Effects of Sample Preparation in Analysis: Spectroscopy

D.B. Williams and M. Watanabe

Dept. of Materials Science and Engineering, Lehigh University, Bethlehem, PA18015, USA

The principal aim of X-ray and electron spectrometry in the analytical electron microscope (AEM) is to determine the local (usually nanometer-scale) elemental composition (via X-ray energy dispersive spectrometry (XEDS) and electron energy loss spectrometry (EELS)). Related phenomena such as the chemical bonding state (via energy-loss near edge structure (ELNES)) and atomic arrangement (via extended energy-loss fine structure (EXELFS)) are also if interest. From the specimen preparation standpoint, therefore, the major concerns for the analyst are that the preparation process preserves the elemental composition and bonding state of the atoms in the bulk sample, during the thinning to electron transparency. In contrast to the thinning of specimens for imaging, we are less concerned about the generation of, or re-arrangement of, crystal defects, so long as such processes are composition–independent, which they usually are. It is possible that specimen preparation may change the local atomic arrangement thus potentially limiting EXELFS but that remains a rarely-used aspect of AEM and this paper will emphasize the chemical composition aspects of AEM only.

By definition, thinning processes attack the surface of the bulk sample by a variety of mechanical (grinding, polishing, microtoming, ion-beam sputtering, cleaving) and/or chemical (electropolishing, electroetching, oxidizing/dissolving, reactive ion etching) processes [1]. While many of these processes clearly alter the chemistry/bonding of the surface under attack, none of the processes affect significantly the internal chemistry of the thin foil. Therefore, it is the surface chemistry (i.e. the surface composition and the surface bonding) effects that must concern the analyst, since any of the above techniques (except perhaps cleaving and microtoming) will in some way modify the surface chemistry.

Before panicking and deciding that thinning will always limit the analysis, so why bother, it is worth remembering that the greatest advantage of AEM is the high spatial resolution due to the small electron probe and the small analysis volume in thin specimens. This combination also results in relatively poor counting statistics for both XEDS and EELS which, in turn, brings with it a relatively poor analytical sensitivity (~ 0.1 wt. %) and limited accuracy of quantification (~ $\pm$ 10%). Therefore, if it is possible to confine the effects of changes in surface chemistry/bonding to a fraction of the thickness of the specimen that is smaller than the error that can routinely be expected in quantification/sensitivity, then specimen preparation effects can be ignored. For example, if typical quantification accuracies are $\pm$ 10% relative then if the combined thickness of the top and bottom surface-modified layers is <10% of the thickness of the analyzed volume, then specimen preparation effects are not limiting the analysis. So the crucial questions to be addressed are a) how thick is the surface modified layers and b) how can they be minimized?

Of the typical thinning processes, mechanical methods of any form can result in significant (> micrometer) sub-surface damage and smearing of the structure. However, mechanical polishing to final transparency is so rarely used that this can be ignored. Most final thinning steps require ion beam sputtering or electro-chemical attack in some form. It has been known since the earliest days of AEM [2] that electropolishing can result in serious changes in the surface chemistry, which prevents realistic analysis of the thin edges of electro-polished specimen unless they are cleaned by a chemical that only attacks the electro-chemical surface product, or by ion beams [3]. So electropolishing is probably the most dangerous specimen preparation tool for the analyst, although by no means one that should be automatically discarded. Ion beam methods have improved significantly over the 30 years since the first primitive instruments appeared [4]. Techniques such as Gatan's PIPS (precision ion polishing system) and focused ion beam (FIB) thinning mean that thin specimens of almost any combination of materials can be produced with surface damage confined to a level that affects only the thinnest regions (< ~5 nm). Even in any

damaged areas, it is residual Ar or Ga that might be the only chemical change of consequence and since the analyst is rarely interested in quantifying Ar or Ga and overlap of the Ar and Ga peaks with other elemental peaks is not a serious problem (one minor overlap is the Ga Kα peak with the Ir Lα peak). For example, figure 1 shows a typical spectrum from a homogeneous Cu-Mn specimen prepared by Gatan's PIPS (a) and the measured Ar composition is plotted as a function of thickness (b). While the effects of residual Ga seem higher in the FIB specimen, as shown in figure 2, the influences of the residual preparation-induced impurities on the overall analyses are very minor. However, it should be noted that re-deposition of marking/protecting materials for FIB specimen preparation, such as W or Pt, may also cause an overlap problem (e.g., the overlap of W Mα with Si Kα).

So, ion-beam thinning in some form should be the specimen preparation method of choice for the analytical microscopist, (or at least the last stage of any multi-stage thinning process) - except perhaps if you are analyzing trace amounts of Ir.

References
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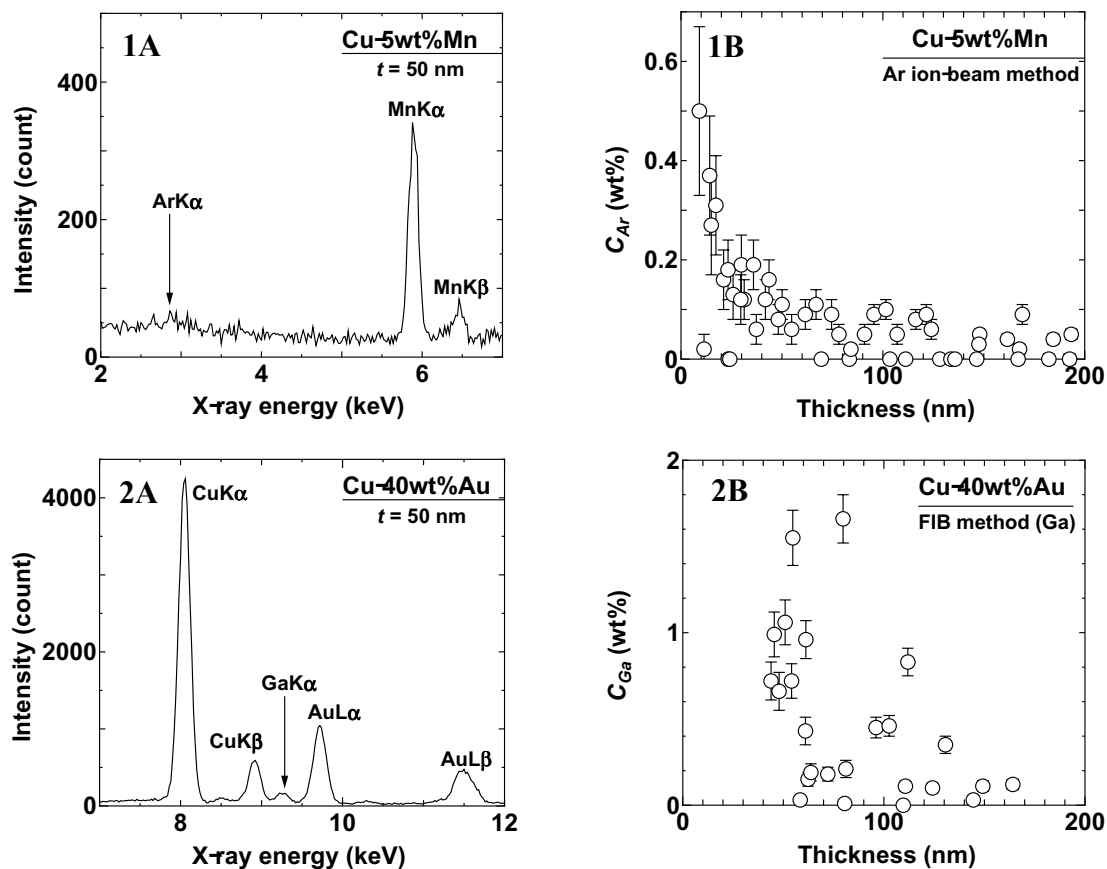[5] This research was supported by NSF DMR 99-72670.

Fig. 1 A typical XEDS spectrum from a Cu-Mn specimen prepared by Gatan's PIPS (A) and the measured Ar composition plotted as a function of thickness (B).

Fig. 2 A typical spectrum from an FIB-prepared Cu-Au specimen (A) and the measured Ge composition plotted as a function of thickness (B).