Selected Article

Determination of Oxygen and Carbon of Silicon for Solar Cells

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Recently, silicon has attracted attention as not only the semiconductor but also as a material for the solar cells. It is known that impurities such as oxygen and the carbon exist in silicon, and there impurities are known to affect its electrical properties. So it is important to control its concentration in low concentration level. Oxygen/ Nitrogen analyzer EMGA series and Carbon/Sulfur analyzer EMIA series has been recognized as a measuring device capable of rapid and accurate in low level of time, and various application developments have been also done in the long history. In this study, we introduce new measurement application of oxygen and carbon in silicon for solar cells as an example of the application.

Introduction

Generally high purity crystalline silicon is required large amount for solar cells; however it is also important material in the semiconductor industry, so the shortage of silicon material is becoming a serious problem in the field of crystalline silicon solar cells. Moreover The solar energy was required several times more costly obtain compared to fossil fuel energy[1]. However recently, a new silicon material manufacturing process known as SOG-Si, or Solar Grade Silicon has been developed for use in the manufacture of solar cells. The purity of this SOG-Si is between 5N and 7N and its manufacturing process is less expensive than the method used to produce silicon for semiconductors. For SOG-Si to be usable in solar cells, its resistance needs to be kept between 0.005 - 0.015 ohm-m. The resistance is affected by impurities such as oxygen or carbon, although the control of purity is need essentially to improvement of its efficiency.

Infrared absorption method (FT-IR) is generally used for oxygen and carbon analysis in silicon and it is standardized in the American Society for Testing and Materials (ASTM). But there is a problem that heavy-doped single crystalline silicon can not be measured because infrared rays are not penetrated though. Moreover, second ion mass spectroscopy (SIMS) has some problems those small measurement areas, necessary ultrahigh vacuum and a long measurement time. So we considered the method to measure oxygen and carbon in the silicon with a high accuracy, using Oxygen/Nitrogen analyzer EMGA -920, and Carbon/Sulfur analyzer EMIA-920V.

Oxygen Measurement in Silicon with EMGA-920

Oxygen/Nitrogen Analyzer EMGA -920

Oxygen/nitrogen analyzer EMGA -920 can measure oxygen and nitrogen at the same time with a high accuracy, in steel, nonferrous metals, and electronic materials and is used for process control, quality management, and also used in research and development of new materials. Figure 1 shows appearance of EMGA-920. The main part of equipment consists of sample fusion and a gas extraction part, and a detection part. The electrical impulse furnace is used for sample fusion and a gas extraction part.

This instrument use the inert gas fusion infrared absorption method (GFA)[2-7]. An electric power of 7 kW which attain to 3000 °C was applied to the graphite crucible in an inert gas (He) to remove and moisture and adsorbing gases from crucible. Then the graphite crucible was heated for sample melting temperature and the signal was adjusted to zero after the amount of carbon monoxide evolved from the graphite crucible became constant, and

then sample was dropped into the graphite crucible. The dropped sample in the crucible is melt and oxygen in the sample was reduced by the carbon of the graphite crucible to form carbon monoxide, which was subsequently measured with an infrared gas detector.

Figure 1　Appearance of EMGA-920

Oxygen Measurement in Silicon with EMGA-920

There was a problem with the repeatability to measure the oxygen in silicon using the method of inert GFA. This causes the oxidation film by the atmosphere, to solve this repeatability problem, it is required essentially to measure the bulk oxygen only after the surface oxide film has been removed. To remove this oxide film, the acid (chemically) treatment with the hydrogen fluoride acid was used. The study that removed the surface oxide film was done inert gas fused infrared absorption in a steel field[8-10]. This study describes a method for analyzing the bulk trace oxygen content of silicon, from which the surface oxide film had been removed using an inert gas fusion impulse furnace.

Figure 2 shows the sequence of the oxygen analyzer as fusion impulse furnace. An electric power of 2900 °C was applied to the graphite crucible for 40 sec to remove and moisture and adsorbing gases. Afterwards, the graphite crucible heated at 1300 °C for 50 sec. After the first 10 sec, the sample was dropped into the graphite crucible, and the oxide film on the sample surface was reduced by the carbon vapor for 40 sec. The treated sample was then left in the graphite crucible for 120 sec to cool, and was then taken out of the graphite crucible. The treated sample was placed back to the holder of the oxygen analyzer. Again, the graphite crucible was heated for 40 sec with 2900 °C. The graphite crucible was then continuously heated for 140 sec with 2100 °C. When the signal of the carbon monoxide from the graphite crucible became constant, the signal was adjusted to zero. Afterwards, the treated sample was dropped back into the graphite crucible for the bulk oxygen to be reduced by the graphite carbon. The evolved carbon monoxide was then

measured using the infrared gas detector.

To confirm whether the silicon re-oxidized upon exposure to the atmosphere, two samples were compared. A silicon sample with its surface oxide film removed by the carbon reduction described above was left for 10 min. at room temperature and 60% humidity. Its oxygen content was compared with that of silicon whose surface oxide had been chemically removed. There was no difference in the total oxygen between the two samples. Oxygen by the re-oxidation of the silicon surface which had been left in the atmosphere for a short time was below the detection limit in this method.
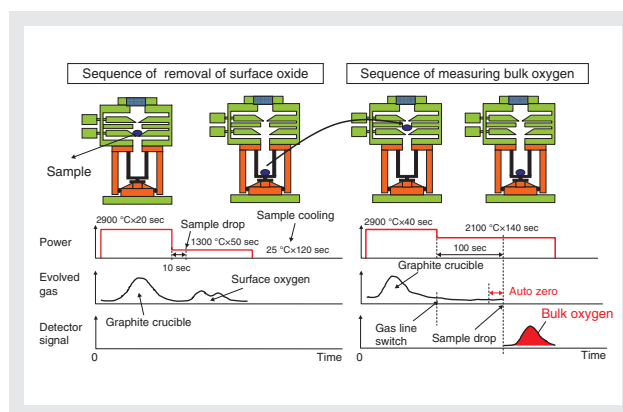

Figure 2　Sequence of surface oxygen film removal and bulk oxygen measurement

Correlation with the Oxygen Measurement Result in FT-IR

The amount of oxygen in various samples was previously measured by FT-IR, and determined to be 12.1 to 15.2 $\times 10^{17}$ atoms/cm^3 (Sample size ; 6×13×2 mm and approx. 0.35 g). 8 silicon samples were measured by this heated carbon reduction method. Table 1 shows the comparison result with GFA and FT-IR. The relative standard deviations of the oxygen in silicon samples with the surface oxide film removed were determined to be 0.8% for 9.8×10^{17} atoms/cm^3, and 2.7% for 13.0×10^{17} atoms/cm^3. The relationship between the oxygen concentrations measured using this method, and those measured by FT-

Table 1　Comparison result with GFA and FT-FIR

| Sample | FT-IR | GFA | |
	Ref.value	Ave.	RSD (%)
		($\times 10^{17}$ atoms cm^3)	
A	-	9.8	0.8
B	12.1	11.9	0.9
C	12.3	12.2	1.6
D	13.2	13.0	2.7
E	13.5	13.4	2.0
F	14.2	14.3	2.4
G	14.6	14.6	2.2
H	15.2	15.2	1.0

IR is shown in Figure 3. The index of correlation was 0.9962.

For Sample A that was doped boron in silicon, FT-IR measurement is impossible. Thus, although it may be unable to measure by FT-IR when boron and phosphorus are doped in silicone at high concentration in order to make the semiconductor of P type or N type, it can measure by the GFA method.
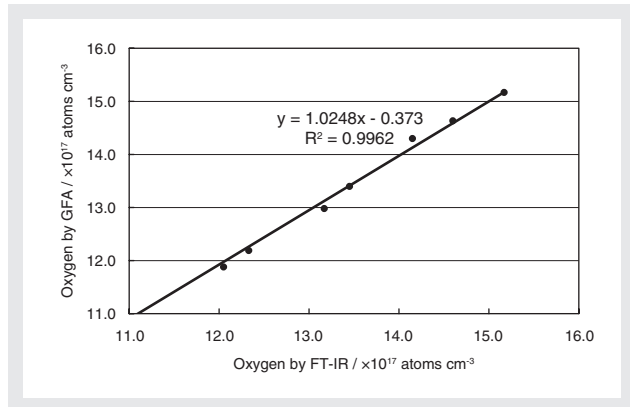

Figure 3   The correlation of the oxygen concentration between GFA and FT-IR

Carbon Measurement in Silicon with EMIA-920V

Carbon/Sulfer Analyzer EMIA -920V

Carbon/Sulfur analyzer EMIA-920V can measure carbon and sulfur at the same time with a high accuracy, in steel, nonferrous metals, steel alloys, special metals, and mineral stone of steel. Figure 4 shows appearance of EMIA-920V.

The principle of this measurement, the combustion oxygen conbusion - Infrared absorption method has been used and two types of combustion, by the tubular furnace with electric heater (EF) combustion and high-frequency (HF) induction heating furnace. EMIA-920V is using high-frequency induction heating furnace, easy to handle and heating furnace to high temperatures can rise quickly. The sample in the ceramic crucible is heated by eddy current caused by high frequency induction current flowing in electromagnetic field.

The sample is burned by heating in oxygen and carbon in the sample reacts with oxygen as carrier gas and generates carbon dioxide (and some carbon monoxide). However, only the sample is difficult to combust, so usually accelerators such as tungsten (W), tin (Sn), copper (Cu), and pure iron (Fe) are used with the sample. Carbon dioxide and carbon monoxide is carried to detector by carrier oxygen gas and detected by non-dispersive infrared detector (NDIR).

Figure 4   Appearance of EMGA-920

Carbon Measurement in Silicon with EMIA-920V

As standard measurement conditions like steel sample for EMIA-920V, W1.5 g and Sn0.3 g as an accelerator are used and HF current is 175 mA. When measuring carbon in silicon, there was the case that standard accelerator did not combust the sample completely, so increased W to 3.0 g to get a larger amount of heat, added pure iron 0.5 g to let it continue the heat that occurred for a long time, and increased Sn to 1.0 g to reduce the viscosity of the molten metal when combusting the sample. However, molten metal eroded to ceramic crucible under the influence that viscosity reduces, and a tailing came to be seen in the carbon extraction peak, and, as a result, carbon measurement value is not stable. So to avoid carbon peak tailing as much as possible, the HF current was set to be 150 mA. Table 2 shows measurement condition for carbon in silicon.

Table 2   Measurement condition for carbon in silicon

HF current setting	step 1	0 mA - 150 mA	5 sec.
	step 2	150 mA - 150 mA	35 sec.
accelerator	Fe	1.0 g	
	W	3.0 g	
	Sn	1.0 g	

Relationship between Grain Size and Carbon Value of the Silicon

The grain size also affects to the result at the time of measurement of carbon in the silicon. When grain size is too big, it's difficult to combust and grain size is too small oppositely, the surface area is large, and it'll be that

carbon value becomes high by influence of the surface pollution or involves air between grains. Silicon (2-3 mm, purity 99.999%) was classified more than 2 mm, 1-2 mm and less than 1 mm by a sieve, and the carbon measurement values, repeatability and extraction peaks were compared by sample mass 0.2 g. Table 3 shows relationship between grain size and carbon value of the silicon.

Table 3   Relationship between grain size and carbon value of the silicon

		(mass ppm)
particle size	average	S.D.
< 1 mm	132.79	12.65
1 mm-2 mm	82.41	1.56
> 2 mm	80.53	6.44

In the case of grain size is less than 1 mm, carbon measurement value becomes high clearl. Figure 5 shows comparison of carbon extraction peak in silicon: grain size (a) 1-2 mm (b) 2-3 mm. The result of Table 3 and Figure 5 shows that a combustion state of grain size 1-2 mm is the best since sharpness and good repeatability of extraction peaks and the standard deviation of measurement value is also small. From these results, when measuring carbon in silicon, grain size 1-2 mm is considered best to use those.
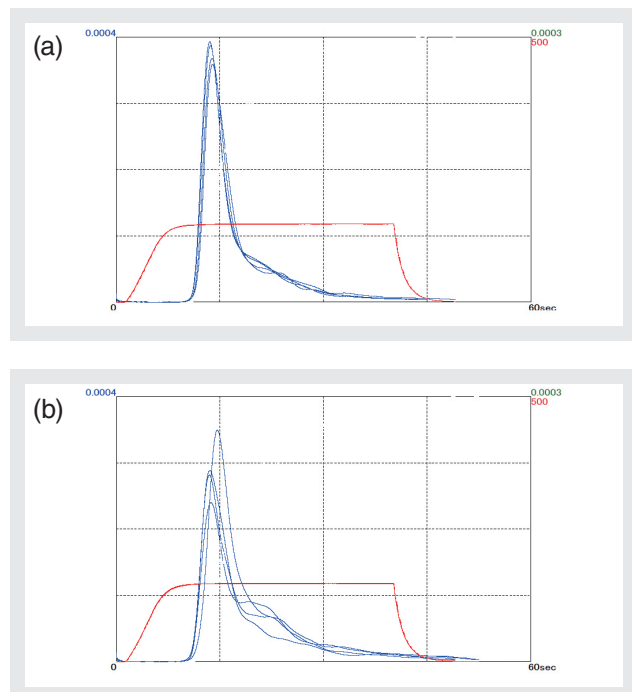

Figure 5   Comparison of carbon extraction peak in silicon: grain size (a) 1-2 mm (b) 2-3 mm

Conclusion

For the determination of oxygen and carbon in silicon, we developed a new separation method for measuring bulk and surface oxygen by means of oxygen/nitrogen analyzer (EMGA-920) and carbon measurement by the optimal silicone grain size by means of carbon/sulfur analyzer (EMIA-920V). This quantitative method is useful for the new development and the improved quality of SOG-Si by measuring oxygen and carbon in silicone correctly. In addition, the development of new materials is performed in future in various fields, and we would like to do an application development suitable for needs in the time quickly and provide it timely.

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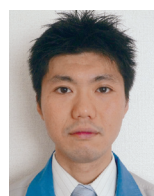
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