Surface and depth profile analysis of glasses by GD-OES

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Radio Frequency Glow Discharge Optical Emission Spectrometry (RF-GD-OES) is a mature technique[iiiiii] for direct elemental analysis of conductive solid samples without complex sample preparation. It has been used for bulk, surface and depth profile analysis of metals, oxides and semi conductive materials[ivv]. RF- GD-OES has been applied on non-conductive materials such as glasses or ceramics to characterise heterogeneity, interphase and chemical gradients. Glasses with increasing structural complexity were selected (homogeneous, multi-layered etc.) to asses the ability of GD to perform elemental depth profiling and evaluate the spatial resolution of the technique. A Jobin Yvon GD-OES system 5000 RF was used for depth analysis. The characterisation (texture, structure and composition) of the glasses was also conducted using electron microscopy (SEM /X-EDS) to assess the chemical and physical gradients in the samples. RF-GD-OES is able to offer a rapid characterisation of the surface of the glasses and elemental profiles in the matrix at a resolution of few manometer along z axis.

Introduction

The scientific community [vi] but also the industries[vii] (materials, electronics etc) ask for a technique requiring no sample preparatio , providing good sensitivity (few ppm), wide elemental coverage (from H to heavy elements), fast acquisition rate and able to detect small concentration gradients over a large analysis area and accurate depth analysis (few nanometer). RF-GD-OES can meet these demands. It can provide direct analysis of glasses and it only requires the use of a primary vacuum, making the analysis easy. Its ability to perform depth analysis down to the nanoscale is particularly useful in alteration studies. It has a fast sputtering rate (µm/min) and operates on a large surface area (2-4 mm). RF-GD-OES could perform quantitative and profile elemental analysis of homogeneous and multi-layered glasses and show chemical gradients in altered materials (atmospheric or leaching solutions).The spatial resolution along z axis for the glasses was estimated to be less than 10 nanometers.

Materials and Methods

Materials

To illustrate our purpose only one sample will be presented. It is an industrial glass provided by the Schott company[viii] as testing material. It is a multilayered sample. The glass surface is covered by three layers measuring respectively 90/120/60 nm (from the surface toward the core) and the shape of the glass is a small square of 5 cm by 5 mm in thickness. The major elements contained in the glass are O, Na, Mg, Al, Si, K, Ca, Ti, Fe, and Sn.. The GDS is performed to distinguish the different surface layers.

Methods

The GDS instrument was a JY 5000RF manufactured by Jobin Yvon Horiba (JY), France. This instrument was equipped with a standard 4 mm JY glow discharge source, an optical spectrometers (polychromator), and Quantum 2000 V1.1 software. The source was operated with constant pressure (Argon) monitored in the source and with the JY class E RF generator and matching box providing optimum power transfer at 13.56MHz from the source to the samples. SEM (Jeol 8400) was also performed for chemical and textural analysis. Data has been acquired at 15keV using a secondary electron detector for morphological image and with the backscattering electron detector for chemical contrasts picture.

Results and Discussion

Schott Glass

The GD depth profile for the Schott glass (Fig. 1) shows the heterogeneous distribution in the matrix. For simplification, only the elements presenting significant variation as a function of time (i.e. depth) are shown (for a total number of 40). These elements are C, O, Na, Si, Ti and Sn. The Sn signal is high during the first 10 seconds then decrease (between 10 up to 50s), and noticeable after in association with Ti. The second sequence (time range 10-50s) shows a peak of Si with a peak of Na between 30-50s which decrease after. The Ti signal increases after 50s and decrease progressively in association with Sn signal and O. Na finally growth from 70s and then stabilises after 100s. The interpretation of this depth profile is that there is a very thin $SnO2$ coating on top of a thicker silicium followeb by a $TiO2$ and Sn02 layer one on top of a vitreous matrix containing Na, where Na diffuses to the interface silicium/TiO2/glass. The detection of Ti on the first layer can be due to the excitation of the third layer by the GD and the relative transparency of the two first layers (SnO2 and Si). The C signal indicate that potential poluution could be existed on the surface of the sample. The time scales are related to the relevant thickness of the layers and to the relative sputtering rates. The SEM observation (Fig.2) of the crater induced by the GD process shows several inhomogeneities with the secondary electron mode (fig.2a) as well as with the back-scattered electron mode(Fig.2b). This double image allows the correlation of the topographic variations of surface to variations of the chemical composition. The black dotted arrow indicates a thin layer of less than 100nm which is assumed to be Sn. It is followed by a darker zone, deeply alterated (presence of a small crater) indicated by the white arrow and attributed to the silicium deposit. The third black arrow indicates the third thin layer Ti rich. The presence of morphological heterogeneity (holes or redeposition zones) indicates that the GD sputtering process induces a thermal constraint which by itself may explain the Na peaks at the interfaces Si/Ti/Glass. However this mechanism of Na diffusion has been related to the preparation process of this multilayer sample. Thus the GD observation could be real and not an artefact [ix].

These results show that GD can give very quickly some results when characterising multilayer glasses.

Conclusion

The potential of RF-GD-OES for depth analysis of glasses has been evaluated through studies on a complex sample. The performances of GD (ease of use, depth resolution and speed) have been shown and the need to couple GD results with microscopic techniques has been clearly demonstrated. Various works are in process to improve the GD performance and extend its capability but the absence of lateral resolution and the atomic information that the technic provides will still require complementary investigations with other methods. A multiple technique approach is however a key in studies on glasses and to that respect the RF-GD-OES comes out as a new and very valuable experiment tool.

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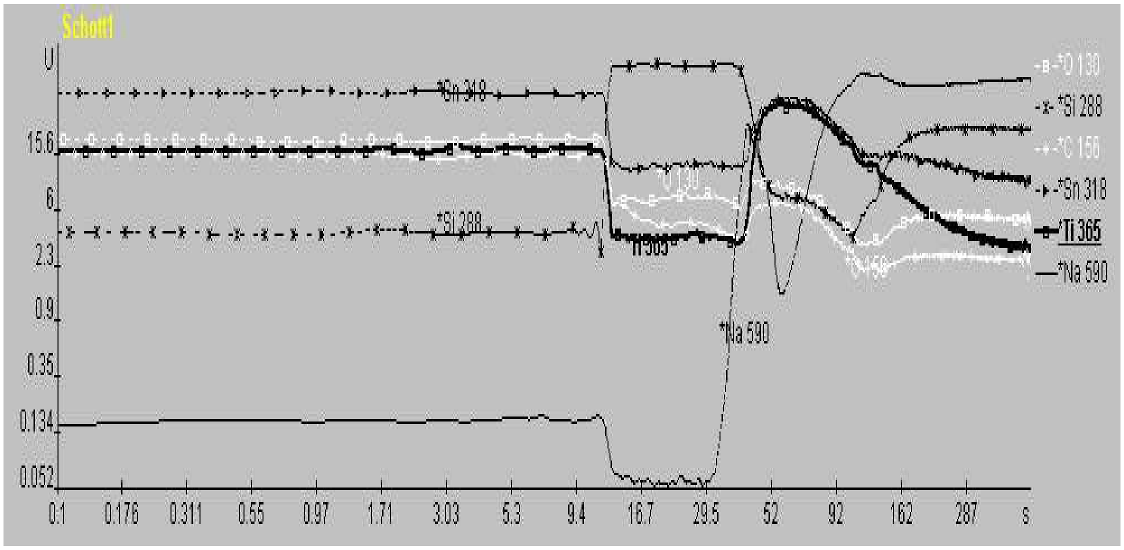

Figure 1 : GDS depth profile of the Schott glass (log-log scale)

Figure 2 : SEM picture of the Schott glass. Left one is secondary electron image; right one is backscattered electron image. (The white bar 1μm length. The arrows indicate the layers deposited)

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[i] Bell and Johnson, Applied Spect. **27**, p. 118-124 (1973)

[ii] Berneron and Charbonnier, Anal. Proc., p. 488-491 (1980)

[iii] Wittmaack, in *Practical surface analysis : Ion and neutral spectroscopy*, edited by Briggs & Seah (1992), **Vol. 2,** , p. 105-175.

[iv] Payling, in *Surface analysis methods in material science*, edited by O'Connor, Sexton and Smart (Springer - Verlag, Berlin, 1992), p. 387-402.

[v] Payling and Jones, Surf. & Interf. Anal., p. 787-795 (1993)

[vi] Rivière J.C., in *Encyclopedia of Analytical Chemistry*, edited by Wiley & sons (Meyers, New-York, 2000).

[vii] De Gregorio, Comm. European Communities, EUR n°6122 (1978).

[viii] Bange K., Schott company, private communication

[ix] Bange K & Rupertus V., Schott company, private communication