Quantitative Analysis of Impurities on Semiconductor Materials

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The quantitative analysis of impurities on wafer surfaces becomes more and more important not only in microelectronics but also in photovoltaics. The manufacturing process plays an increasing role for the purity of semiconductor materials. Metal contaminations can be integrated in the growing oxide layer during the sawing process and diffuse into the bulk material during subsequent high temperature process steps. Also organic contaminations on the surface of the silicon wafers may have a detrimental impact on further process steps. Thus, a sensitive and quantitative determination of organic and inorganic contamination is an important step of quality control and process monitoring. This contribution presents different analytical methods as well as examples on photovoltaic silicon wafers.

1 Introduction

As the development in solar cell efficiency is still not at the end of their possibilities very pure silicon material and also increasing high quality wafer surfaces are needed. During the sawing process the silicon is bare for the first time and the very reactive surface is predestined to bond metal contaminations, which are introduced by the sawing wire, into the oxide layers [1]. Also, organic impurities are introduced by further process steps from different cleaning solutions, the environment as well as packaging materials [2]. Therefore, process control of impurities for both, organic and inorganic contaminations is of high importance.

We discuss here different methods for sensitive and reliable analysis of organic and inorganic surface contamination. Besides the ICP-MS analysis to determine inorganic impurities also two supplementary methods to determine organic contaminations, on the one hand as integral total organic carbon analysis and on the other hand as lateral resolved surface energy maps, are presented [3].

2 Experimental details

2.1 Analysed samples

Analysed samples for the following described methods were six inch silicon wafers after wire sawing out of the brick.

For the analysis of metal impurities by ICP-MS wafers with and without visible stains were used. The wafers received different pre-cleaning processes and thus have different optical appearance. While batch #1 received a pre-cleaning procedure only by water, for batch #2 a 10 Vol.-% NaOH/IPA solution (volume ratio 1 : 1) was used.

For the analysis of organic impurities by a TOC analyser and contact angle measurements six inch wafers after different cleaning processes were analysed and the results compared to each other.

2.2 SE-ICP-MS

For the analysis of inorganic contaminations surface extraction and subsequent mass spectrometry with inductively coupled plasma (SE-ICP-MS) was used.

After the surface extraction, described in section 2.4, the final solutions were measured by the high resolution (HR-) ICP-MS Element XR (Thermo Fisher Scientific, Dreieich, Germany). Calibration was done by standard addition with commercial available multi-element standard solutions for ICP (Carl Roth GmbH + Co. KG, Karlsruhe, Germany).

Typical limits of detection are in the range of 1E7 atoms/cm^2 to 1E11 atoms/cm^2, depending on the element. The method provides an integral result for the whole wafer surface.

2.3 SE-TOC

For organic contaminations the total organic carbon (TOC) analyser multi N/C UV HS (Analytik Jena, Jena, Germany) was used. After extracting the surface of the wafer according to the methods in section 2.4 the final solution was measured by the TOC analyser.

Due to the acidity of the etching solution the inorganic carbon could be removed by purging with nitrogen and therefore only the organic carbon will be measured in the instrument. After purging, all organic components are oxidised by UV or higher en-

ergetic light and/or sodium persulfate. The formed carbon dioxide is measured by a sensitive NDIR detector.

The method provides the sum of organic impurities on the whole wafer surface and has a limit of detection of about 1E13 carbon atoms/cm^2.

2.4 Surface extraction of wafers

For the surface extraction of solar silicon wafers the sandwich method is most recommendable. Briefly, a pair of identically wafers is needed and was extracted by the sandwich method [4], which is shown in figure 1. 1 mL of an etching solution containing HF, HNO_3 and water (volume ratio: 1 : 1 : 23) was applied to one wafer surface and afterwards covered with the second identical wafer. After ten minutes of extraction time the wafers were separated and the extraction solution was collected by a microliter pipette. After final dilution with ultrapure water the solution was analysed by ICP-MS or TOC analyser.

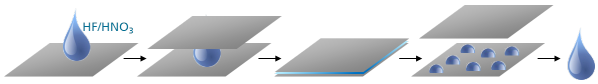

Figure 1: Schematic representation of the sandwich method as preparation technique for ICP-MS and TOC analysis.

Blank samples were produced from 1 mL etching solution and the appropriate amount of ultrapure water for dilution (same as in samples) to determine the background of the procedure.

If only one wafer is available the droplet scan method can be used (figure 2). Therefor 0.25 mL of the mentioned etching solution was applied in one droplet to the wafer and manually driven over the whole surface, before it was collected by a microliter pipette. To ensure that all trace elemental contaminations from the surface were collected, a second droplet scan was performed in the same manner and merged with the first droplet before final dilution with ultrapure water. Blank samples contained 0.5 mL of etching solution and the appropriate amount of ultrapure water for dilution.

All used chemicals were of ultra-purity and purchased from Carl Roth GmbH + Co. KG (Karlsruhe, Germany).

2.5 Contact angle measurements

Samples were analysed by an OCA20 (DataPhysics Instruments GmbH, Germany) measuring instrument for their contact angles. The contact angle is the angle of a droplet of liquid at a solid surface. It depends on the interaction between the liquid and the solid phase.

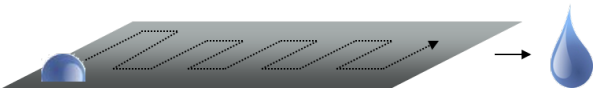

Figure 2: Schematic representation of the droplet scan method as preparation technique for ICP-MS and TOC analysis.

For a standard six inch wafer a pattern consisting of 30 equidistant measuring spots was measured. At each point a droplet of water (18.2 MΩ from Purelab Ultra, ELGA, Germany) and diiodomethane, respectively, was placed on the wafer surface by a vertical syringe. The used method is known as sessile drop technique. The contact angles on two opposite sides of the droplet were measured automatically by the software and the mean value was calculated. Finally the droplet was sucked by another syringe to remove it. Thus, overlapping of droplets can be avoided and the method can be automated.

From the determined contact angles of water and diiodomethane, respectively, the surface energy could be calculated according to the model of Owens and Wendt [5]. Used surface tension values were 46.8 mN/m and 1.3 mN/m for the polar and 26.0 and 49.5 mN/m for the disperse proportion for water and diiodomethane, respectively.

3 Results and discussion

3.1 Metal impurities

Due to the sawing process and the usage of slurry different metal contaminations can occur on the final wafer surfaces. Two wafer batches from the same sawing process which have received different pre-cleaning were analysed for their inorganic impurities by high resolution mass spectrometry. Batch #1, which only received a pre-cleaning by distilled water, shows visible stains on the surface. In contrast, batch #2 had a stain-free surface after the pre-cleaning with NaOH/IPA (figure 3).

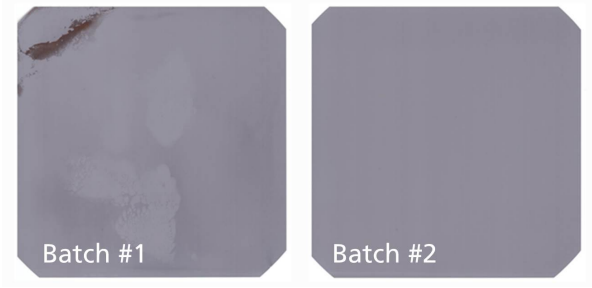

Figure 3: Two different wafer batches after different pre-cleaning processes. Batch #1 with visible stains and batch #2 without stains.

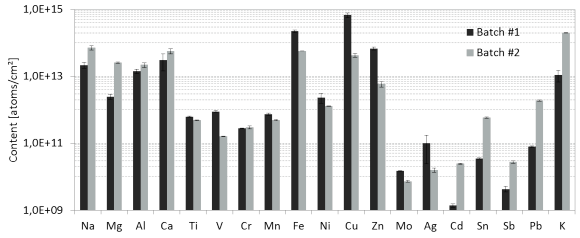

Figure 4: ICP-MS results of the two wafer batches in logarithmic scale.

For the analysis of the metal impurities the wafer surface was extracted by the sandwich method, described in section 2.4, and measured by ICP-MS. Results, which are presented in figure 4, show significant variations between the two wafer batches. All contamination levels were above the determined limit of detection (LOD), which is not shown in the graph.

For wafers from batch #1, which showed visible stains, higher contents of V, Fe, Ni, Cu, Zn and Ag were found. Highest values were found for Cu and Fe with 6.8E14 atoms/cm^2 and 2.2E14 atoms/cm^2, respectively, and can be removed by a factor of 4 for iron and a factor of 16 for copper using alkaline pre-cleaning methods.

There were higher inorganic impurities of Na, Mg, Cd, Sn, Sb, Pb and K found, among them K showed the highest contents (2.0E14 atoms/cm^2). The higher level of alkali and earth alkali elements may occur from the usage of NaOH/IPA as pre-cleaning solution.

3.2 Organic impurities

For the determination of organic impurities two different methods of analysis were used. On the one hand the wafers were analysed for their total organic carbon content, which results in an integral value of contaminations of the whole wafer surface. On the other hand the contact angles with water and diiodomethane were determined for wafers from the same batches and the surface energy was calculated from the obtained values. With the latter method a lateral resolved distribution of organic contaminations could be displayed and local enrichments of impurities could be detected by this method.

The analysed wafers were taken from different steps of the solar cell manufacturing process. TOC values show high organic contamination especially at the beginning of the process and decreasing contents after the first two cleaning steps (figure 5). All values were above the limit of detection, which shows, that the method is sensitive enough even for the analysis of RCA cleaned wafers [6].

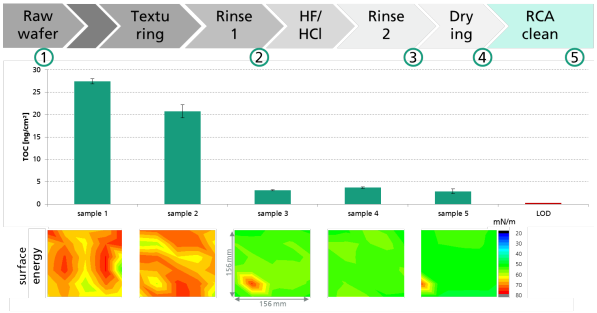

Figure 5: Results of organic impurities after different cleaning steps: the graph shows total organic carbon contents of wafer surfaces, while the appropriate surface energy values calculated from contact angles are shown below.

The contact angles with water and diiodomethane of the same wafer batches were determined and the surface energy maps were calculated. Again, the first two wafer batches show, like the TOC values, higher contamination. With progressing cleaning procedure the surface energy decreases significantly and also, the homogeneity across the wafer rises.

Increasing purification of the wafer surfaces results in decreasing TOC contents and likewise decreasing surface energies. Therefore, it can be said that two useful methods are available which correlate well with each other. As the TOC method results in integral values and the surface energy provides certain lateral resolution the two methods complement each other and provide information about the amount and distribution of organic contamination, even though the chemical structure of the molecules is still unknown.

4 Conclusion

Not only metal contamination but also organic impurities do have a detrimental impact on the following solar cell process, as they can not only cause problems during etching processes but also cause increasing surface recombination velocities which result in lower efficiencies of the later mounted modules.

In this contribution it could be shown, that there are several analytical methods available to determine those impurities with sufficiently high sensitivity. For inorganic contaminations ICP-MS measurements after previous surface extraction is a very powerful tool. Moreover, two techniques were presented for the determination of organic contaminants. On the one hand TOC analysis can give an integral value of the organic impurities and on the other hand contact angle measurements, provid-

ing surface energy maps, give an impression of local distribution of organics. Even though the chemical structure cannot be identified, both methods are rapid and reliable tools for the process control and may support further work to improve the purification process of wafer surfaces.

Acknowledgment

The authors like to thank the Federal Ministry of Economics and Energy (contract numbers 0325777E and 0325805I) for financial support.

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