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M.P. Seah, A.G. Shard

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The matrix effect in secondary ion mass spectrometry

by

M. P. Seah and A. G. Shard

Analytical Science Division, National Physical Laboratory, Teddington,
Middlesex TW11 0LW, United Kingdom

ABSTRACT

Matrix effects in the secondary ion mass spectrometry (SIMS) of selected elemental systems have been analyzed to investigate the applicability of a mathematical description of the matrix effect, called here the charge transfer (CT) model. This model was originally derived for proton exchange and organic positive secondary ions, to characterise the enhancement or suppression of intensities in binary systems. In the systems considered in this paper protons are specifically excluded, which enables an assessment of whether the model applies for electrons as well. The present importance is in organic systems but, here we analyse simpler inorganic systems. Matrix effects in elemental systems cannot involve proton transfer if there are no protons present but may be caused by electron transfer and so electron transfer may also be involved in the matrix effects for organic systems. There are general similarities in both the magnitudes of the ion intensities as well as the matrix effects for both positive and negative secondary ions in both systems and so the CT model may be more widely applicable. Published SIMS analyses of binary elemental mixtures are analyzed. The data of Kim et al., for the Pt/Co system, provides, with good precision, data for such a system. This gives evidence for the applicability of the CT model, where electron, rather than proton, transfer is the matrix enhancing and suppressing mechanism. The published data of Prudon et al., for the important Si/Ge system, provides further evidence for the effects for both positive and negative secondary ions and allows rudimentary rules to be developed for the enhancing and suppressing species.

1. Introduction

It has been known from the earliest days that the absolute intensities in secondary ion mass spectrometry (SIMS) are not simply related to amounts of matter in the analytical volume. In dilute systems, where concentrations were significantly lower than 1%, linearity could be assumed and amounts of matter were linearly related to the signal. Coupled with the very high sensitivities of SIMS for many elements, this led to the flowering of SIMS for depth profiling measurements of delta and similar layers for the microelectronics sector [1,2]. The non-linearity at higher concentrations could be avoided by analysis using Auger electron spectroscopy (AES) [3] or X-ray photoelectron spectroscopy (XPS) [4] where these non-linearities were very much weaker and could be computed relatively easily [5-7]. This provided a situation where a good “work-around” was possible; it was inconvenient but problems could be solved. In more recent studies of organic materials, however, the XPS is insufficiently detailed in its characterization and SIMS must be used to identify the different materials [8-10]. This area of organic nano- and layer-analysis is one where SIMS can be very powerful. However, for this, we are now forced to address the problem of signal non-linearity at non-dilute levels.

In one of the earliest studies of quantitative SIMS, Andersen and Hinthorne [11] applied the Saha-Eggert ionization equation to show that in mixtures of elements, the positive ion yield could be related to the neutral yield by an equation involving the important factor $\exp(-E_I/kT^+)$ where E_I was the ionization potential and T^+ was the effective temperature in the sputtered plasma at the surface. A similar factor, $\exp(E_A/kT)$, was obtained for the negative

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