresponding potential (bottom graph). The topography reveals a step of 40 nm height located at the p-n-junction which was created on the wafer during surface cleaning by oxidation and the silicon oxide removal by HF. The step is probably due to a higher oxidation/etching rate on n-type silicon.

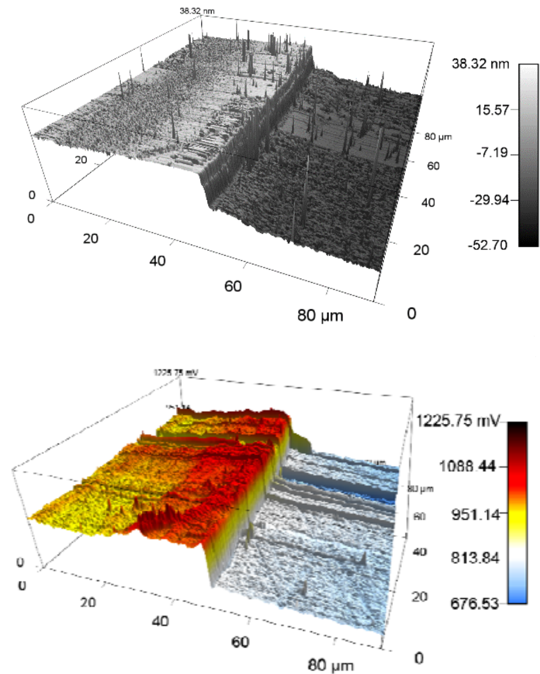

Figure 3: 3D representation of the topography (top) and the potential (bottom) distribution at the edge of the sharp p-n-junction reference sample. The pn-junction is located precisely at 49 µm, while the jump in potential indicates the change from n- (right side) to p-type (left side). Single peaks are known to be artefacts of the AFM measurement caused e.g. by particles on the surface or phase hopping.

The linescan of the potential and the height step displayed in Figure 4 proofs the p-n-junction to be a sharp junction which is exactly located at the already

described 40 nm step. The total change in potential at the pn-junction is at around 250 mV, which is lower than the expected difference of approximately 750 mV of the quasi-Fermi-level splitting in Si under illumination conditions. In [2] this discrepancy is explained by surface states and stray capacitances, while stray capacitances seem to have minor influence compared to the surface states. Changes in the signal strength may be a function of illumination, too. Fluctuations of the halogen lamp or different shading by the cantilever, located between lamp and sample, may lead to slightly different results.

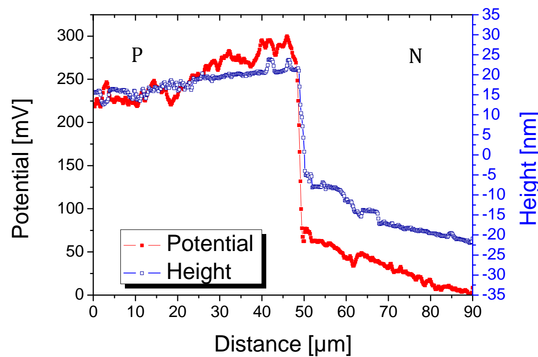

Figure 4: Linescan of surface potential (red) and topography (blue). The sharp drop at around 50 µm indicates the pn-junction as well as the 40 nm step which was created by oxidation of the surface and etching the oxide.

Further measurements, which are not shown here, on the boron ink samples lead to the conclusion that the location and behaviour of the p-n-junction heavily depend on the edges of the ink stripes. Carefully adjusting the inkjet parameters finally leads to ink stripes which show a sharp drop in thickness of the inks' edges (cf. Figure 5).

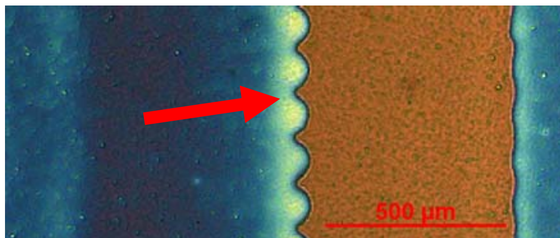

Figure 5: Microscopy image of a well prepared inkjet stripe. The symmetrically arranged semicircles at the edge of the ink correspond to the ones in Figure 6.

KPFM investigation of a sample prepared in this way reveals a sharp and homogeneous emitter, as shown in Figure 6 (bottom). Compared to the topography of the reference sample, the topography of the boron ink sample (top) reveals again a small step (around 20 nm), which was created by oxidation of the surface and etching the oxide, in the Si height, although it is superimposed by the surface roughness of the chemical polished silicon.

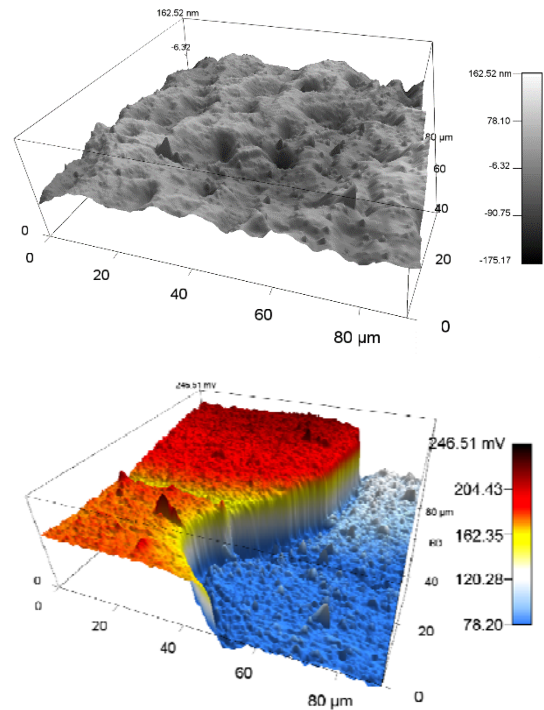

Figure 6: 3D representation of the surface potential at the edge of a boron-containing ink stripe. The pn-junction follows the former s-shape (Fig. 5) of the boron ink, while the surface potential jumps to p-type towards boron-containing ink (left side). Single peaks are known to be artefacts of the KPFM measurement caused e.g. by particles on the surface or phase hopping.

The increasing potential following the s-shape in Figure 6, precisely located at 65 µm in a single linescan in Fig. 7, is explained by a rapidly increasing thickness of the boron-containing ink (cf. Figure 5). If the inkjet conditions are not chosen well, as exemplarily presented in Fig. 2 , it is believed that up to a certain thickness limit (before diffusion) the boron-containing ink does not act as an infinite source of boron atoms and therefore shifting the Fermi-level slightly towards midgap (at the surface). It could be shown that this phenomenon can be avoided by developing sharp boron ink edges.

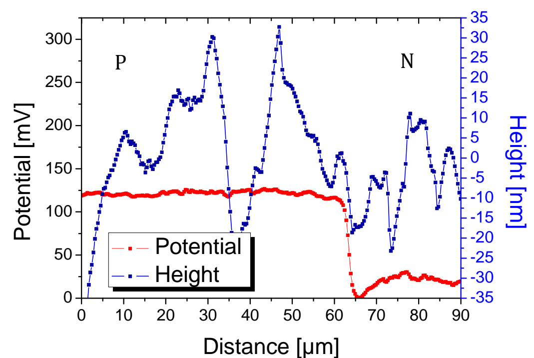

Figure 7: Linescan of the surface potential (red) and the topography (blue). The sharp drop of the potential at around 65 µm indicates the pn-junction. The surface roughness is enhanced compared to Figure 4 due to the lack of mechanical polishing of the investigated wafer and uncorrelated to the surface potential.

4 CONCLUSIONS AND OUTLOOK

For solar cell concepts like IBC featuring locally doped regions it is necessary to develop measurement techniques capable of imaging and quantifying the local doping level. KPFM is found to be capable of doing this with a sub-micron resolution. Provided that the preparation of the inkjet processed samples is done under the described conditions, it could be shown that, a precise and sharp p-n-junction can be created by using locally deposited boron containing inks as dopant source on standard chemically polished wafers.

5 ACKNOWLEDGEMENTS

Part of this work was financially supported by the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (FKZ 0325581) and RENA GmbH within the "UHRWERK" project (FKZ 0325374 A). The authors thank Dr. Oliver Doll from Merck for providing the boron containing ink. The content is the responsibility of the authors.

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