Application Note

High Purity Silane Analysis
For Solar Applications

PROBLEM

Silane gas, used in the production of polysilicon and amorphous silicon thin films, is one of the basic source materials in solar device fabrication. For high quality solar device characteristics, the silane used must have very low levels of contamination in the part per billion (ppb) range. PPB purity analysis of silane requires precise and accurate instrumentation and exacting method development. Instrumentation used during the silane analysis must be leak free due to the pyrophoric nature of the gas with oxygen, creating silicon dioxide and water, as well as conversion to silicon dioxide and H₂ when very little water is present.

BACKGROUND

Modern manufacturing processes for the semiconductor industry require ultra-high purity in the bulk gases used for processes such as PVD, CVD and etch. Contamination levels, in most instances, are in the parts per billion regime. Contaminants such as H₂O, CH₄, CO, and CO₂ are of particular interest in photovoltaic (PV) device manufacturing since these contaminants in 100% silane (SiH₄) feedgas can lead to defects in the devices. CVD processes for active thin films must especially exhibit extremely low levels of particulate and elemental contamination to ensure acceptable solar energy conversion to voltaic energy. To guarantee delivery of silane to PV processes at the necessary purity levels, a reliable and accurate analytical tool capable of detecting water, carbon oxides, and hydrocarbons is required. Preferably, the analytical tool should be adaptable to in-line or at-line analysis of the incoming feed gas.

The analysis at the ppb-level for H₂O, CH₄, CO, and CO₂ in bulk silane poses significant problems for conventional analytical equipment. The most significant of these problems is the performance of the analysis in a matrix of a pyrophoric gas. Historically, the only truly reliable method of determining whether silane is of sufficient purity is growing epitaxial silicon films using the source gas and measuring the resistivity of the film produced. Obviously, epitaxial film growth is a laborious method for process control purposes. Analyses of captured silane samples, as well as at-line analytical tools such as GC/MS and APIMS, have been deployed but the instrumentation is very difficult to maintain and operate due to special requirements that are needed to obtain ppb level of analysis. It is also necessary to keep the equipment and sampling line free of moisture.

SOLUTION

The MultiGas® FTIR model 2032 Purity Analyzer provides an effective solution for bulk silane purity analyses at the ppb level. This analyzer is ideally suited for high purity analysis within different matrix gases. It is equipped with a 5μ thermo-electric (TE) cooled detector and has a usable infrared range from about 6000 cm⁻¹ down to 2000 cm⁻¹ that makes the instrument extremely sensitive for the detection of most volatile hydrides as well as the air components.

High purity analysis requires exacting method development, beginning with accurate zeroing of the analytical tool for the contaminant(s) to be analyzed. This requires that the FTIR spectrum of a sample of extremely clean SiH₄ (with less than 1 ppb of H₂O, CO, and CO₂) must be collected. This spectrum will be used to reference (zero) the contaminant responses of the air components that are to be detected by the MultiGas 2032.

The purity of the “zero-gas” silane is facilitated through the use of a gas manifold such as that shown in Figure 1. This gas manifold incorporates point-of-use purifiers through which the sample gas stream is “zeroed” (using a Matheson TriGas silane purifier) and the N₂ purge used for the optics (using a SAES nitrogen purifier) is scrubbed of contaminants. The H₂O, CO and CO₂ in the purge and zero gases are removed to levels of less than 1 ppb.

Figure 1 - Gas Management Panel attached to MG2032 back, showing N₂ purifier used on the N₂ purge inlet line, as well as the SiH₄ purifier used to create the pure silane spectrum used in the method.
SOLUTION (CONT'D)

Prior to running the silane zero gas through the MultiGas 2032, the gas feed lines and sample chamber (collectively called the sample loop in this document) within the instrument are purged to the point where they are dry and free of volatile contaminants. If this is not done, then residual moisture that is adsorbed on the surfaces of the sample loop will contaminate the lines and optical equipment, forming silicon deposits. Moisture and other volatile contaminants can be reduced within the FTIR by applying a steady purge of purified, dry N₂ through the FTIR sample loop (flow rate 1 - 2 slpm) and the optical purge loop (flow rate 4 – 5 slpm) while simultaneously “baking” the unit out overnight at elevated temperatures to assist in removal of moisture from the walls. In some instances (high moisture environments) a second bakeout may be required to stabilize the background moisture signal. The background moisture level that can normally be achieved using this approach is approximately 150 ppb. Once the FTIR as well as the sample loop has been purged and baked out, it is ready for conditioning through exposure to the silane gas. Once the line is conditioned, it is best to retrain the silane sample in the line either using a constant purge or trapped silane in the line in order to reduce the conditioning time needed to remove the moisture provided all safety measures are in place for any leak that might occur.

Once the sample loop has been conditioned, the silane feed gas is then diverted through the silane purifier. This purifier must also be conditioned. In the case of the silane purifier from Matheson TriGas, the manufacturer recommends a silane purge of only 0.5 slpm for 5 minutes to condition the purifier; however we have found that, in practice, it may take longer. In some cases, it may take up to 3 hours to obtain a steady-state value when using a new purifier. As conditioning proceeds, the moisture signal, as determined through the monitoring of the H₂O concentration using the MKS 2032 analyzer, eventually reaches a steady-state.

Figure 2 shows the MultiGas 2032 signal for water vs. time used for the initial establishment of the 100% silane spectrum and then analysis of the raw silane gas. The trace that can be seen in the scan is the signal strength for the water level in the silane sample that is flowing through the silane purifier. Once the signal reaches steady state, (the red box in Figure 2) the user presses the “100% Zero Gas” button to automatically replace the spectrum in the method with the one that is collected on the FTIR. Once that spectrum has been replaced then the analysis of the raw silane sample can be made.

The spectrum of silane that is supplied with the original method must be replaced with one created on the FTIR instrument in use. This is only done once and is required because the signal from the 100% silane spectrum has many fully absorbed regions in the IR spectrum and this causes differences in the detector responses from instrument to instrument. Once replaced, this 100% silane spectrum is permanent until something is changed on the FTIR. With the Auto-Reference method deployed by MKS, once the FTIR has been baked out and the 100% silane spectrum obtained, there is no need to switch the sample line to N₂ or any other gas other than the raw silane that is to be analyzed. The Auto-Reference method automatically creates a background spectrum without the need for purging the gas cell with an inert gas. This greatly reduces the chance of contaminating the sample line with any air or moisture.

Figure 2 - Sample was diverted to Purifier and H₂O concentration was monitored. Second switch was after the H₂O concentration was at equilibrium.
SOLUTION (CONT'D)

Once the 100% silane spectrum has been established, the silane stream is then diverted through the by-pass line for the analysis of the raw sample impurity content. The vertical yellow bars shown in Figure 2 indicate the region of the scan that was used for analysis of the unpurified/raw sample after it reached steady-state showing 37 ppb H₂O.

While Figure 2 only shows the results of the analysis of silane for moisture, similar analyses for other contaminants can be simultaneously determined from the FTIR spectra collected under steady-state conditions. Of all the air components, only CO is unable to be analyzed using the FTIR when running 100% silane, as CO absorbance is fully obscured by the silane peaks.

In determining which contaminants can be effectively analyzed using the MultiGas 2032 Purity Analyzer, it is important to consider interferences due to the overlap of absorption bands of the contaminant with those of the matrix gas. Experimental evaluations have shown that moisture and CH₄ have detection limits of around ±30 ppb, while CO₂ has a limit of ±3 ppb. These detection limits show that the MultiGas 2032 has excellent characteristics as an analytical tool for silane quality assurance in PV manufacturing. Table 1 shows the results for the high-purity analysis of a SiH₄ cylinder using the MG2032 Purity FTIR.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Cylinder Concentration</th>
<th>Est. Detection Limit in 100% SiH₄</th>
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<tbody>
<tr>
<td>H₂O</td>
<td>37 ppb</td>
<td>30 ppb</td>
</tr>
<tr>
<td>CO₂</td>
<td>&lt;3 ppb</td>
<td>2.7 ppb</td>
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<tr>
<td>CH₄</td>
<td>35 ppb</td>
<td>30 ppb</td>
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<tr>
<td>C₂H₆</td>
<td>&lt;270 ppb</td>
<td>270 ppb</td>
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<tr>
<td>C₂H₄</td>
<td>&lt;1300 ppb</td>
<td>1330 ppb</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>&lt;120 ppb</td>
<td>120 ppb</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>&lt;690 ppb</td>
<td>690 ppb</td>
</tr>
<tr>
<td>HCl</td>
<td>&lt;30 ppb</td>
<td>30 ppb</td>
</tr>
<tr>
<td>HF</td>
<td>&lt;6 ppb</td>
<td>6 ppb</td>
</tr>
</tbody>
</table>

Table 1. Quantification Results of the SiH₄ Cylinder

CONCLUSION

When used with proper sample loop conditioning and purification of the purge gas and calibration zero gas (employing both a N₂ and a SiH₄ purifier), the MKS MG2032 Purity FTIR is an effective analytical tool that can perform low ppb level detection of contaminants such as H₂O, CO₂, CH₄, HCl, and HF directly within a silane gas matrix.

In Table 1, Column #1 is the impurity component that was analyzed; Column #2 shows the cylinder concentration as determined by the FTIR method; and Column #3 is the method detection limit within a 100% SiH₄ matrix for each component analyzed (based on three times the standard deviation of the residual of the quantified area using the 100% purified silane sample).

The experiments summarized in Table 1 also showed that some of the C₂ and C₃ hydrocarbons may be analyzed within the SiH₄ matrix, but the estimated detection limits were on the order of 100’s of ppb and, in the case of ethylene, around 1.3 ppm. However, these detection limits are too high for use in purity analyses for the Solar Industry requirements.