Characterization of patterns of Localized Doping Using Stamping technique for Selective n-Emitter Solar Cell Structure

A. Mangkornkaew¹ and T. Fangsuwannarak¹
1 School of Electrical Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima, Thailand 30000

E-mail: thipwan@g.sut.ac.th

Abstract. In the present, a novel cost-effective process scheme for single step selective emitter diffusion was implemented. It is based on the fabrication of acid-resist pattern using a stamping technique with collaboration of a spin on dopant (SOD) and chemical etched-back emitter methods. The SOD diffusion process provided heavily doping n-emitter. Acid-resist pattern without exploitation of a complex method as a photolithography, was stamped as a metal contact pattern for prevention of a localized heavy-dope region from etching back. Phosphorus doping profiles were controlled by etching back time to provide the formation of n-type selective emitter. Sheet resistance is tunable from 10 to 180 Ohm/Sq on localized n-layer. After removal of the patterned acid-resist, the selective n-emitter solar cell structure was obtained under one-step diffusion to achieve a better blue-light response and low contact resistance.

1. Introduction
Today, photovoltaic (PV) technology is not only important to require renewable energy but also has more concern to clean environment and sustainable energy sources. One of the challenges for commercial PV cell manufacturers adapted is to further reduce the cost and to simultaneously improve the efficiency of PV cells. One key limitation of present silicon industrial solar cells is the production based on homogeneous emitter region with a low sheet resistance of about 50-70 Ω/Sq. Meanwhile, a junction depth of about 0.5-1 μm is required for a compromise between a sufficient contact quality of silver grid metallization and a low recombination rate at the front surface. It causes a problem of shorter life time of generated charge carriers because a low sheet resistance of homogeneous emitter from high dopant concentration provides high density of carrier recombination centres [1, 2]. Thus, conventional PV cell efficiency is usually below 17%. The increase in sheet resistance of n-emitter enables to reduce the Auger recombination, resulting in a better blue-light response and thus a higher I_sc. Moreover, it is also able to provide a better front surface passivation, leading to a higher V_oc [3]. Nonetheless, another effect considered due to low dopant concentration is a severe contact quality between metal and silicon emitter, resulting in a lower fill factor and solar cell efficiency decreased [4]. In order to improve solar cells efficiencies, optimization of emitter to require higher blue response and better contact quality has been investigated. One of the most potential method is selective emitters (SE) that feature a heavily-doped contact area underneath the metallized region and a lightly-doped emitter area between front fingers. Crystal silicon SE solar cell is able to provide its efficiency improvement with a competitive production cost [5, 6].
In the present, commercially available researches involve dopant ink through an additional screen printing step and laser-based SE process, which are available for forming different regions including heavily-doped emitter region with about below 50 Ω /Sq and lightly-doped emitter region with about 90-110 Ω /Sq. Si ink based SE technology has achieved an efficiency of up to 19.2% on screen-printed c-Si solar cells [7,8]. However, both of the SE processes have relied on more masking steps, laser ablate openings and scribe grooves. These additional processes affect the rising cost, the complex laser processing, and the use of relatively expensive materials and equipment, which cause the main reasons for the industry’s reluctance to adopt these technologies. Therefore, simple SE processing to replicate that based on low cost materials is required.

A stamp-patterning fabrication using a cheap flash foam is an alternative patterning technique to rapidly transfer acid-resist pattern in both micro-scale and nano-scale structures that is applicable to devices on planar, curved, flexible, or soft substrates, especially when low cost processing is required [8]. Although the stamping and etching steps are added in the process, the using repeat of inexpensive flash foam and etching solution is a highlight advantage. This approach is related to a pattern fabrication with stamping process to produce acid-resist area localized underneath the metallized region. A selective emitter structure with one diffusion step to form n-p shadow junction with highly doping concentration. This paper highlights the ability to achieve a wide range of dual doping concentrations using the flash form stamp and additional etch-back processing step. The study of variation in sheet resistance via etched back processing times is demonstrated. The localized emitter feature which is patterned by using flash foam stamp, is characterized.

2. Experimental Details
Sol-gel consists mainly of phosphorus solution as a SOD source, Tetraethylorthosilicate (TEOS, 98% Fluka), Ethanol absolute (EtOH, 99% BDH) and H2O with a volume ratio of 5:10:1.5. Subsequently, the mixed solution was stirred for 5 minutes at 70°C to ensure homogeneity. Phosphoric acid (H3PO4, 85%Ajax) was then added by a volume ratio of TEOS: H3PO4 at 3:1 and stirred for 40 minutes. The obtained mixture solution was cooled down to room temperature for 30 minutes.

P-type poly-crystalline silicon wafers (~1 Ω·cm) as substrates were textured by HF chemical etching and then were cleaned by standard Radio Corporation of America (RCA) method and subsequently were treated in dilute hydrofluoric acid (HF) for 1 minute. The mixture of SOD solution was spun on the Si substrates at 2-speed steps at 1000 rpm/min for 10 seconds and 3000 rpm/min for 30 seconds. Subsequently, the wafers coated by SOD film were sintered at 1000°C for 60 minutes. The high heat-treatment acts as a thermal diffusion to drive the phosphorus atoms through the silicon wafer for formation of the shallow n++/p junction. The low sheet resistance of n++ emitter layer was measured by a 4-point probe technique.

Flash foam stamp (FFS) acts as photosensitive material, is a type of micro porous polymer. FFS surface exposed by flash light will be burnt and sealed solution. A grid mask on top of the flash foam is exposed transferring the grid pattern to FFS. Surface morphologies of FFS comprising 2 regions: a liquid sealed part and an unsealed part, are created on a FFS. Acid resist solution was stored in the FFS and then stamped onto poly-Si substrate to flow through the unsealed pattern area. The acid resist features the grid metallization pattern stamped on n++ emitter surface, thus the heavily doping area was kept fixed by the acid resist. After drying at 120°C for 30 minutes, to minimize the dopant concentration the etching step as a etched-back emitter method was processed in HF:HNO3 solution with the volume ratio of 200:1 in times variation. The influence of etching time on a decrease in sheet resistance of emitter layer was investigated.

3. Results and Discussions
FFS feature was changed when the FFS below the designed grid mask was exposed by light flashing. Fig.1 (a)-(b) shows FFS pattern composed of 2 different surface morphology areas: porous area (unsealed area) and sealed solution area. As can be seen the scanning electron microscope (SEM) image in Fig.1(c), the locally unsealed region shown as porous openings has the size less than 20 μm, which allows the solution flowing through. The size of FFS pattern obtained is consistent with the
mask designed in a feature of PV grid contact pattern. Acid resist solution was stamped onto n\textsuperscript{++} Si surface by flowing through the patterned FFS.

![Pattern images of FFS after transferring grid layout to feature in (a), magnified image in (b) and unsealed surface SEM image in (c).](image)

Fig. 1 Pattern images of FFS after transferring grid layout to feature in (a), magnified image in (b) and unsealed surface SEM image in (c).

After etching back n\textsuperscript{++} Si emitter, different values of emitter sheet resistance were obtained by varying the etching times as shown in Fig. 2. The sheet resistance of the processed emitters on poly-Si wafers was measured with a four-point probes technique. Each wafer was measured on five positions. Etching time extension from 0 - 45 second is able to provide the sharply change of emitter sheet resistance from 10 Ω/Sq to 180 Ω/Sq in average. It is found that sheet resistivity of n\textsuperscript{++} emitter is adjustable from varying etching times. The higher resistivity range is usually required between 90-110 Ω/Sq that is form as a lightly doped emitter region for PV efficiency improvement.

![Sheet resistance at different emitter etching times.](image)

Fig. 2 Sheet resistance at different emitter etching times.

As shown in Fig. 3 the dark color pattern on poly-Si wafer showed the acid resist region which is able to prevent chemical etch in heavily doped area. When the n\textsuperscript{++} Si surface was patterned by FFS stamp to transfer acid resist as a grid pattern on the surface, the n\textsuperscript{++} emitter region was changed into lightly doped region during etched-back process. After removing acid-resist, the feature in dark color of localized n-Si emitter after etched-back process is shown in Fig.4 when we used the emitter etching time about 37 sec. Meanwhile, n\textsuperscript{++} Si region featured light color, thus selective emitter performing the both of lightly doped region (110 Ω/Sq) and heavily doped region (< 20 Ω/Sq) are clarified as shown in light color pattern and dark color pattern, respectively. It is noted that different phosphorus
concentration regions is fabricated by simple stamping technique without complex process as a photolithography.

![Image](Fig. 3 Grid pattern images of acid resist pattern in dark color to be transferred from designed FFS.)

![Image](Fig. 4 Grid pattern feature of SE surface after etched-back process: lightly doped region with dark color and heavily doped region with light n++ Si.)

4. Conclusion
The results of this study were revealed that the simple stamp coating is a potential method to produce a selective emitter in only one thermal diffusion step with one additional etching back step. By transferring grid pattern to n++ Si emitter region, locally lightly dopant regions were performed at 37 seconds for etching time without employing a complex procedure of photolithography. The n++ Si region coverage with patterning acid resist was provided with less than 20 Ohm/Sq and there was 110-120 Ohm/Sq at lightly doped region. The SE pattern was controlled by designing the feature of FFS. The proposed simple process employing stamping technique also shows clearly the potential to become more cost-effective than existing selective emitter processes relying on other additional complex procedure and expensive tools such as laser doping and photolithography steps.

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