Surface Contamination of Silicon Wafer after Acid Texturisation

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Introduction

The acid texture bath that is commonly used in crystalline silicon solar cell manufacturing is a mixture of $HF/HNO_3/H_2O$ [1]. While the influences of metal contamination on silicon wafer surfaces as well as several cleaning methods were intensively investigated in the previous 30 years [2] the effect of metal contaminations in texturisation baths has not yet been studied intensively. Few papers are investigated in metal assisted chemical etching [3],[4], where Ag and Pd are used as catalysator for the texturisation.

Metal contaminations in texture baths originate from the used chemicals and from the etched silicon wafers. Depending on the final wafer application, for example high efficiency cell processing or etching and cleaning of upgraded metallurgical grade (umg) silicon, different demands on the purity of used chemicals have to be met. Interesting is the influence of metal contamination in acid texture baths in regard to the texture behaviour of silicon wafers.

Experimental

Monitoring of acid texture bath in an inline process system

For the monitoring of the acid texture bath silicon was enriched in this bath in an inline process system. After enrichment the bath was filled up with HF and HNO_3 (p.a., Honeywell) to get a preset concentration. For enrichment, umg-silicon wafers from the Silicon Material Technology research centre (SIMTEC) at Fraunhofer ISE were used.

The concentration of HF, HNO_3 and silicon was measured by ion chromatography [5, 6]. The metal concentrations in acid texture bath were measured by ICP OES.

At each process point during the silicon enrichment, four silicon wafers (Deutsche Solar, p-doped, 1Ohmcm, 210µm) to lifetime samples. After the wet etching process, the wafers were cleaned using a KOH-, HCl- and a final HF-Dip.

Two silicon wafers undergone a long temperature step (Diffusion, ~800°C and 1h) and the other two wafers a short temperature step (SiriON-Stack [7] on both sides, 400 °C and 10 min). After POCl-diffusion, the silicon wafers were dipped in 10w/w % HF for PSG-etching. Afterwards, these wafers were also coated with a SiriON-Stack on both sides for passivation. The lifetimes of the silicon wafers were measured by QSSPC.

Texture behaviour in metal contaminated acid texture baths

Silicon wafers (fz-Si and mc-Si, 5x5cm², 0.5-2 Ohmcm) were etched in a mixture of $HF/HNO_3/H_2O$ at 10°C for 20 sec. The metal contamination of the acid etching bath was generated by dissolving different metal nitrates (Ni, Fe, Cu, Al, Cr) (Merck, pa). After silicon wafer have been dipped in etching bath and rinsed with DI-water, they were dried with N_2-gas.

The texture behaviour was investigated in regard to microscope and texture parameters like abrasion and reflexion. The surfaces of the silicon wafers were chemically analysed by droplet collection (DC) with 1w/w% HF. The 1w/w% HF samples are then analyzed by atom adsorption spectrometry or inductively coupled plasma mass spectrometry.

Results and Discussion

Monitoring of acid texture bath in an inline process system

The process conditions at the Photovoltaic Technology Evaluation Centre (PVTEC) at Fraunhofer ISE differ in some aspects from common industrial production conditions; therefore, such accumulation steps necessary to achieve high silicon contents in the texture bath were undertaken. The silicon is enriched in the acid texture bath in inline process system (mc-silicon at SIMTEC Fraunhofer ISE).

The concentration of HF and HNO_3 in the acid texture bath is refilled after enrichment to preset concentrations. Only at the last experimental points were HF and HNO_3 not set up to preset concentrations.

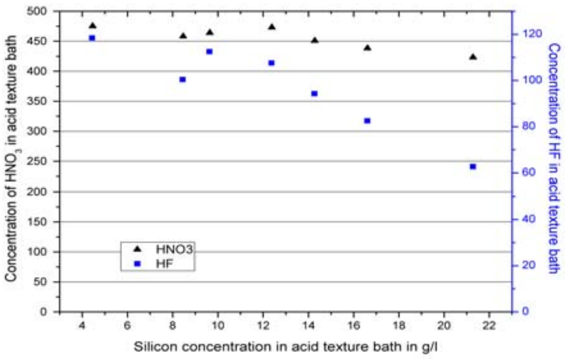


Figure 1 Concentration of HF and HNO_3 are measured by ion chromatography. The presented points of concentrations are the process concentration after enrichment with silicon and dosing with the acids.

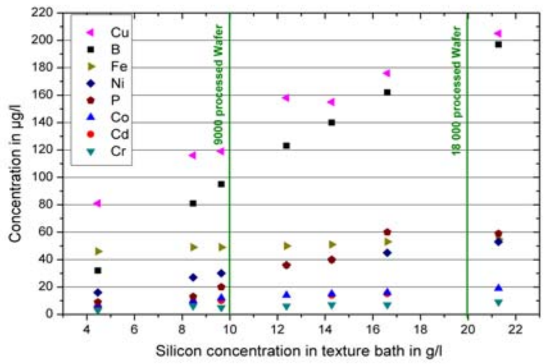


Figure 2 Results of ICP OES measurement. The concentration of the elements in the acid texture bath is applied to silicon content in the acid texture bath. 10 g/l silicon content is corresponds to ~9000 processed silicon wafers in an inline etching system.

The increasing of metal concentration in the acid texture bath is dependent on entry of silicon wafer and dosed chemicals. In the experiments, the increasing effect of chemicals is negligible. In the last three process points the concentration of HNO_3 and HF decreased, while the metal concentration increased. Therefore the entry of metals into the acid texture bath mainly depends on the silicon content.

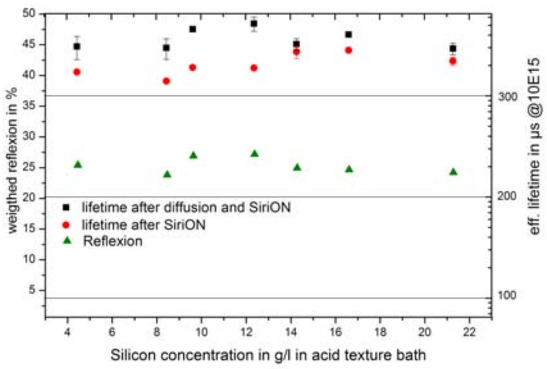


Figure 3 Weighted reflectance and lifetime of silicon wafer measured by QSSPC are applied to silicon concentration in an acid texture bath.

The reflectance of silicon wafers depends on the texture behaviour of the acid texture bath. The texture behaviour is influenced by the concentration of the main components in this bath, especially HF, HNO_3, H_2SiF_6 and the content of NO_x as well as by the temperature. In our experiments, the silicon content increased and the concentration of metals is varied in a small range in the texture bath, but no influence on the reflectance was determined.

The lifetime of silicon wafers also remained unchanged with increasing silicon content and subsequent increasing metal content. This behaviour can be explained as following: on one hand, it is possible, that the metal contaminations do not precipitate on the silicon surface; on the other hand, this can also be a result of the cleaning sequence after the texturisation.

The etching mechanism on the silicon surface has been described by Steinert [8]. In the important oxidation step, many highly reactive species like the nitrosyl cation are involved. This NO^{+}-ion has a very high oxidation potential. It is therefore very unlikely, that metals are reduced and deposited in such an environment.

The entry of metals from the silicon wafers into the acid texture bath leading to a contamination with trace impurities during processing of silicon wafers in the texture bath can therefore be estimated to be not critical.

Texture behaviour in metal contaminated acid texture baths

The concentration of metals in the acid texture bath is increased with growing silicon content in the texture bath. Depending on the silicon material the metal concentration is increased in the acid texture bath. During the texturisation of multicrystalline silicon wafers in a small scale experiment, the concentration of metals was varied from 0 to 1000mg/l to study the effect of metal contaminations on the texture behaviour.

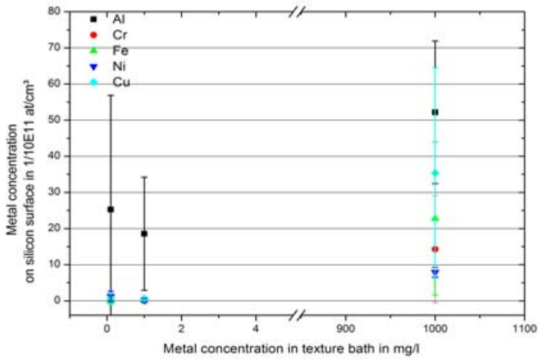
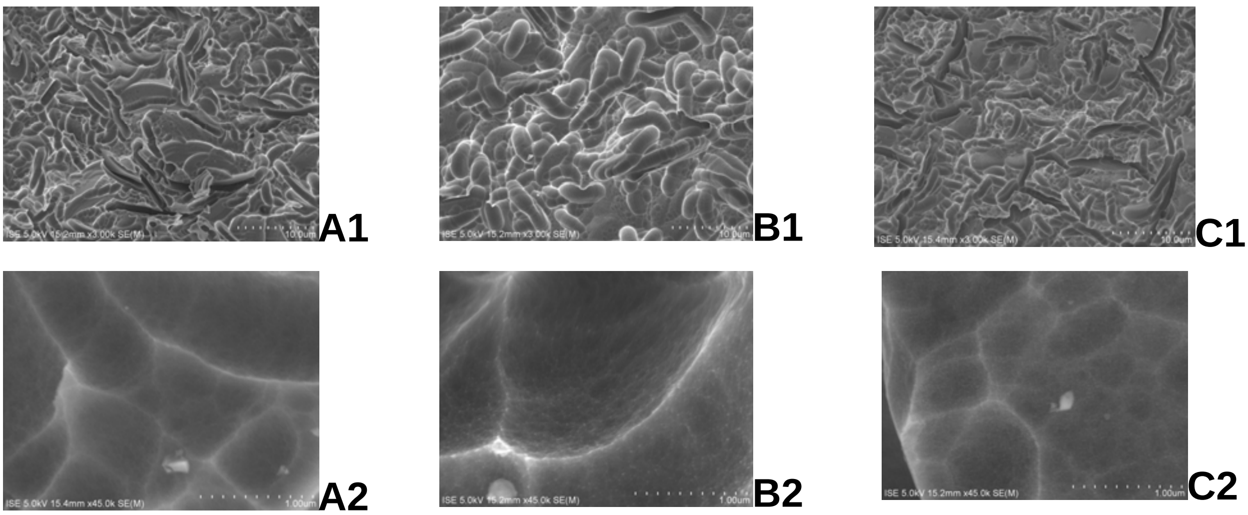


Figure 4 The metal concentration on the silicon surface is applied against the metal concentration in the acid texture bath.

The metal concentration on the silicon surface remained constant with increasing metal concentration in the acid texture bath. The maximum solubility of metals in acid solutions is >1000mg/l. The deposition of metals on the silicon surface with increasing metal concentration in the acid texture bath was not found under 1000mg/l. By 1000mg/l metal ions in the acid texture bath metal ions are found on silicon surface after texturisation. It is assumed that the maximum solubility is achieved and the metals are dropped out.

The metal impurities in the acid texture bath are present as ions, such as Fe^{3+}, Fe^{2+} and Cu^{2+} in the acid solution. They are well dissolved and enclosed in a salvation shell. The only mechanism that can lead to a precipitation of these ions is the chemical reduction of them.

It is known from experiments with metal-assisted texturisation, that the presence of metals can change the texture behaviour. In our experiments, we did not find a change of the surface structure that can be assigned to an increasing metal concentration in acid texture bath.



Picture 1 SEM pictures with a magnification of 3k (1) and 45k (2) of etched wafer in clean etching bath (A), in 1mg/l metal contaminated etching bath (B) and in 1000mg/l metal contaminated etching bath (C).

The textured silicon surface was examined using scanning electron microscope (SEM) pictures with a magnification of 3k and 45k. The surface is strongly etched, but no influence with increasing iron concentration in the acid texture bath can be determined.

The investigated silicon surfaces do not show any anomaly from typical acidic texturized silicon wafers. Ellipsoidal cavities are randomly distributed over the surface. The different sizes of the cavities contribute slightly different etching times and therefore to different stadia of the texture development. The texture behaviour is therefore independent on the contamination degree with metal.

Summary

ICP OES is a suitable tool for the monitoring of the enrichment of metal impurities during the etching of upgraded metallurgical (umg) silicon. The entry of metal impurities from silicon in the acid texture bath was investigated, but the influence on the texture behaviour is negligible. In lifetime experiments, no influence on the carrier lifetime was observed even at high impurity contents.

The measurement of the surface contamination of wafers, textured in highly metal contaminated acidic texturing solutions showing constant surface concentrations up to a contamination level in the solution of 1 g/l metal lead to the conclusion, that metal does not precipitate from HF/HNO_3 solutions.

On a macroscopic and microscopic level, the metal contaminations do not show any influence on the silicon surface’s morphology.

References

1. Röver, I., et al. *Reactivity of crystalline silicon in the system HF-HNO_3-H_2O (a novel study)*. in *Proceedings of the 19th European Photovoltaic Solar Energy Conference*. 2004. Paris, France: WIP-Munich, ETA-Florence.
2. Kern, W., A.R. Karen, and K. Werner, *Preface to the first edition*, in *Handbook of Silicon Wafer Cleaning Technology (Second Edition)*. 2008, William Andrew Publishing: Norwich, NY. p. xxv-xxvi.
3. Lipinski, M. and J. Cichoszewski. *Silicon solar cells with texturization by metal assisted chemical etching*. in *Proceedings of the 24th European Photovoltaic Solar Energy Conference*. 2009. Hamburg, Germany.
4. Tsujino, K., M. Matsumura, and Y. Nishimoto, *Texturization of multicrystalline silicon wafers for solar cells by chemical treatment using metallic catalyst.* Solar Energy Materials and Solar Cells, 2006. **90**(1): p. 100-10.
5. Zimmer, M., et al. *In-line analysis and process control in wet chemical texturing processes*. in *Proceedings of the 22nd European Photovoltaic Solar Energy Conference*. 2007. Milan, Italy.
6. Oltersdorf, A., et al. *Analytical research of the acid etching bath by ion chromatography*. in *Proceedings of the 23rd European Photovoltaic Solar Energy Conference*. 2008. Valencia, Spain.
7. Seiffe, J., et al. *Alternative rear surface passivation for industrial cell production*. in *Proceedings of the 23rd European Photovoltaic Solar Energy Conference*. 2008. Valencia, Spain.
8. Steinert, M., et al., *Reactive species generated during wet chemical etching of silicon in HF/HNO_3 mixtures*. Journal of Physical Chemistry B, 2006. **110**(23): p. 11377-82.