Glow discharge mass spectrometry (GDMS) is a well established technique for bulk solids analysis. Compared to glow discharge optical emission spectrometry (GD-OES), GDMS uses the energy of the GD plasma to make ions from the sputtered sample rather than photons. The ions are sampled into a mass spectrometer under high vacuum for analysis of the ionic species. The relatively low amounts of spectral and detector background in MS make GDMS the most sensitive, commercially available, bulk analysis tool. Indeed, GDMS is the preferred analytical technique for the certification of high purity materials such as used in the semiconductor industry. Analogous to inductively coupled plasma mass spectrometry (ICP-MS), differences exist in the types of mass analyzers used in GDMS, which have a direct bearing on the respective analytical characteristics, applications, and costs. The two types of mass analyzers are the high resolution magnetic sector and the quadrupole mass filter. Any comparison between GDMS and GD-OES must first involve a comparison of the characteristics of the available mass analyzer systems.

### Table 1: GDMS and GD-OES comparison

<table>
<thead>
<tr>
<th></th>
<th>Magnetic Sector</th>
<th>Quadrupole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution (m/ m)</td>
<td>Up to 10,000</td>
<td>1</td>
</tr>
<tr>
<td>Analysis time (20 elements)</td>
<td>30 - 60 min.</td>
<td>15 - 30 min.</td>
</tr>
<tr>
<td>Spectral interferences</td>
<td>Few</td>
<td>High</td>
</tr>
<tr>
<td>LODs</td>
<td>&lt; 1 ppb</td>
<td>&gt; 10 ppb</td>
</tr>
<tr>
<td>User sophistication</td>
<td>MS to Ph.D. level</td>
<td>MS or excellent technician</td>
</tr>
<tr>
<td>Cost</td>
<td>&gt; $400,000</td>
<td>&gt; $180,000</td>
</tr>
</tbody>
</table>

Other than the fundamental differences between GDMS and GD-OES, there are more important practical differences which will determine the appropriateness of the two methods. These differences are described below.

### 1 Sample types

While GDMS is the technique of choice for high sensitivity metals and semiconductor analyses, there are no commercially available radio frequency-GDMS sources. Thus, bulk non-conductive materials must be ground to a powder, mixed with metal, and pressed to form a conductive disk. The analysis of thick oxide or polymer layers is not available directly. In some cases, a conductive metal mask (called the secondary cathode) is placed over/around the sample, but this approach has not gained wide acceptance. On the other hand, there is a radio frequency (RF) source for GD-OES that permits the direct analysis of metals, glasses, polymers, and non-conductive films.

### 2 Analysis time

Because of the need for low pressures for GDMS analysis, extensive pumpdown times are required. For many analyses, pump down times of more than 15 minutes may be required. Longer times are required for ultimate sensitivity or gaseous element analyses.

It is important to realize that the presence of
residual gases (air and water) on the sample surface or in the source greatly affect the performance of the GDMS experiment in terms of absolute sensitivity and spectral interferences. On the other hand, even in the case of gaseous element analysis, the RF-GD-OES pump down time is more on the order of 1 minute. The actual analysis time for GDMS depends on the level of sensitivity required and the type of mass analyzer employed (quadrupole analyses are usually much shorter than sector). Analysis times are typically 15 minutes to 1 hour, depending on the desired sensitivity. Depending on the spectrometer employed (sequential or simultaneous), the RF-GD-OES analyses are typically less than 5 minutes.

3 Complexity of instrumentation

The need for high vacuum integrity, the high level of contamination effects, and the complexities of tuning and maintaining a sector mass spectrometer require a very high level of operator sophistication, usually a Ph.D. The requirements are less for quadrupole instruments. Conversely, the RF-GD-OES instrument can be operated by a skilled technician.

4 Elemental coverage

GDMS analysis produces ions from all of the elements present, with the mass analyzer being able to detect all masses (isotopes). In this way, GDMS offers complete elemental coverage in any analysis. The primary difficulties come from spectral interferences. For example, Si, N2, and CO all exist at nominal mass 28 amu, and thus are not separated with a quadrupole instrument. Most mass interferences occur in the low mass range, < 80 amu. By comparison, RF-GD-OES employs a scanning monochromator which can access a wide wavelength range (VUV-NIR) to cover the most sensitive transitions for each element. Of course, if a polychromator is employed, there must be a PMT positioned for each element to be determined.

5 Quantification

In GDMS analysis, the elemental sensitivities are very uniform, and are not very sensitive to matrix identity and experimental conditions. For this reason, strict matrix matching is not required for quantification. Calibration curves are not used in GDMS, relative sensitivity factors (RSFs) are generated from standards. On the other hand, RF-GD-OES can use similar matrix standards to generate calibration curves which may, or may not, need to be run very often. The quality of quantification in RF-GD-OES is less sensitive to contaminants than GDMS.

6 Sensitivity

When talking about sensitivity in GDMS and RF-GD-OES, the key point is knowing whether a sector or quadrupole mass analyzer is used. The sensitivity of sector-based systems is far greater than RF-GD-OES. On the other hand, RF-GD-OES is very comparable, if not better than, quadrupole GDMS for many elements.

7 Cost

As with any analytical method, the initial capital costs depend on the level of sophistication built into that particular system (e.g., a polychromator is more complex than a monochromator), as described for GDMS above.

8 Depth profiling

The fact that all GDMS mass analyzers are sequential in nature is a serious limitation in depth profiling applications. Even though the ablation rates in GDMS are ~5X slower than in GD-OES, the user is very limited in the number of elements which can be effectively monitored. In addition, the models and methods for computing quantitative depth profiles by GDMS are at a very primitive stage in comparison to RF-GD-OES.