Electronic Supplementary Material (ESI) for Journal of Analytical Atomic Spectrometry.

Supporting information

A correlative method to quantitatively image trace concentrations of elements by combined SIMS-EDX analysis

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For comparison of the information depths of EDX and SIMS, Monte-Carlo based simulations were carried out. The EDX information depth was investigated by simulating the electron beam induced X-ray generation using CASINO v2 [1]. Pure copper was selected as the target sample for simulation and the number of primary electrons impinging the sample was set to 10^5. All the simulations parameters were set to similar values as in the experimental parameters of the SEM-EDX analysis.

The SIMS information depth was investigated using SD_TRIM_SP code.[2] It is based on the simulation codes TRIM[3,4] and TRIDYN[5,6]. Oxygen ion irradiation on Cu was simulated with the ion bombardment energy of 16 keV at normal incidence, which corresponds to the experimental conditions for imaging in SIMS mentioned above. During the simulations, the KrC potential has been used for interatomic interactions, the Oen-Robinson model for electronic stopping and the Gauss-Mehler method with 16 pivots for integration. The surface binding energy is calculated using $sbe(i,j) = 0.5\left(Es_i + Es_j\right)$, where sbe is the surface binding energy for the target of consideration and Es_i is the atomic surface binding energy[2].

It is known that SIMS is a surface technique whereas EDX in general has a large information depth in bulk samples. The results of the simulations are shown in Fig. S1. The range of the primary electrons and their energy range are shown in Fig. S1 (a). Similarly, the ion trajectories related to are shown in Fig. S1(b). As the simulation parameters correspond to typical experimental conditions, the results for Cu can be treated to broadly represent most inorganic materials. To highlight the difference in length scales, Fig S1(b) is also presented as an inset in Fig S1(a). To compare the information depth quantitatively, the depths from which the X-rays (for EDX) and secondary ions (for SIMS) emanate are compared in Figs. S1(c) and (d) respectively. From Figs. S1 (a)-(d), it is evident that there is a large difference in the information depths between the two techniques. While the X-rays emerge from several hundreds of nanometres depth, secondary ions emerge from the first few monolayers. Hence, addressing this difference is important in any method which combines EDX and SIMS data. The current method described in the main manuscript overcome this because of the fact that the diffusive flux is not depth dependent in the diffusion couple. Hence, the composition is essentially depth invariant. In this way, we overcome the issues related to the difference in information depths between EDX and SIMS techniques.

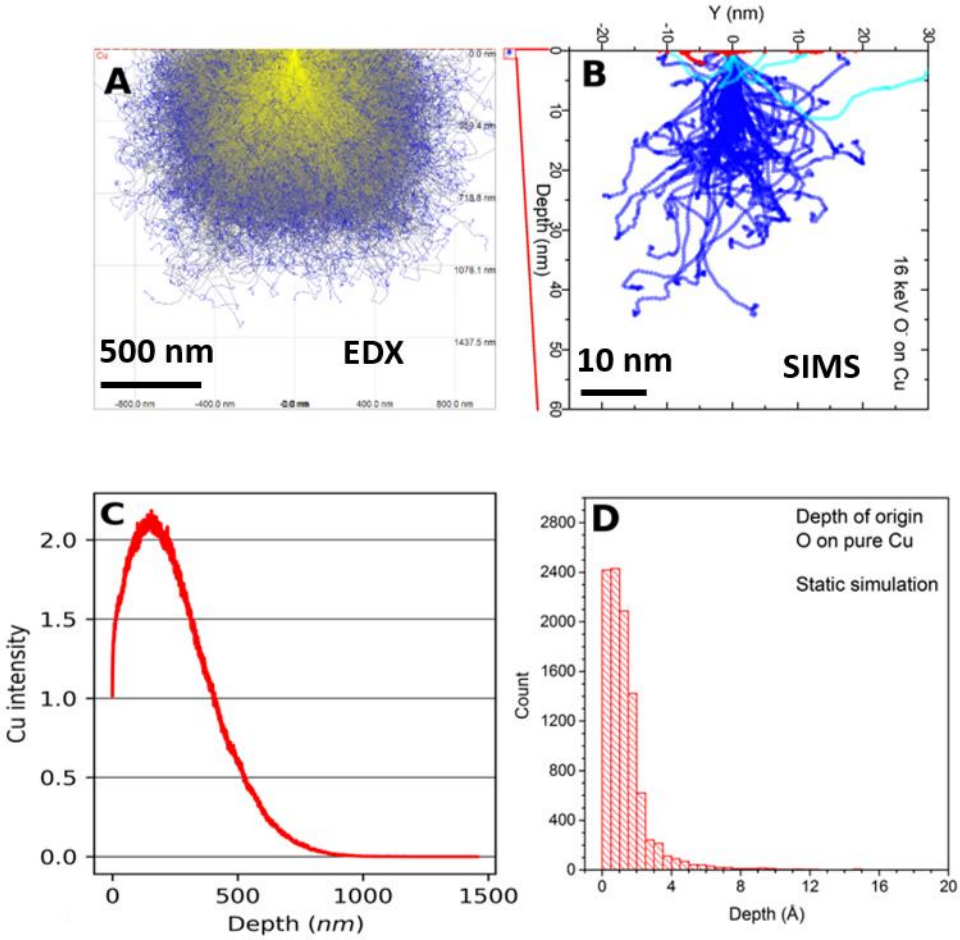

Figure S1: Monte-Carlo simulations for electron-solid and ion-solid interactions were carried out to compare the information depths between (a) EDX and (b) SIMS techniques for the experimental conditions used. Pure Cu was taken as the target sample with irradiation of 20 keV electrons for EDX and 16 keV O^- ions for SIMS. The colours in (a) indicate primary electron energy from yellow (20 keV) to blue (0 keV). The colours in (b) indicate sputtered Cu atoms (red), implanted primary oxygen atoms (blue) and backscattered primary oxygen ions (cyan). The depths from which the X-rays (EDX) and secondary ions (SIMS) emerge are compared in (c) and (d) respectively.

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