CASE
STUDY

ICP-Mass Spectrometry

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Photovoltaic Silicon Impurity Analysis by ELAN DRC ICP-MS

Rising energy and oil prices in light of the economic slowdown, and a heightened awareness of the environment, have led to an increase in global incentives for the diversification of energy sources and greater utilization of renewable energy segments. With the increased interest in renewable energy, there are growing opportunities for photovoltaics (PV). According to market research, PV is expected to account for over 50% of the world's total electricity generated by renewable energy sources by 2070. The PV market overall has grown to $19 billion globally and is predicted to continue over the next decade at over 30% per year. Wafers are the principal raw material used to produce solar cells, which are devices capable of converting sunlight into electricity. Today approximately 90% of the world-wide PV installations use mono- or multi-crystalline silicon wafers in the solar cells and silicon wafers represent half or more of the cost of silicon solar cells.

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LDK Solar (NYSE: LDK) is a pure-play manufacturer dedicated solely to the design, development, manufacturing and distribution of multicrystalline solar wafers. The manufacturing process is based on proprietary production processes utilizing both virgin and recycled polysilicon for ingot production. LDK's headquarters and large scale, state-of-the-art manufacturing facilities are located in Hi-Tech Industrial Park, Xinyu City, Jiangxi province in the People's Republic of China. The technology center is involved in investigating new technologies and developing new processes such as pure silicon material, crystal-silicon growth, big crystal ingot, great size silicon wafer and thin wafers.

High competition and achieving cost effectiveness through innovation are the broad characteristics of the PV industry. Reducing the cost to produce PV Si is one of the key challenges facing the PV industry, and it has been reported that about 40% of inventions focus on reducing the cost of manufacturing/fabrication of PV Si. The technology center also collaborates with leading domestic and foreign researchers.

Impurity level is the key factor for cost control and yield optimization, since metallic impurities are prevalent contaminants in PV Si and can severely degrade the performance of the final devices either by forming metal silicides and/or by acting as recombination centers. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) is currently the most powerful and useful trace analysis tool capable of quantitatively measuring the total elemental impurity concentrations in PV Si of varieties forms down to ppbw level (parts per billion weight).

During the past decade, PerkinElmer has built a PV focus team allowing a deeper understanding of this fast moving industry. Shortly after the 1993 introduction of the first ELAN® ICP-MS, the PV industry recognized the many possibilities of this new technology. Over the years, PerkinElmer has provided the most powerful analytical tools available coupled with unrivaled speed of analysis and best-in-class ease of use.

What might not be apparent is our application-focused solution with innovative thought leadership and public outreach programs that will bring insights from top scientists, industry experts and government agencies directly to customers. One key component of the initiative is to deliver state-of-art instrumentation that combines the necessary product offerings with the applications, methodologies, standard operating procedures and training required to complete specific analyses.

Due to the advantages of excellent sensitivity and high sample throughput, ICP-MS has become the industry standard technique for the characterization of trace metal contaminants in PV Si. For quality control purposes, there are two types of Si that are routinely analyzed, bulk Si and the surface of Si wafers. Bulk Si analysis can be performed by totally digesting the Si using a very aggressive acid. Vapor phase decomposition (VPD) is the most common method used for the analysis of Si wafers. However, it is extremely important to address the significant solvent-related and silicon-based polyatomic interferences which form, as well as matrix suppression effects due to the high Si content. These issues arise when analyzing solutions with dissolved silicon matrix directly.

Among these complexities of impurity measurements by ICP-MS, boron and phosphorus are of particular importance since they function as dopants, must be below threshold levels and must be in a specific balance for proper solar

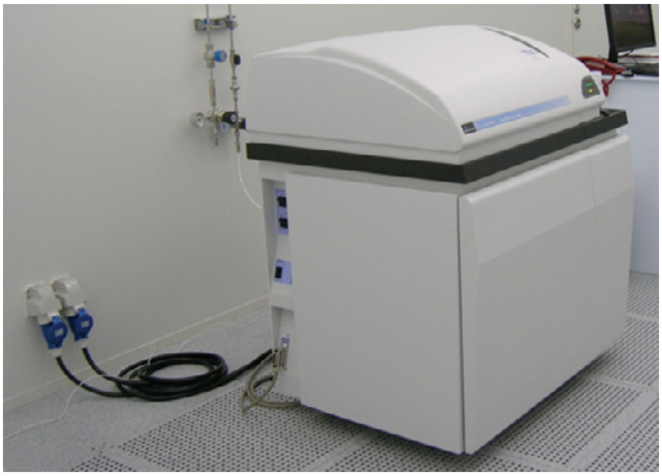

Figure 1. ELAN DRC II ICP-MS in the class-100 clean room at the Technology Center of LDK Solar Limited.

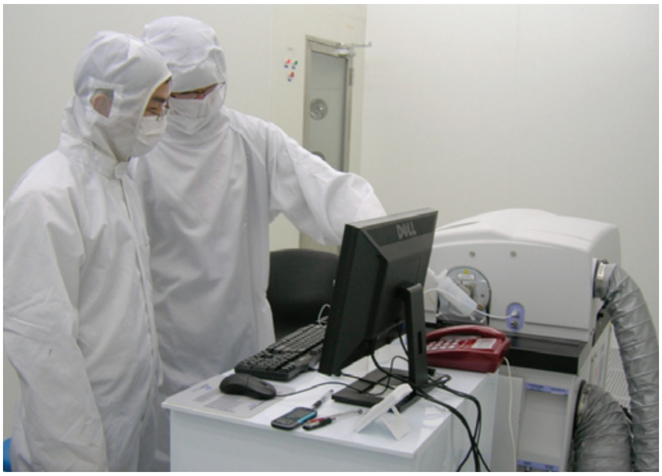

Figure 2. Scientists and industry experts share insights and experiences with customers.

cell performance, However, boron and phosphorus are classically difficult elements to accurately determine. More importantly, common sample preparation procedures for the analysis of boron in PV silicon wafers mostly involve the addition of very aggressive acid, such as sulfuric acid, to remove bulk silicon completely due to the higher temperature evaporation process. The addition of mannitol is also recommended to retain boron in solution while heating. However, these two procedures pose higher risk of contamination and increased interference on method detection limits. Thus, although the current technology innovation of ICP-MS makes it relatively unaffected by both of the sample matrix and instrument stability, the sample preparation is of paramount importance to achieve current quantitative measurement for lower detection limits and speed of analysis requested by PV industry. Direct analysis is more attractive because it does not contaminate the sample and generally does not require bulk silicon removal via time-consuming hot plate evaporation.

While cold plasma has been shown to be effective in reducing argon-based interferences, it is even more prone to matrix suppression than hot plasma. Additionally, because of the low plasma energy, other polyatomic interferences which are not seen under hot plasma conditions may be preferentially formed. Collision cells using multipoles and low reactive gases have proven useful in reducing polyatomic interferences. This approach necessitates the use of kinetic energy discrimination (KED) to remove the unwanted by-products. However kinetic energy discrimination results in the loss of sensitivity, which is an issue when analyzing at sub ppbw levels. Additionally, sensitivity loss is more significant for lighter analytes.

Figure 3. Modifying the conventional sample pretreatment procedure of PV Si brings new simplicity to ICP-MS measurement established for rapid, sensitive and selective analysis.

The dynamic reaction cell (DRC™) is another technique which uses a quadrupole mass filter where both RF and DC voltage can be applied. The advantage of this configuration is that ions of a specific mass range pass through the cell, while ions outside of this range are ejected from the cell. This process is known as dynamic bandpass tuning (DBT). With this patented technology, the ELAN DRC II ICP-MS does not need to use cool plasma and also avoids the use of KED because it is a technique of chemical resolution to remove the interferences. As a result of this capability, undesirable by-product ions do not form within the cell, even when very reactive gases are used, such as NH_3 and O_2. Samples containing up to 2000 ppm silicon in solution can be directly introduced into plasma for analysis without problems which greatly reduces the operator's workload.

Another advantage of the ELAN DRC II ICP-MS is that it always operates under robust hot plasma conditions, effectively decomposing the sample matrix and eliminating the need for matrix-matched standards or method of standard additions (MSA). Since matrix-matched calibration curves are not required to analyze PV Si samples, the method detection limits (MDL) achieved on the ELAN DRC II ICP-MS are independent from the sample matrix and can be determined from the simple acid calibration blank.

The instrument also has the ability to combine elements run in DRC mode (with reaction gas) with elements run in standard mode (without reaction gas) in a single analytical run, eliminating the need for running the sample twice or under two different plasma conditions. Both DRC and standard condition elements were determined in the same multi-element run with the total measuring time (3 replicates) less than 3 minutes per sample for a total of fifteen analytes. This feature of time-efficiency highlights the suitability for the routine quantification of trace impurities in PV industry.

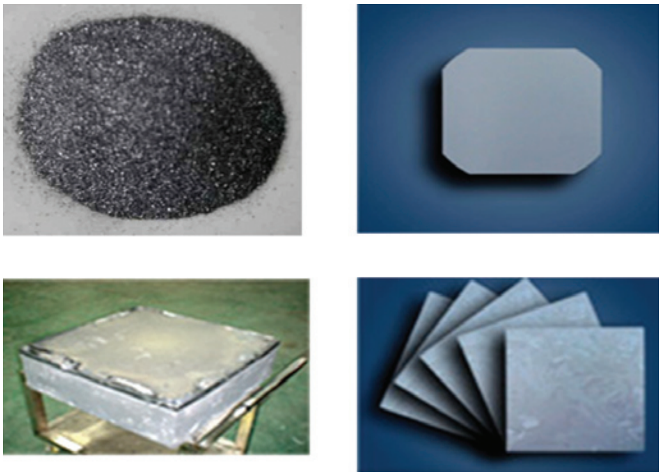

Figure 4. Trace elemental impurities in PV Si in several forms can be quantitatively and accurately analyzed by ELAN DRC II ICP-MS with the total measuring time (3 replicates) less than 3 minutes per sample following an appropriate sample pretreatment process.

For method validation, a PV silicon wafer sample was taken in six replicates treated with proposed application methods, and then analyzed by ICP-MS. The results agree well with the detailed specification of analyzed sample characteristics. In addition, the mean results of ICP-MS were confirmed by Glow Discharge Mass Spectrometry (GDMS) analysis at the technology center. The matched data of two different technologies highlights the advantage of ELAN DRC II ICP-MS for the fast determination of impurities in the application of PV industry, while GDMS is primarily not as cost effective and time efficient.

As a world leader in analytical instrumentation, with the application-focused total solution and close attention to customer's specific needs, PerkinElmer is the premier partner for PV industry. The ELAN DRC II ICP-MS provides the appropriate tool for obtaining accurate low level data quickly and with minimal complexity of sample preparation, to the trace interference-free analysis of PV Si. This technology can result in a major benefit to a laboratory because it can be readily and easily used without time consuming changes in the instrument configuration.

Reference

1. SEMI PV1-0709 - Test Method for Measuring Trace Elements in Silicon Feedstock for Silicon Solar Cells by High-Mass Resolution Glow Discharge Mass Spectrometry.

2. SEMI E45-1101 - Test Method for the Determination of Inorganic Contamination from Minienvironments Using Vapor Phase Decomposition-Total Reflection X-Ray Spectroscopy (VPD-TXRF), VPD-Atomic Absorption Spectroscopy (VPD-AAS), or VPD/Inductively Coupled Plasma-Mass Spectrometry (VPD/ICP-MS).

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