LIBS TECHNIQUE FOR FAST IMPURITIES IDENTIFICATION IN METALLURGIC GRADE SILICON

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ABSTRACT:
Thanks to the rapid growth of the photovoltaic market the silicon demand is continuously increasing. The shortage of purified silicon between 2004 and 2008 induced a strong price increase and triggered a capacity expansion as well as the introduction in ingot production of the so called “upgraded metallurgical grade silicon” (UMG-Si) as a feedstock. However, new solar grade silicon might contain significant higher fractions of impurities. It is well known their impact on the final cell quality but the debate is open about what are the acceptable contamination levels within the purified silicon feedstock also because it is well known that during the growth process and cell manufactory the material quality improves. In the recent period in the market there is an increasing availability of silicon feedstock at lower cost but its quality is not always guaranteed.

In this paper we report a new fast in line characterization tools for feedstock analysis based on the Laser-induced breakdown spectroscopy. We applied this technique to the characterization of metallurgic grade silicon feedstock with the aim of valuate the applicability of this technique in the photovoltaic industry as in-line portable characterization tool. Different silicon grade feedstock were analyzed and selectivity and detection limit for the main impurities present in the silicon feedstock were determined.

Keywords: Metallurgical Silicon, LIBS, Metallic impurities

1 INTRODUCTION

The photovoltaic market is still dominated by wafer-based crystalline silicon photovoltaic modules although thin film technology is continuously increasing its share. One of the reason for the growing interest in thin film technology is the reduction of material usage and, as a consequence, a potential cost reduction. However, also crystalline silicon based solar cell producers are looking for cost reduction solutions and a possible way could be the use of the so called “upgraded metallurgic grade silicon” (UMG-Si) as a feedstock (Table I).

New solar grade silicon might contain significant higher fractions of impurities. As recently reported by del Coso [1] the cost advantage due to a feedstock cost reduction is practically lost if cell efficiency is reduced, due to quality degradation, by an absolute 1.7% for present module technology.

Typical impurities present in silicon produced by a metallurgical process are B, P, Fe, Cu, Cr, Ti, Al, Na, O and C (Table II). The debate is open about what are the acceptable coo presence of boron and phosphorus [2] and impurity levels within the purified silicon feedstock [3] also because it is well known that during the growth process and cell manufactory the material quality improves [4].

Several analytical techniques for monitoring impurities in silicon wafers are available like neutron activation analysis [5], secondary ion mass spectrometry [6], atomic absorption spectrometry [7], vapour-phase decomposition [8] total reflection X-ray fluorescence analysis [9] and inductively coupled plasma mass spectrometry [10].

However the accepted limit for most of the impurities is well below the detection limit of the more diffuse and non invasive characterization techniques available.

Photovoltaic industry ask for a non destructive and fast technique with a sufficient sensibility for an in line control of the incoming feedstock.

In this paper we report an in line characterization tools for feedstock analysis based on the Laser Induced Breakdown Spectroscopy (LIBS). LIBS is a well known technique for qualitative and quantitative analysis specially in the metallurgic field [11]. Recently LIBS has been explored also as a method for chemical analysis of silicon for photovoltaic application [12, 13].

Table I World Wide silicon consumption and silicon purity classification

<table>
<thead>
<tr>
<th>Element</th>
<th>MG typical (ppmw)</th>
<th>SoG feedstock (ppmw)</th>
<th>EG ref. cell (ppmw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>7</td>
<td>0.45</td>
<td>0.1</td>
</tr>
<tr>
<td>P</td>
<td>7</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Al</td>
<td>&gt;300</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>Fe</td>
<td>&gt;300</td>
<td>50</td>
<td>0.01</td>
</tr>
<tr>
<td>Ti</td>
<td>&gt;300</td>
<td>50</td>
<td>0.01</td>
</tr>
<tr>
<td>Cu</td>
<td>&gt;5</td>
<td>5</td>
<td>0.01</td>
</tr>
<tr>
<td>Ni</td>
<td>&gt;10</td>
<td>1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Cr</td>
<td>&gt; 5</td>
<td>0.2 – 1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Zn</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>20</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>20</td>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>

Table II Typical elements and concentration in silicon

- 90 % of the Solar Cells produced are based on Silicon (~50% SC, ~50% MC)
- PV uses 30 % of the total World Wide wafer based Silicon produced
- Metallurgic Grade (MG)
- Solar Grade (SoG)
- Electronic Grade (EG)
2 AIM OF THE WORK

The aim of the measurements is using LIBS to assess the overall impurities present in MG feedstock, and verify feasibility of SoG feedstock test. Delivery of quick analytical response at acceptable cost and turnaround time due to absence of sample preparation and analysis in air. Focus on the critical elements that decrease the cells quantum efficiency (Fe, Ti, Cu, Cr, ...). Assess the doping impurities (B, P) compensation ratio.

3 LIBS

LIBS is a simple emission spectroscopy resolved in time. By focusing a high power laser pulse, a very small, hot plasma is produced. In the lens spot temperature of several thousand degree is reached, so any molecular or solid structure is broken, moreover under certain condition (energy - time scaling) the plasma would be considered in Local Thermodynamic Equilibrium, so bound electrons in atoms are distributed following Boltzmann law, ratios from ions and neutral atoms are regulated by Saha equation. For trace elements the plasma can be considered as a thin source so the line intensities are linear with concentration, but for matrix elements (i.e. elements with concentration of some %) the plasma has to be regarded as a thick source, lines are often self-absorbed and calibration curves are necessary or a more realistic model for line intensities has to be used.

Heavy metals show very intense and rich spectra in the UV-Vis region. So LIBS is very suitable as tools for heavy metal detection in different matrix.

4 EXPERIMENTAL DETAILS

The main limitation for this technique was the limited sensibility but with the increasing availability of new and more sensitive CCD based spectrometers its application field can be extended.

We applied this technique to the characterization of metallurgic grade silicon feedstock with the aim of valuate the applicability of this technique in the photovoltaic industry as in-line portable characterization tool. Different silicon grade feedstock were analyzed and selectivity and detection limit for the main impurities present in the silicon feedstock were determined.

Two different setup have been used: the system in LaserPoint ships an Nd:YAG laser (40 mJ per pulse) and a non intensified detector.

The Geostudi prototype system can be divided in three logical units: Laser; detection apparatus; control and analysis unit. The laser is a Nd-YAG deliver up to 150 mJ per pulse @ 1064 nm. The repetition rate is 10 Hz. The beam is guided within an articulated arm into a head probe mounting the focusing lens and the collection optics. The optical signal is delivered into the entrance slit of the spectrograph via an optical fiber.

The spectrograph, a 50 cm focal length, ships two grating, a 2400 gg/mm HG, for LIBS that allows 0.2 Å sampling step, and a 150 gg/mm RG for LIF application. All the functions of the spectrograph (i.e. slit width, grating selection, wavelength position) are controlled by PC by serial communication port. Spectra were acquired by an ICCD camera that has an active matrix of 1024x128 pixel bat in this configuration is used as linear detector. The ICCD doesn't need external pulse generator, the whole control is carried out with a single PC board. The detector head would be cooled down to -20 degree with a single stage Peltier driven by the PC board.

5 MEASUREMENTS

Different types of silicon samples have been analyzed with LIBS:
- MG feedstock, as received, ingots
- MG feedstock, powder, mixing with high purity KBr, disk form
- SoG feedstock (B analysis), slices

Acquisition conditions:
- MG: 30 shots (3s acquisition time), delay 3 µs, gate 3 µs
- B: 500 shots (50s acquisition time), delay 3 µs, gate 3 µs

Figure 1 General setup of LIBS system

Figure 2 Schematics of transportable LIBS system

Figure 3 High resolution spectra of MG feedstock powder in KBr
Spectral lines of most trace elements can be observed in spectra form metallurgical grade silicon. Mg, Ca, Fe, Cu, Al can be easily detected by strong resonance line doublets or bands (Figure 4-7).

![Figure 4 Fe II lines in MG feedstock powder in KBr](image)

![Figure 5 Cu and Ti lines in MG feedstock powder in KBr](image)

![Figure 6 Ti lines in MG feedstock powder in KBr](image)

![Figure 7 Mn lines in MG feedstock powder in KBr](image)

Detection limits (Table III) of each element has been determined from spectra on metallurgical grade silicon by using the following criteria: $LOD = \frac{3 \times rms}{Peak\text{Height}}$.

**Table III** Spectra lines used for element identification and quantification and detection limit.

<table>
<thead>
<tr>
<th>Element</th>
<th>Spectral line [Å]</th>
<th>LOD (ppmw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>2139</td>
<td>0.5</td>
</tr>
<tr>
<td>Fe</td>
<td>2382</td>
<td>20</td>
</tr>
<tr>
<td>Mg</td>
<td>2795</td>
<td>0.2</td>
</tr>
<tr>
<td>Al</td>
<td>3093</td>
<td>70</td>
</tr>
<tr>
<td>Cu</td>
<td>3248</td>
<td>3</td>
</tr>
<tr>
<td>Ca</td>
<td>3934</td>
<td>4</td>
</tr>
<tr>
<td>Sr</td>
<td>4078</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Modified data:

<table>
<thead>
<tr>
<th>Element</th>
<th>Spectral line [Å]</th>
<th>LOD (ppmw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>3791</td>
<td>0.5</td>
</tr>
<tr>
<td>Ga</td>
<td>2944</td>
<td>0.01</td>
</tr>
<tr>
<td>Ti</td>
<td>3361</td>
<td>80</td>
</tr>
<tr>
<td>B</td>
<td>2498</td>
<td>20</td>
</tr>
</tbody>
</table>

Slices of SoG feedstock have been analysed for the characterization of Boron (Figure 8) that can be detected at 249.8 nm and 249.7 nm. High Born concentration (more than 100 ppmw) allow the detection at 208.9 nm.

![Figure 8 Boron lines (249.8 nm and 249.7 nm ) from Three different concentrations (45, 170, 2300 ppmw)](image)

A calibration curve (Figure 9) has been derived from Boron spectra and the results are shown in the picture below.

![Figure 9 Calibration curve for boron](image)

**5 FURTHER APPLICATION**

LIBS was also used to analyze the compositional profile (Figure 10), 2 microns CIGS > 10 shots before reaching CIGS-Mo interface.

![Figure 10 LIBS profiling in CIGS structure](image)

The gradient composition of the elements is easily detectable.

**6 CONCLUSION**

We have demonstrated that LIBS technique, even in basic configuration, can allow fast and complete characterization of impurities above 10 ppmw in MG Silicon feedstock (even if P needs further investigation).
We have demonstrated as well, that many elements between 1 and 10 ppmw can be detected. Fast analysis is possible, spectra acquisition time can be as low as 3 to 50 seconds. In these configurations, typical MG Silicon feedstock can be accurately characterized. Fe and Cu, two of the main detrimental contaminants, can be detected even in SoG Silicon feedstock.

As further development, composition profiling of CIGS cell structures was demonstrated, with a resolution in the range of 200 nm/shot.

As future development optimization element by element of delay and gate time, could lead to significant improvement of LOD. Analysis in modified ambient (He) lead to LOD of B as low as 60 ppbw; this procedure can be extended to other impurities in SoG Silicon feedstock.

A Calibration-Free data analysis technique will allow semi-quantitative characterization of elements when standards are not available [14].

REFERENCES