

Emergence and consequences of lateral sample heterogeneity in glow discharge spectrometry

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ABSTRACT

Conventional glow discharge emission or mass spectrometry requires the assumption that the surface of the sample is homogeneous. However, recent developments in glow discharge imaging appear to offer an opportunity to obtain three-dimensional concentration maps, in which this assumption is no longer necessary. Here, experiments, models, and a summary of earlier work are combined to examine the sputtering behavior of elemental and morphological heterogeneities in a sample. The theoretical model reveals gaps in current knowledge of glow discharge sputtering of heterogeneous samples, particularly indicating that heterogeneity in the sample leads to roughened crater bottoms and how additional morphology can evolve. Additionally, a three-dimensional profiling microscope is used to characterize the effects of surface inclusions on the sputtering process in a DC glow discharge in a reduced-pressure argon environment. Findings have important implications for bulk analysis, depth-profiling, and elemental surface mapping with glow discharge spectrometry.

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1. Introduction

Quantitative depth profiling with glow-discharge (GD) sources is used with both optical spectroscopy and mass spectrometry for the elemental characterization of thin films [1], semiconductors [2], and several other classes of materials [3]. In depth-profiling applications, it is necessary to determine the sputtering rate of the sample to determine the depth corresponding to each subsequent spectrum [4,5]. In turn, the rate of sputtering is largely derived from Eq. (1), which was described by Boumans in the early 1970's, during the early days of glow-discharge spectrometry [4,5].

$$Q = C_Q \cdot i_g \cdot (V_g - V_0) \quad (1)$$

In this equation, Q is the sputtering rate and V_g and i_g are the discharge potential and current, respectively. The other two variables – C_Q and V_0 – are dependent on the material of the cathode and the

discharge support gas. The threshold voltage, V_0 , is a minimal potential required to sustain the discharge and induce sputtering [6]:

$$V_0 = \frac{(m_i + m_t)^2}{4m_i m_t} U_0 \quad (2)$$

Variables m_i and m_t are the masses of incident and target particles and U_0 is the heat of sublimation for each material. The material-dependent sputtering constant, C_Q (with units of $\mu\text{g} \cdot \text{W}^{-1} \cdot \text{s}^{-1}$), is empirically observed to be related to the atomic weight and the heat of sublimation of the sample also, but this term is not entirely predictable, especially for multi-element samples.

Preferential sputtering (more rapid removal of some elements than others in the same sample) within macroscopically homogeneous samples has been described previously [7,8]. The principles behind these earlier studies have enabled quantitative mass spectral and emission measurements of bulk materials that have components with different sputtering rates. When GD spectrometry is used for bulk analysis, a pre-burn period is employed, which establishes an equilibrium of surface concentrations before the analytical measurement is begun [8].

Flat-bottomed craters are generally presumed to indicate even sputtering across the surface of a sample [9,10]. However, finer

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observation commonly reveals a roughened surface on the crater bottom that can arise from microscopic heterogeneity within a sample. Disparity in the sputtered depth across the surface of a sample is a greater problem when macroscopic inclusions are present, which results in variation in the depths and sputtering rates between entire regions of a sample. Glow discharge depth-profiling methods typically employ algorithms that use the composition of the sample to estimate the sputtering rate [11–13]. A necessary assumption of these techniques is that the elements observed in the spectra are homogeneously distributed about the lateral dimensions of the sampled area [14]. However, this assumption is not always valid; some materials have laterally heterogeneous structure [15] and others have unexpected inclusions [16] that can alter the characteristics of the material.

Several researchers have described problems that arise from sample heterogeneity in glow discharge spectrometry. In the early 1970s, Dogan, Massman, and Laqua [7] observed the difference in the height of two materials in the same sample that sputtered at different rates. They expanded this study with electron micrographs that revealed topographic structures in the crater bottom and described how variations in sample composition ultimately resulted in changes in the I-V characteristics of the source and in the associated sputtering behavior. Their work addressed both microscopic heterogeneity in alloyed materials and how these differences were likely to translate to macroscopic variations [7]. Later, Weiss [8] described the sputtering-based enrichment of carbon on the surface of graphitic steel and explained some of the associated quantitative calibration techniques.

Over the past decade, several optical techniques have been developed to view spatially resolved emission across the surface of glow discharge samples [17–20]. These techniques utilize pulsed glow discharges in 0.1 to 4.0 kPa of argon to temporally and spatially isolate emitting species near where they were sputtered from the surface. Higher pressures shrink the mean free path, which limits the lateral diffusion of atoms in the time between their removal from a sample surface and emission they yield in the negative glow region of the discharge [18]. These techniques generally provide lateral spatial resolution on the order of hundreds of micrometers, making them appropriate for the characterization of macroscopic variation across the surface. Ideally, spatially resolved measurements would be coupled with depth-profiling techniques to produce a three-dimensional map of a sample. However, this goal can be achieved only with a full understanding of how lateral variation affects the sputtering process.

Other surface-analysis techniques (e.g. Auger electron spectroscopy [21], x-ray photoelectron spectroscopy [22], and secondary ion mass spectrometry [23]) offer three-dimensional spatial resolution, but generally do so by sputtering and sampling small parts of the surface sequentially [21–23]. Due to this point-by-point approach, high-resolution images can require many hours to raster across a sample. Glow discharge spectrometry offers the advantage over these other surface-analysis techniques of simultaneously sputtering away an entire surface layer of the sample, enabling a much faster analysis [24]. However, simultaneous sputtering creates a complication for heterogeneous samples, especially when quantification of both concentration and depth are desired.

Several aspects of depth-profile GD analysis can limit precision and accuracy. Instrumental conditions can play a role if redeposition occurs [25], electric fields are uneven [26], or conditions in the discharge change [26]. Interfacial effects can also be important if the transition between layers is large enough [27]. In such situations, errors from earlier layers are propagated through the sampling process such that each subsequent interface appears broadened [28]. The paucity of high-quality layered standards is also limiting in many cases.

Of course, depth quantification is further complicated by the need to convert emission signal to concentration (y-axis of a depth profile) and time to depth (x-axis). This two-part quantification problem has been described in detail elsewhere [29]. Additionally, variation at a sample interface can be dealt with mathematically to deconvolve unevenness

that can evolve at such interfaces [30]. However, all these methods currently require the assumption that the layers are generally homogeneous.

The present study focuses on challenges for GD depth profiling that arise because of the expectation of laterally homogeneous samples and how observations of intentionally heterogeneous samples provide insight into how heterogeneity in GD samples is manifested in an analytical signal. These studies include an examination of how theory that assumes lateral homogeneity can be affected by sample inclusions. Experimental results indicate also the manner in which heterogeneities and surface morphology affect signals from both the minority inclusion and majority constituent of the sample.

2. Materials and methods

2.1. Simulation program

The simulation program was written in LabVIEW™ 14 (National Instruments, Austin, TX). The operational principles behind the simulation's operation can be found in Fig. 1; the program itself is available as electronic supplementary information.

2.2. Sample preparation

Simulated metal inclusions were inserted into samples by drilling small holes of the same diameter as a piece of the selected metal wire. Care was taken to ensure that the holes extended only part way through the sample. A small segment of wire was then pressed into each hole after which the sample was ground flat. All samples were ground and polished with 4/0 grit polishing paper before analysis. Copper (1 mm, bare copper wire, p/n 155452A, Fisher Brand), aluminum (1 mm, 99.999% Al, Alfa Aesar, p/n MFC00134029), and silver wire (2 mm, 99.9% Ag, Acros Organics, p/n 317720010) were all inserted as inclusions in brass. Microscopic examination of these inclusions found no observable gaps between the materials before they were sputtered with the glow discharge. A scratched brass sample was created by dragging a stainless steel screw across the brass surface after grinding and polishing.

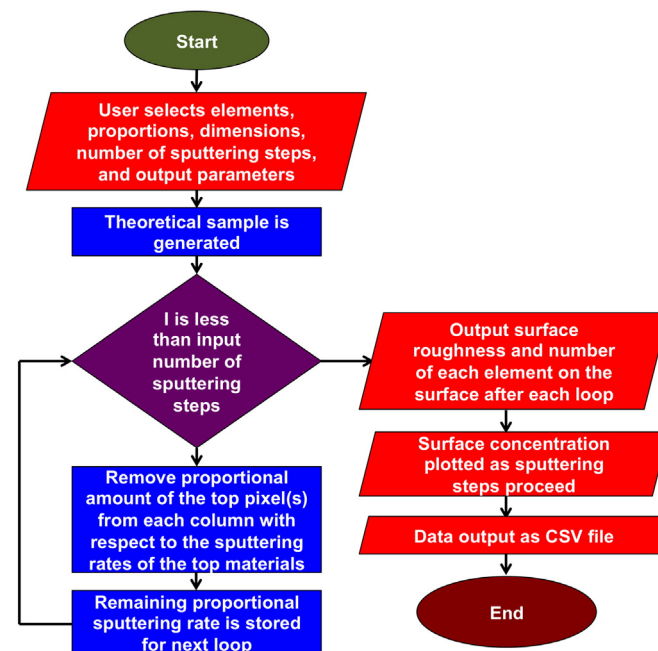


Fig. 1. Flow chart of essential operations of the sputtering-simulation program. Operational program can be found in electronic supplemental material.

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