Gettering of silicon by HCl gas

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Purpose of the work: In standard silicon solar modules, the costs of silicon wafers amounts up to 50% of the total costs. The reason is mainly the high costs for semiconductor quality wafers, as the purification steps are time and resource consuming. In order to save material costs, much research towards low - quality solar grade silicon and purification processes is made. Another approach is to use the concept of a crystalline silicon thin film (cSiTF) solar cell. Only a small amount of the expensive high purity silicon is needed for the epitaxial deposition on a substrate of metallurgical grade silicon (mg-Si). The resulting product is called epitaxial wafer equivalent (EpiWE) because it can be processed in a standard wafer cell production.
However, the metallurgical silicon used as substrate has a very high amount of doping and metallic impurities such as Fe, Cu, and Au. These contaminations severely degrade the minority carrier lifetime by forming recombination centres [1]. Therefore, the amount of impurities has to be reduced in order to prevent diffusion to the active layer. Since unidirectional solidification of the ingot cannot reach the appropriate impurity level, an effective gettering method is considered to be the following step.

Approach: Gettering of metal contaminations by HCl is known in the microelectronics during oxidation of wafers. The gettering effect is suggested to base on the formation of volatile metallic chloride species. The approach followed in this work is to treat the metallurgical silicon substrate by HCl gas, in the same CVD reactor prior to the deposition of high-purity silicon. The gettering mechanism as well as the reduction of the metal concentration is investigated in detail. For the analysis of metallic impurities, we apply standard analysis techniques like Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), and Instrumental Neutron Activation Analysis (INAA). The achievement of the gettering is controlled by comparing the amounts of trace elements before and after the gettering process. Using Fourier Transformed Infrared Spectroscopy (FTIR) we are able to investigate the exhaust gas and its components during the gettering process to optimize the method.

Scientific innovation and relevance: Gettering by HCl gas diluted in hydrogen is a new technique with promising results to reduce the metal contents. It enables in-situ processes, and by combining HCl gettering with HCl texture and emitter epitaxy, it seems to be possible to establish a fully dry in-line process for the wafer-equivalents. Neutron Activation Analysis shows to be a suitable measurement tool, which will be investigated for spatially resolved measurements and higher throughput.

Results: Gettering of the substrates was investigated on lowly contaminated multicrystalline and metallurgical silicon wafers. Lifetime measurements were performed, showing clearly the gettering effect by HCl gas. Gettering at 850°C with HCl concentrations between 5 and 16% shows a clear decrease of the total interstitial iron concentration of more than two orders of magnitude [2]. Lifetimes as high as the reference wafers, which were treated with the higher established method of phosphorus gettering, could be reached.
On metallurgical silicon, a decrease of the impurity concentrations was detected by Neutron Activation Analysis. This method was successfully developed for the detection of relevant impurities for solar cells. Microscopic examinations show that surface clusters are preferentially etched by HCl gettering, resulting in holes in the wafers.
Figure 1 shows the concentrations of several transition metals in mg-Si measured by NAA. The samples were taken from the top, middle and bottom of the silicon ingot, which was obtained by unidirectional solidification. An increase of the impurities from the bottom to the top is noticeable due to the small segregation coefficients of the respective metals in liquid and solid silicon.

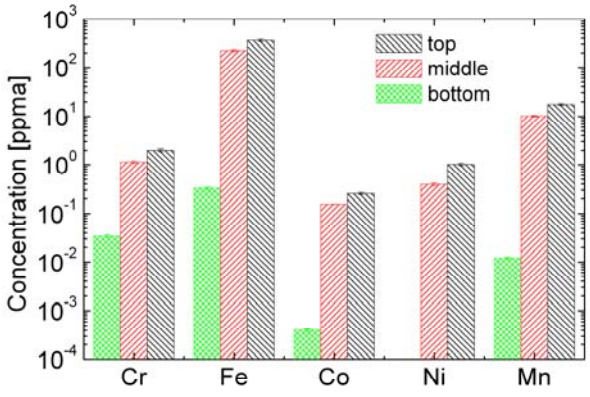

Figure 1. Impurity concentrations measured by NAA as they depend on the wafer position in the crystallised silicon ingot

Conclusions: HCl gas gettering shows promising results on multicrystalline and metallurgical grade silicon by decreasing the amount of impurities dramatically. The NAA method will be optimized for the routine application in photovoltaics.

References

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