3.1 Introduction

The main point of spectrometry performed point-by-point using an electron probe of nanometre dimensions is to acquire chemical and electronic information about the defects and interfaces which control structural, electronic and optical properties of materials. According to some, our civilisation now depends upon electrical current sheets travelling along the interfaces between silicon and its oxide; others claim that it depends upon load transfer across the interfaces between weak, ductile metals bonded to strong but brittle fibres. Every polycrystalline material depends upon its grain boundaries, whether for strength or for optical transparency. Analytical electron microscopy, particularly EELS acquired using STEM, is the unique experimental method available to probe the interfacial density of states as well as the chemistry and the structure of such interfaces. Although it is a relatively new technique still improving, it has already solved a number of problems which could not otherwise be tackled. However, its main fundamental limitation is the damage caused to the material by the intense focused probe of electrons in the time required to extract the desired information.

3.2 Spatial Information

The preferred method of deriving spatial information from EELS is to compare directly spectra from one probe position to the next, for example the 'spectrum-line' methods introduced by Colliex and co-workers [1] and the changes in the EELS as the probe is moved from one atomic column to the next: Batson [2], Browning et. al. [3], and Muller et. al. [4]. In spite of the complications in interpretation of spectra, subtraction of one spectrum from another taken from a neighbouring position is assumed to reveal the difference in the density of states accessible to the appropriate core electrons: thus changes in the d-band occupancy at grain boundaries in transition metals can be observed [5], Muller [6], Botton and Humphreys [7], Ozkaya et. al. [8], and differences at the cores of dislocations studied [9]. It is unlikely that complications such as excitons will prove difficult, since they cancel out in the difference spectrum. Such
experiments seem poised to become an important new field of solid-state spectroscopy, unrivalled for spatial resolution and directness of approach. These experiments are scarcely possible in XAS with its unfocused beam. It is irresistible to reproduce, in Fig. 3.1, Batson's [2] demonstration of the change in oxidation state of silicon across a silicon-silica interface; column-by-column changes can be followed in the Si L_{23} edge. This is at the limit of achievable spatial resolution using 100 kV instruments: using equation (2.3), we find that the impact parameter with a value of 0.4 nm probably dominates the effective spatial resolution in the spectral information.

![figure 3.1](image_url)

Figure 3.1. Spectrometry at the highest spatial resolution, as exemplified by Batson [2]. The white blobs are Annular Dark Field images of atomic columns of Si atoms in crystalline silicon, merging into the oxide which is dark and without structural detail because it is amorphous and has lower scattering power. The Si L edge reveals changes in the electronic state of the Si almost column-by-column across the interface.

However, even in robust metallic samples, radiation damage by the focused probe may be what limits observation of localised states at grain boundaries (Ozkaya et. al. [8]). In these cases, progress can be made by using the 'spatial difference method' where one acquires a spectrum from a large area containing the boundary, and then one from a neighbouring region but excluding the boundary. The difference between the two spectra reveals the extra empty states at the boundary, and of course any impurities which may be segregated there. Thus radiation damage is avoided but at the cost of reduced spatial resolution.