High spatial resolution studies of surfaces and small particles using electron beam techniques

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ABSTRACT

A brief review is given of studies of surfaces and small particles using electron beam techniques. The principal tools are secondary, Auger and backscattered electrons, either energy-filtered using various types of analyzers, or as a stronger signal with coarser energy filtering. These tools have been deployed in wide-beam surface science instruments, but also increasingly in scanning electron and scanning transmission electron microscopes, especially in ultra-high vacuum instruments capable of analyzing clean surfaces. The different choices that need to be made are illustrated with examples of clean surfaces, thin films and catalyst particles at high spatial resolution.

Keywords: UHV electron microscopy; secondary electrons, Auger electrons, backscattered electrons, surfaces, small particle catalysts

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1. Introduction to surface microanalytic techniques

Most physics-based techniques can be classified as scattering experiments: a particle is incident on the sample, and another particle is detected after the interaction with the sample. Surface sensitive techniques are no exception; we have an incident electron probe, with a well defined energy E_0, and maybe a well defined wave-vector k_0, or equivalently momentum $p_0 = \hbar k_0$. The response particle in our case is another electron. If we understand the nature of the scattering process, then we can interpret the experiment and deduce corresponding characteristics of the sample. Here we concentrate on secondary, Auger and backscattered electrons in section 2, while recognizing the strong connection with energy loss electron spectroscopy (EELS) and X-ray emission spectroscopy, which are discussed in other papers in this volume. Quantification of Auger electron spectroscopy (AES) is discussed in section 3.

These signals can be measured on a microscopic scale in several ways. Scanning Electron Microscopy (SEM) has various operational modes, which depend on the detection system, and on whether the energy E and/or the wave vector (momentum) $k(p)$, and maybe other attributes, are measured. Scanning Auger Microcopy (SAM) is the child of AES and SEM, and is fairly widely available as an ultra-high vacuum (UHV), clean surface instrument. UHV-SEM-SAM has been developed in several laboratories, including the University of Sussex, and UHV-STEM (scanning transmission EM) especially at Arizona State University, and the potential of high resolution SAM has been evaluated. Particular developments of surface sensitive SEM and SAM are explored here in sections 3 and 4.

All these techniques are useful for studying surfaces and small particles. The reason is that either the probe or the response particle has a short mean free path, λ, and so is sensitive to scattering events close to the surface. The prime example here is AES, where the emerging electrons in the energy range 100-2000 eV have λ for *inelastic* scattering in solids typically in the range 0.5-2.5 nm. By using an analyzer to measure only those Auger electrons that have not lost energy, the signal from subsurface layers is strongly attenuated. Even without an energy analyzer, secondary electrons are also fairly surface sensitive, with λ values up to 10 nm. But low energy secondary electrons can be even more sensitive to surface layers, via changes in the work function. This feature enables UHV-SEM to detect sub-monolayer quantities of adsorbates in favorable cases. Several practical examples and many references are given in a graduate teaching and source text by one of the authors [1]. Some of these examples are highlighted here.

There is also great interest in other techniques, which, while not being chemically specific as SAM, have much greater signal levels and/or better signal/background levels. The use of secondary and backscattered electrons, and low voltage microscopy are examples. These developments are discussed in the context of research on small particles in section 5.

2. Chemical and electronic state information, and instrumental effects

If we bombard a sample with electrons, or with other particles such as photons or ions, electrons will be emitted which have an energy spectrum, shown schematically in Fig. 1a. Secondary electrons are the signal normally used to form an image in the SEM, and AES uses Auger electrons to determine surface chemical composition. As an example, Fig. 1b shows the energy level scheme associated with the Si $KL_1L_{2,3}$ transition, one of a set of KLL transitions, the strongest of which is at ~1620 eV, with λ in solid silicon observed to be just below 2 nm.

The close relationship between the various possible processes indicated in Fig 1b has been well known for a long time [1, 2], though not always emphasized in the subsequent literature. All processes stem from the initial ionization event, which kicks out one (secondary) electron, leaving a core hole, and converts the incident electron into the energy loss electron that is measured by EELS. The relaxation event that follows may result in an X-ray, or the corresponding energy may be converted into an Auger electron that is measured in AES. For low energy transitions, Auger emission is strongly favored. The Auger process thus involves three electrons, and leaves the atom doubly ionized. The Auger effect is due to the Coulomb interaction between the core hole and the ejected electron, which leaves the other hole behind. The Auger efficiency $\gamma = 1 - \varpi$, where the X-ray fluorescence yield is ϖ; the proportion of K-shell Auger emission is greater than 0.5 up to about $Z = 30$ (zinc). Auger energies, and approximate relative transition rates are well known, and are typically displayed in every surface science laboratory. Accurate intensities, both experimental and theoretical, are however another story: the spectrum shown in Fig. 2 was one of the first to be calibrated on an absolute intensity scale [4]. The theory is rooted in atomic physics [5], and is only modified slightly by solid state and surface effects, as discussed in outline here and in more detail elsewhere [1, 3].

The width of the Auger peak is typically 1-2 eV, due to a rather short lifetime before Auger emission. The Auger peak width can be further broadened by overlapping peaks, by wide valence bands, or by analyzers set to increase sensitivity at the expense of resolution. The state of

matter affects the line-shape, and causes energy shifts. If the transitions involve the valence band, then we refer to LVV etc, or more generally to core-valence-valence (CVV) transitions. For example, Si LVV has a transition at ~90 eV; this transition is sensitive to chemical state; Al LVV has a different line-shape in metallic Al and in aluminum oxide, and Ni MVV in Ni silicides of various compositions [1,6,7]. Many authors have studied the corresponding core level shifts in photoelectron spectroscopy (UPS and XPS). More details, applications to semiconductor and other surfaces, and further references are given in references [1, 7-9].

Auger electron energies have historically been given by approximate formulae, e.g. by Chung and Jenkins [10]:

$$E(KL_1L_2) = E_K(Z) - 0.5 \{E_{L1}(Z) + E_{L2}(Z)\} - 0.5\{E_{L1}(Z+\Delta) + E_{L2}(Z+\Delta)\}, \qquad (1)$$

where the use of the average energy is due to being unable to distinguish which electron filled the core hole. The correction Δ has been used to indicate that the final emission is from an ion, not a neutral atom, which shifts the final energies downwards slightly. Calculations need to take into account whether the atom in question is *L-S* or *j-j* coupled; for example the main KLL transition in silicon has a $^1D_2$ final state. Si KLL is primarily a case of *L-S* coupling, since the atomic number is small, whereas Ge KLL is in the intermediate coupling regime [11]. A high-resolution spectrum shows these effects, as for Ge LMM in Fig. 2 and for Si KLL and Ag MNN later in Fig. 5. What one can see in the spectrum depends on both energy resolution and signal to noise ratio (SNR), and if X-ray excitation is used, the secondary electron background can be much reduced over electron excitation. So the peak to background ratio, while very useful for analysis as we shall see later, does depend on the analyzer settings, the mode of excitation, and the excitation energy.

The problem of measuring the electron energy spectrum is non-trivial. There are various possible geometries for the analyzers, and the measurements can be performed in an angle-integrated or angle-resolved (AR) mode. Electrostatic electron energy analyzers in common use for bulk samples are the cylindrical mirror analyzer (CMA) and concentric hemispherical analyzer (CHA) [1,12]. They can be operated with retardation, so that the pass energy is less than the energy of the electron being analyzed; this is easier for the CHA, with retarding lenses in front of the analyzer, and can lead to good energy resolution in the resulting spectrum.

If the analyzer is retarded to a constant pass energy, then the spectrum reflects $N(E)$, which is often peaked at low energies, since secondary electron emission is strong. If there is no

retardation, or if the pass energy is a constant fraction of the analyzed energy, then the spectrum reflects $EN(E)$. In many older instruments, this signal was differentiated to improve the SNR [6]. Here we concentrate on $EN(E)$ signals, which, with single particle counting digital detection schemes, have as good a SNR as possible, i.e. provided practical issues such as reducing the effects of stray (magnetic) fields on the analyzer transmission at low energies are solved [13].

If one can detect neighboring energies in parallel, so much the better; this can be done relatively easily with the CHA, but is more difficult with the CMA. Many electrostatic analyzers have been developed to exploit parallel recording, often in energy, but sometimes in angle or beam position. These parallel angle-resolving analyzers have been most successful in the synchrotron environment [14], but parallel energy recording is being pursued in connection with scanning microscopes; a recent example from the York group is described in refs [15]. Parallel angle-resolving analyzers are capable in principle of measuring AR-effects in samples, such as crystallographic and so-called holographic effects, but this large topic is not discussed here.

The magnetic sector, and the related Omega filter spectrometers are used for EELS in conjunction with TEM or STEM. They have very good energy resolving power, but collect electrons only over a small angular range; this is well suited to the strongly forward peaked scattering that occurs at TEM energies (≥ 100 keV) with thin film samples, but is not good for bulk samples at lower beam energies. In recent developments, EELS is being pushed towards single column resolution, and ≥ 300 keV, aberration corrected, field emission probes may make this spatial resolution almost routine. The energy resolution can also be impressive [8], and will improve in future, with additional energy filtering of the source. The signal is integrated down the column, and so this form of (high energy) EELS is not specifically surface sensitive. But once we have thin samples, distinctions between the surface and the bulk become blurred: we simply evaluate the usefulness of each technique for solving specific problems.

3. Quantification of Auger spectra

The general equation governing the Auger electron current, I_A caused by a probe current I_p can be written down easily, but really needs a schematic drawing, such as Fig. 3. For a bulk sample, the incoming electron causes an electron cascade below the surface, whose spatial extent is typically much greater than the imfp. For example, the spatial extent is about 0.5 μm at an incident energy $E_0 = 20$ keV, but also depends on the material and the angle of incidence, θ_0. As

a result Auger electrons can be produced by the incoming primary electron beam, and also by the backscattered electrons as they emerge from the sample; the Auger signal intensity thus contains the backscattering factor, R, which is a function of the sample material, E_0 and θ_0.

The ratio I_A/I_p can be expressed as a product of terms describing the production and detection of the Auger electrons, as first developed by Bishop and Rivière [2], and the same formulation has been used many times since [e.g. 4, 16]. The Auger yield Y is the number of Auger electrons emitted into the total solid angle ($\Omega = 4\pi$ sterad). It is therefore not dependent on the details of the analyzer. The detection efficiency D of the analyzer can be written as ($T.\varepsilon$), where T is a function $f(\Omega_a/4\pi)$, Ω_a being the solid angle collected by the analyzer, and ε is $f(\Delta E/E)$, most simply $\varepsilon = (\Delta E/E)$. Thus

$$I_A/I_p = Y.D = [\sigma\gamma R].\sec\theta_0.N_e(T.\varepsilon). \tag{2}$$

Here we have Y expressed as the cross-section for the initial ionization event (σ), the Auger efficiency (γ), discussed in outline in the previous section, and the factor R. The $\sec\theta_0$ term describes the extra ionization path length caused by having the primary beam at an angle θ_0 to the sample normal. Finally N_e is the effective number of atoms/unit area contributing to the (particular) Auger process.

What we actually want to know is: given a measured signal I_A, how many A-atoms are there on the surface? Typically there is not a unique answer to such a simple question, because the signal depends not only on the number of atoms but also on their distribution in depth. There are two cases that can be solved uniquely, which are instructive in showing how such analyses work. The first is when all the atoms are in the surface layer: then $N_e = N_1$, and if one knew all the other terms in the equation, we could determine N_1. The second case is when the atoms are uniformly distributed in depth: in this case we can show that $N_e = \lambda N_m$, where N_m is the bulk (3D) density of A-atoms. Both these cases are illustrated in detail elsewhere [1, 16].

Batchelor *et al.* [16], amongst others, have performed an experimental and computational study of Auger signals from bulk elemental samples. These studies show that the dependence of the Auger peak height on primary beam energy E_0 explores the variation of (σR); the variation with θ_0 is determined by ($R\sec\theta_0.T$). The dependence on atomic number Z is complicated, since all the above material variables and the Auger energy are properties of the individual element in question.

To make these comparisons, a particular ionization cross-section was taken, and the Auger backscattering factor $R = 1 + r$ calculated with this cross section, where r is defined as

$$r = (1/\sigma(E_0)\,\sec\theta_0)\iint \sigma(E)(\mathrm{d}^2\eta/\mathrm{d}E\mathrm{d}\theta)\sin\theta\mathrm{d}\theta\mathrm{d}E, \qquad (3)$$

where the normal electron backscattering factor η is given by

$$\eta = \iint (\mathrm{d}^2\eta/\mathrm{d}E\mathrm{d}\theta)\sin\theta\mathrm{d}\theta\mathrm{d}E. \qquad (4)$$

This means that the Auger backscattering factor can be written as $R = 1+\beta\eta$, where the factor β is typically greater than 1, and depends on the energy and angular distribution of backscattered electrons, and the Auger energy in relation to the beam energy. Comparison of the energy dependences of the cross sections and other checks on absolute values has advanced knowledge of which cross sections are reliable [4,16,17].

The peak to background ratio (P/B or PBR) can be measured accurately and is very useful as an approximate compensation (although it may somewhat over-compensate) for topographic effects [6]. This angular dependence is rather flat as shown by Batchelor *et al.* [16] for Cu, Si and W Auger electrons measured in two different instruments. At high incidence angle, there is much less variation in the back scattering factor as a function of atomic number, and the background becomes dominated by secondary electrons, which have similar excitation mechanisms to Auger electrons. This is mirrored in the PBR as a function of E_0. Above 15-20 keV both Cu L_3MM and Si KLL show no dependence on E_0; this effect sets in at lower E_0 for lower energy transitions, where the background comprises secondary rather than backscattered electrons [16].

Detailed study of the basic quantification equation leads to some interesting physics, and often to a determination of one or more parameters of the experiment, but it does not lead directly to easy sample analysis. For this we have to keep many of the experimental parameters fixed, and use standard samples for comparison. Ratio techniques are common in all forms of quantitative analysis, principally because they allow one to eliminate instrumental variables [1,2,12]. The measurement is then the value of (I_A/I_p) for the sample (s), ratioed to the same quantity for the (pure element) standard (el). Comparing the terms in the quantification equation, the only terms which do not cancel out, for bulk, uniformly distributed samples, are

$$(I_A/I_p)_s/(I_A/I_p)_{el} = (R_s\lambda_s/R_{el}\lambda_{el}).(N_s/N_{el}); \qquad (5)$$

the factor in the last bracket is what we want to know, and the previous term is a 'matrix dependent' factor. Without detailed calculation it is not obvious how such terms behave, but they

can sometimes vary slowly. For example, it has been shown that the matrix dependent factors often vary linearly with composition in binary alloy systems [18].

A typical 'surface science' application of AES is to distinguish layer by layer from other types of growth. Layer growth is a case which one can work out easily if we disregard (the minor) changes in the backscattering factor; the experimental ratio is (I_A/I_p) for a multilayer divided by (I_A/I_p) for a monolayer (ML). Here we assume that there are N_1 atoms in the first layer, N_2 in the second and so on, and their spacing is d. Then we can work out the signals at coverage θ between n and $n+1$ ML from both layers and substrate, as summations that take attenuation into account. For example, if $n = 1$, and we neglect attenuation within the first layer

$$N_e = N_1[(2-\theta) + (\theta-1)\exp(-d/\lambda\cos\theta_e)] + N_2, \tag{6}$$

where the first (second) term in square brackets correspond to the proportion of the first layer which is uncovered (covered) by the second layer, and so on.

This relation leads to a series of straight lines, often plotted as a function of deposition time, from which the λ can be deduced in favorable cases. The simplest case, where there are the same numbers of atoms in each completed ML, can be worked out explicitly. In that case, the slope of the second ML line ratioed to that of the first ML gives $\exp(-d/\lambda\cos\theta_e)$, from which d/λ can be extracted if the effective analyzer angle θ_e is known. This effective angle is given by

$$\cos\theta_e = (1/\Omega_a)\iint \cos\theta_a.\sin\theta_a d\theta_a d\phi_a, \tag{7}$$

where the integrals are taken over the analyzer acceptance; the angular integration is performed numerically. There has been much discussion over what λ really is in such experimental comparisons; it is now accepted to be the attenuation length (AL), which is shorter than the imfp due to elastic (wide angle) scattering [19]. However, as pointed out by Cumpson & Seah [20], unless the integration of (7) is performed separately (as implied here), the AL also depends on the type of analyzer used and the angular range accepted; thus in some papers the AL is not a material constant, and one should beware of using published values uncritically. This topic has been revisited in several updates of databases: at NPL in the UK [4, 20], NIST in the USA [21], as well as by other groups [22].

There are many layer growth analyses in the literature, in some cases with a large number of data points showing relatively sharp break points at well-defined coverage, such as for Ag/W(110) [23]. Here we consider the case of Fe/Ag/Fe(110) [24, 25]. Ag/Fe(110) is a typical layer plus island growth system, with two layers before islands form, the first of which has the

c5x1 structure, which has a nominal coverage of 0.8 ML, and the second is close to a compact Ag(111) layer. There is nothing unusual about the Ag/Fe(110) interface; it is very similar to Ag/W(110). However, deposition of Fe on thin films of Ag/Fe(110) results in some interdiffusion, the extent of which depends on the Ag film thickness, deposition and annealing conditions. This example is shown in Fig. 4, where the ratio of Ag/Fe AES intensities is plotted against Fe coverage, and is compared with a layer growth calculation [25].

The lower curves are calculated assuming no surface segregation, the two curves reflecting some uncertainty in the correct inelastic mean free path for the Auger electrons, as discussed in [22]. For deposits of less than 1 ML at room temperature, the data follow this layer growth curve, more or less. But between 1 and 2 ML, there is clearly some segregation, where the calculation assumes that all of the first 0.8 ML Ag has moved to the surface; this is clearly not a bad approximation. But annealing to around 250°C results in more segregation, and deposition at 250°C results in almost complete segregation. Results for other Ag layer thicknesses show a similar trend; interdiffusion at the ML level proceeds even at room temperature, and there is long range interdiffusion already at a few 100°C.

4. Scanning electron and Auger microscopy

In a UHV, clean surface environment, there are several SEM-based techniques that are surface sensitive at the ML and sub-ML level. In several papers, the Sussex group has shown that the low energy secondary electron signal is very sensitive to work-function and other surface-related changes; by biasing the sample negative to a bias voltage V_b between -10 and -500V, we can obtain biased secondary electron images (b-SEI), and ML and multilayer deposits can be readily visualized and distinguished [24-26]. In extreme cases, such as Cs/W(110) and Cs/Si(001), sensitivity approaching 0.01 ML has been demonstrated [27].

Following on the discussion in the previous section, we can think about the extraction of Auger data from energy-selected line scans and images, and quantification of such information. We need to use ratio techniques for several reasons. First, typical samples are not flat, and may be extremely rough, or can involve changes in backscattering factor. This leads to variations in ($r\sec\theta_0.T$). Second, one needs to have Auger information, which (if possible) is independent of these changes in the background spectrum, and of beam current fluctuations. The first goal is not entirely possible, but one can make a good attempt. By taking line scans or images at one or

more energies in the background above the peak (B and maybe C), then difference techniques can be constructed to extract better Auger information. The ratio most commonly used is a quasi-logarithmic measure of Auger intensity based on two channels only,

$$I(\text{difference})/I(\text{sum}) = (A\text{-}B)/(A\text{+}B), \tag{8}$$

which is a first approximation to $(2EN(E))^{-1}.d(EN(E))/dE$ in the fixed retard ratio mode [6]. The simplest linear measure is based on an extrapolation of the background from C to B to A. Assuming these channels are equally spaced, then the

$$\text{Peak to background ratio } (P/B) = (A\text{-}2B\text{+}C)/((2B\text{-}C). \tag{9}$$

This measure is usually noisier than the ratio based on the two channels A and B, as discussed in some detail by Frank [28]. This is because one is in effect measuring the background slope at each pixel, as well as the peak height, a situation paralleled in analysis by EELS [8].

A particular problem faced by analysts in the 'real world' is that their samples contain many different elements; they may have rough surfaces, and this may interfere with quantitative analysis. However, they may not be so concerned about quantitative information at every point in the image; association of specific types of qualitative information with each point may be more informative. This type of ratio technique as applied to SEM/SAM started with work by Browning [29]. Prutton and El-Gomati's group at York has furthered these techniques, originally developed for satellite imaging by NASA/JPL, as described in more recent papers [15, 30]. Similar 'spectrum-imaging' techniques have been developed for EELS data [8].

In such an approach an SEM picture is taken of the whole field of view and a survey spectrum is taken from this area. This may show many peaks, some of them very small. The spectrum is used to identify energies (channels) at which information will be recorded at each point on the image, typically a peak (A) and a background (B) channel at higher energy, for each of the elements of interest. Before images are made with this information, scatter diagrams (which plot where individual image points fall as a function of specific peak height ratios) are constructed. These show that the ratio data cluster in well defined regions of the scatter diagram, and it is easy for the analyst to identify the clusters as particular phases, at least tentatively.

At this stage, one can place a software 'mask' over the data and use all the data which fall within this mask to form an image. In Browning's original work, an unknown phase was identified which contained Ti, Si, some S and also P. By setting limits on the various ratios, an image was then produced from the stored data set, which shows the spatial distribution of this

particular range of compositions. In this case it was shown that the 'phase' was formed in the reaction zone between the SiC fiber and the Ti alloy that made up the composite material.

A simpler two-component system, such as an evaporated tungsten pad on silicon can be used to explain the principles clearly. There is no real limitation to 2D data; experiments with 3D data sets have been reported [30]. These 'associative' or pattern recognition techniques are very powerful, but they do require that a lot of effort be expended on a particular small area. This concentration on one small area may well result in radiation or other forms of damage, as with EELS, and it is always possible that you could have got the answer you really needed faster by another technique. At high spatial resolution one needs to beware of various artifacts associated with sharp edges, essentially because part of the information comes from backscattered electrons. Some of these effects were studied early on by El Gomati *et al.* [6], and are discussed in several papers from the York group [15, 30], and in the book by Smith [12].

The development of SEM/STEM and AES/SAM at the highest resolution has been pursued at Arizona State University in what has become known as the MIDAS project, a Microscope for Imaging, Diffraction and Analysis of Surfaces. Figs. 5-7 are shown here to illustrate this project [1, 31]. The innovation as regards electron optics is to use the spiraling of the low energy electrons in the high magnetic field of the objective lens to contain the secondary and Auger electrons close to the microscope axis. These electrons are further controlled by auxiliary magnetic fields (parallelizers) in the bores of the lens, and by biasing the sample negatively. A special combination Wien filter/ deflector is then used to deflect the low energy electrons off axis through a right angle, while keeping the 100 keV beam electrons on axis. The low energy electrons then enter a commercial CHA. Because they spiral in the high **B** field and their angle to the axis decreases as the field weakens, quite a large proportion of the emitted electrons can be collected. This higher collection angle compensates for the lower yield at higher beam energy, and the smaller current available in the fine probe. In effect, a high magnetic field/ parallelizer/ CHA combination represents a different type of electron energy analyzer, which is uniquely adapted to high spatial resolution studies [32].

The quality of the spectra obtained is relatively high, both with respect to energy resolution (Fig. 5a) and to sensitivity (Fig 5b). Auger mapping is obtained by taking images *A* and *B* and using ratios $(A-B)/(A+B)$ as explained above. Fig. 6 shows the comparison of the b-SE image, with good SNR, and the Auger image, with relatively poor SNR, even after smoothing.

For imaging, we have to be clear about distinctions between 'image' and 'analytical' resolution. This is because of the non-local nature of the Auger signal, firstly from backscattered electrons as discussed already, but also at high spatial resolution because of the finite Auger attenuation length, and non-local excitation. Image resolutions below 3nm have been obtained on bulk samples in this instrument.

In the case of thin film substrates, we strongly reduce the backscattering contribution, so that the image and analytical resolutions converge on the image resolution, which in practice may well be limited by the probe size. Such high resolutions are of interest in small particle research, particularly in catalysis. Work on such samples is illustrated in Fig. 7, which shows energy-selected images of small Ag particles on a thin carbon substrate [33]. Here it is not so clear what the quantification routine ought to be, and in practice the raw *A* and *B* and simple difference (*A-B*) images for various elements are displayed. Even for small Ag particles, backscattering effects can be seen in the intensity of both carbon Auger images (Fig. 7c and d), but the carbon background is largely removed in the Ag difference image (Fig. 7f). Secondary electrons (Fig. 7e) show very similar information to energy-selected images, via the higher secondary yield of Ag. Even more interesting is that, for particles of size at or below the Auger attenuation length, the number of atoms in the cluster is measured by the integrated intensity of the particle, rather than the image size of the particle, and that such images can be internally calibrated, using large particles such as A in Fig. 7f. On this basis, it was concluded that particles such as B in this panel contained <10 Ag atoms.

We should note that, because of the high yield for Ag MNN Auger electrons, this is a favorable case; we are still quite a way from detecting arbitrary minority species on such small particles. Moreover, we are much more likely to be able to detect them first with a high SNR, qualitative, technique, such as b-SEI, than with low SNR, quantitative AES/SAM. There are further illustrations of this point coming from MIDAS. For example, oxygen KLL at 505 eV has a relatively low Auger yield. Small oxide particles on copper can be seen very readily in high-resolution b-SE images. Indeed the presence of oxide can be seen in the shape of the (secondary electron) spectrum background, whereas wide beam Auger declares the surface to be clean [34]. This discrepancy is due both to the fact that the oxide particles cover a small fraction of the surface, and that oxides in general have a very high secondary electron yield. Non-conducting

samples in general are difficult samples for analysis by AES/SAM, for which special techniques for discharging the surface have been developed [35].

5. Recent applications to small particles and catalysis

Because of their unique electronic, optical, magnetic and chemical properties, small particles play an important role in heterogeneous catalysis, quantum dots, and other nanophase systems. To understand nanoparticle systems fully and to utilize their unique properties more effectively, we need to study their physical and chemical properties, their interactions with supports or substrates, and their collective behavior [36]. TEM/STEM, associated spectroscopy and spectrum-imaging techniques provide ultra-high resolution information on the atomic arrangement, chemical composition, and electronic structure of nanoparticle systems as demonstrated in this special issue. Transmission-based techniques, however, have stringent conditions on the samples that can be examined: useful information can be extracted only from very thin areas of a sample because of severe absorption of electrons in thicker regions. The preparation of suitable samples for transmission observation may also pose a formidable problem for certain materials. These limitations preclude the application of TEM/STEM techniques to extracting information about the surface properties of thick or bulk samples.

Fortunately, the recent rapid development of the high-resolution SEM makes it possible to examine bulk samples on a nm or even sub-nm scale. The high-stopping power of electrons at low energies significantly reduces the electron-specimen interaction volume as well as the range that an electron can penetrate into the sample. Low-voltage SEM (LVSEM) offers new opportunities for imaging a wide variety of bulk samples with high spatial resolution [37]. For example, highly dispersed metal nanoparticles as well as detailed surface topography of supported catalysts can now be routinely examined [38].

Reducing the primary energy E_0 of the incident electrons has profound effects. Both elastic and inelastic mean free paths, λ, decrease with decreasing E_0. The *electron range*, which is a measure of the penetration depth of the incident electrons, and the *interaction volume*, a measure also of the lateral diffusion, are significantly reduced at low electron energies. These effects have been modeled using Monte Carlo simulations of electron trajectories, as shown here in Fig. 8a and b. With $E_0 = 30$ keV, a penetration depth ≥ 10 μm can be reached in bulk silicon; but 1-keV electrons can only diffuse as deep as 0.04 μm into the sample. The interaction volume

of the 1-keV electrons is about 10^7 times smaller than that of the 30-keV electrons. This tremendous reduction in the interaction volume for low-energy electrons makes it possible to perform high-resolution backscattered electron (BE) imaging and chemical microanalysis with characteristic X-ray photons in the modern FE-SEM instruments.

The BE signal is one of the most useful signals available in a SEM instrument. For a homogenous bulk sample, the electron backscattering coefficient, η, is almost independent of the electron beam energy E_0 in the range 5-100 keV; it increases monotonically with the atomic number Z of the sample. Below 5 keV, however, the dependence of η on the atomic number of the sample is not monotonic; with decreasing E_0, η decreases for high-Z but increases for low-Z materials. When a small particle is located on, or inside, a substrate, the electron-specimen interaction is more complicated, especially with low-energy electrons. Depending on the size and location of the small particle as well as E_0, the electron-particle interaction can play a dominant role in determining the scattering processes of the incident electrons [38]. For example, when a 20-nm Pt particle is embedded inside a carbon support (Fig. 8c), 20 nm below the carbon surface, a large fraction of the 3-keV electrons are first backscattered by the Pt particle, then travel through the carbon, and exit the carbon support as backscattered electrons. On the other hand, most of the 30-keV electrons pass through the 20-nm Pt particle without being backscattered (Fig. 8d).

The value of η for a particle-substrate composite strongly depends on E_0 and the size and location of the particle. A 20-nm Pt particle located on the surface of a carbon support may give a very high contrast in BE images obtained with 3-keV electrons since $\eta_P = 0.6$ for the platinum-carbon composite sample and $\eta_C = 0.1$ for the carbon support. A contrast

$$C = 100\% \text{ x } (\eta_P - \eta_C)/(\eta_P + \eta_C) = 71\% \tag{10}$$

is then obtained for this Pt particle in high-resolution BE images. On the other hand, a 20-nm Pt particle embedded 20 nm below the surface of the carbon support may not be easily observed in BE images obtained with 30-keV electrons (Fig. 8d) since the electron backscattering coefficient for the particle-carbon composite sample ($\eta_P = 0.05$) does not change appreciably from that for pure carbon. If 3-keV electrons are used (Fig. 8c), this Pt particle, however, can be easily observed with a contrast of about 53% since now $\eta_P = 0.33$, much larger than that of pure carbon. Electron interactions with small particles embedded in a matrix are complicated, especially at low electron energies.

Imaging and analysis of small particles, especially metallic nanoparticles in supported catalysts, are critical to understanding the structure-activity relationship of heterogeneous catalysis. BE images can provide information about the size and spatial distributions of metal nanoparticles. By varying the energy E_0, we not only can obtain the lateral distribution of the metal nanoparticles but also their depth distribution, providing surface as well as subsurface information about bulk catalyst samples. As an example, Fig. 9a and b, obtained with 3-keV and 30-keV electrons respectively, shows BE images of the same area of an industrial Pt/C catalyst, revealing different sizes of the Pt particles and their spatial distribution. The two images provide complementary information about the catalyst: some larger Pt particles embedded deep inside the carbon support, and these particles are only revealed in the image obtained with 30-keV electrons. The contrast or visibility of metal nanoparticles in BE images depends on many parameters, including the size, location and the average atomic number of the particle as well as E_0. For example, in Fig. 9a particle A is much brighter than particle B, but the two particles almost have the same visibility in Fig. 9b.

Monte Carlo calculations of the electron backscattering coefficients have been used to understand the contrast of BE images of Pt nanoparticles in carbon supported Pt catalysts [38]. Fig. 10a shows the energy dependence of $\eta(E_0)$ for Pt particles located on the external surface of a carbon support; the values of $\eta(E_0)$ for pure carbon and pure Pt are also shown for comparison. With increasing electron energy, $\eta(E_0)$ first increases, reaches a maximum, and then slowly decreases. There exists an optimum electron energy, E_{op}, which gives a maximum value of backscattering coefficient $\eta_{max}(E_{op})$, for each given size of a Pt particle; the value of E_{op} increases with the size of the Pt particle. This maximum value is reached when the range (R) of the incident electrons approaches the diameter (d) of the Pt particle; $\eta_{max}(E_{op})$ is estimated to be about the same for all sizes of particles. The value of η_{max} may be related to the scaling parameter $\alpha = d/R_{op}$ which is about unity for all particle sizes.

The dependence of the electron backscattering coefficient $\eta(d)$ on the size of a Pt particle is also complicated: in low-voltage BE images, a smaller Pt particle may give a higher image-intensity than that of a larger Pt particle. For high E_0, however, the image intensity of a small Pt particle increases monotonically with its size. Thus, interpretation of high-voltage BE images of small Pt particles located on the surface of bulk substrates is straightforward, while that of low-voltage BE images is more complex. Another factor affecting the interpretation of high-

resolution BE images is that small nanoparticles are often embedded in a substrate. For example, some small Pt particles shown in Fig. 9a with diffuse contrast (e.g. particle B) are definitely located inside the carbon support. To understand the contrast of Pt particles located at various depths within the carbon support, Fig. 10b shows the dependence of $\eta(D)$ on the location of a 40-nm Pt particle for various beam voltages. Regardless of E_0, $\eta(D)$ is highest when the Pt particle is located on the external surface of the carbon support (D = -20 nm). For E_0 < 5 keV, $\eta(D)$ decreases monotonically with D until it finally reaches the backscattering coefficient of bulk carbon. For E_0 > 5 keV, $\eta(D)$, however, first decreases, reaches a minimum, increases again to a maximum, and then slowly decreases to the value of bulk carbon. It is interesting to note that with 10-keV electrons a 40-nm Pt particle located a distance 40 nm below the carbon surface may have a visibility higher than that of a similar particle located a distance 20 nm below the surface.

These Monte Carlo calculations clearly show the complex nature of the contrast of small metal particles in high-resolution BE images, especially in low-voltage BE images. We can see from the above examples that more research is needed to understand the very interesting but complicated electron scattering processes from particle-matrix composites [38]. However, comparing high-resolution BE images with corresponding SE images (see below for discussion) taken at different E_0, useful information about the depth distribution of nanoparticles, as well as the lateral position, can be extracted. The recent development of high-efficiency backscattered electron detectors for low-energy electrons will make low-voltage and high-resolution BE imaging a very powerful technique for studying surfaces, small particles and supported catalysts.

High-resolution SE signals can be readily used to provide detailed surface features of supported catalysts; for example, in Fig. 9c and d, the detailed pore structure of the carbon support as well as some small particles are clearly revealed with high contrast. Experiments with higher-energy electrons, such as those shown in figure 7, have shown that the integrated SE intensity from a small particle with a radius less than the mean escape depth of the collected secondary electrons is proportional to the total number of atoms within the particle, suggesting that the number of emitted secondary electrons is proportional to the total stopping power of the small particle. Unlike in BE images, small metal particles embedded deep inside the support may not be observable in high-resolution SE images. Only those metal particles that lay on, or very close to, the sample surface can give observable image contrast [38].

Supported bimetallic catalysts are becoming increasingly important, both in order to understand the nature of complex nanoparticles, and for their industrial applications. One of the most urgent issues in designing and fabricating nanostructured bimetallic nanoparticle catalysts is to control the outmost surface layer composition of the individual nanoparticles, and to understand how it changes with gas environment, bulk composition, and the sample preparation procedures. Recent experiments in applying atomic resolution EELS to the study of supported bimetallic catalysts have provided valuable insights into the nature of surface composition and electronic states of individual bimetallic nanoparticles. But this technique is usually applicable only to nanoparticles that hang over the vacuum or are positioned very near the edges of the support materials [39, 40].

SAM, on the other hand, can provide surface compositional information of bulk samples as discussed in section 4. Although it is difficult to image the surface composition of bimetallic nanoparticles in industrial heterogeneous catalysts, nanometer resolution SAM images of supported bimetallic catalysts have been obtained [41], providing useful information on the surface segregation of bimetallic nanoparticles. Figure 11a shows a high-angle annular dark-field (HAADF) image of a zeolite-supported PdM (M: another transition metal), a real industrial bimetallic catalyst, revealing the presence, size and spatial distribution of the small metal or alloy nanoparticles. The very weak contrast of the nanoparticles is due to the thick zeolite support and the low average atomic number of the bimetallic nanoparticles. The HAADF image, however, cannot provide any useful information about the surface composition of the individual nanoparticles. On the other hand, the Pd (A-B) Auger elemental map of Fig. 11b clearly shows that some of the small nanoparticles are located on the surface of the zeolite support, and that the surface composition of these bimetallic nanoparticles is rich in Pd. When this type of basic understanding of the nature of bimetallic nanoparticles is integrated into the catalyst synthesis strategy and is correlated to the performance of the catalyst, significant progress can be achieved in developing much-improved nanostructured heterogeneous catalysts.

6. Discussion and conclusions

This article has introduced a range of surface and near surface analytical techniques, from which the leading *clean surface* scanning electron microscopy, SEM, techniques have been developed. Chemical analysis on a microscopic scale was developed for the case of Auger

electron spectroscopy, AES, in sections 2 and 3, with simple analytical models, and examples from the recent surface and analytical literature. Scanning Auger microscopy, SAM, was introduced in section 4, and the development of a 100 kV high spatial resolution field emission (FE)-SEM-SAM, the MIDAS project, in which the authors were involved, was described in some detail. In section 5 we discussed the development of FE-SEM at lower beam voltages, < 5kV, analytic microscopy based on such instrumentation, and the interpretation of secondary and backscattered electron signals based primarily on Monte Carlo modeling. Most of the experimental examples given are close to current technical limits.

There are several avenues for further technical development left to explore in future. First, there are related analytical techniques at high beam voltage (100-300 kV), in which state of the art imaging of bulk samples, or especially thin films, is combined with analytical spectroscopy: AES, EELS, X-ray spectroscopy, in addition to 'Z-contrast' imaging. All these instruments are in need of more incident electrons at a given spatial resolution, in order to improve the signal to noise and signal to background ratio. Some of these spectroscopies, EELS especially, have been transformed by parallel recording of the energy spectrum and associated spectrum-imaging techniques [8], but this not yet been systematically applied to AES/SAM with *in-situ* experimentation [31-33]. The recent development of aberration correctors and their deployment in STEM instruments will enable higher beam currents to be delivered to a small probe. It is at present uncertain where the major effort using such correctors will be deployed, since these instruments are also in the process of transforming atomic resolution imaging [42].

Another state of the art development, which we have not discussed here, is coincidence spectroscopy, in the form of Auger-secondary, EELS-secondary or EELS-Auger coincidence, in both wide beam [43] and microscope [44] instruments. These techniques, borrowed from particle physics, have the potential to increase the signal to background ratio of particular transitions greatly, and such studies are clearly fascinating in relation to studying the underlying physics. But they have as yet made little or no impact on practical quantitative analysis, in part because the count rate needs to be small to use coincidence as a discriminator. Thus the improved PBR is typically bought at the expense of a much lower SNR in a given time. By comparison with particle physicists, microscopists are impatient [45].

More importantly, all the above developments are expensive and are available in a few centers of expertise. In surface analysis, strong end-product applications are needed to justify

investment in new instrumentation; any technique that is more convenient and/or less expensive, and has high throughput, is seriously to be welcomed. The commercial development of low voltage FE-SEM with electron and X-ray analysis should be seen as a major step forward in this respect. Small particle catalysis, backed by multi-billion dollar industries, is likely to prove a fruitful testing ground for deciding in practice which *in-situ* instruments and electron energy ranges are of most use for what particular type of problem. This suite of techniques could eventually mount a challenge to the high spatial resolution EELS technique, in a similar manner to low voltage FE-SEM, which is providing a challenge to more specialist surface instrumentation, as described here in section 5.

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Figure Captions

Fig. 1: a) Electron energy spectrum, showing secondary, Auger, energy loss and backscattered electrons; b) Si KLL Auger scheme (after reference 1 and previous authors).

Fig. 2: High resolution AES spectrum of Ge LMM for 5 keV incident energy [4]. The strongest peaks, within the L_2 $M_{4,5}M_{4,5}$ series at 1145 and L_3 $M_{4,5}M_{4,5}$ series at 1180 eV have $^1G_4$ symmetry; the smaller peaks at higher E consist of 3 overlapping lines with ^3F symmetry [5].

Fig. 3. Schematic diagram of electron scattering in a solid, indicating the incident and detected angles, θ_0 and θ_a, plus the role of backscattered electrons in determining the Auger signal strength. The escape depth is qualitatively the thickness of the region from which most of the detected Auger electrons originate, of the same order as the inelastic mean free path λ discussed in the text (after references 1 & 16).

Fig. 4: AES deposition curves for Fe/1.8MLAg/Fe(110), showing a) rearrangement of the Ag layer between 1 and 2ML, and segregation on annealing, or during deposition at elevated temperature. The Fe/5MLAg/Fe(110) curves b) show less complete segregation. The parameter p is the amount interchanged with the surface in the model [25].

Fig. 5: Pulse counted Auger electron spectra obtained with the 100 keV probe in MIDAS a) Si KLL from clean Si (10 nA probe current, 10 min acquisition time for 512 point spectrum); b) Ag MNN from 100 nm wide island on Si(001) and from < 0.5 ML Ag layer between the islands (1.6 nA probe current, in 10 min. (upper data) and 20 min. (lower data) for the two cases respectively) [31]

Fig. 6: Energy selected electron images, Ag MNN Auger intensity map derived from those images and biased secondary electron image of three-dimensional silver island on Si (001), with probe current 1.5 nA, 20 min. acquisition time for energy selected images; 0.3 nA and 1 min. for b-SEI [31].

Fig. 7: Energy selected electron images of the same area containing small Ag particles on a thin amorphous carbon substrate obtained using different signals in MIDAS a) Ag MNN; b) Ag MNN + 20 eV; c) C KLL; d) C KLL + 20 eV; e) low energy SE and f) P_{Ag} - B_{Ag} [33]. See text for discussion.

Fig. 8: Monte Carlo simulations of the electron trajectories: 30-keV (a) and 1-keV (b) electrons in bulk silicon; 3-keV (c) and 30-keV (d) electrons in a composite sample consisting of a 20-nm Pt particle embedded inside a carbon support. Total number of electron trajectories: 30,000 in (a) and (b), 500 in (c) and (d) [38].

Fig. 9: High-resolution backscattered electron ((a) and (b)) and secondary electron ((c) and (d)) images of the same area of a carbon supported Pt catalyst. Images (a) and (c) were obtained with 3-keV electrons while images (b) and (d) were obtained with 30-keV electrons. These images provide information about the size, lateral and depth distribution of the Pt nanoparticles (see text for detailed discussion) [38].

Fig. 10: Monte Carlo calculations of the electron backscattering coefficients of Pt nanoparticles positioned on a bulk carbon support: (a) as a function of electron energy for various sizes of Pt particles, and (b) as a function of the distance (D) between the center of a 40-nm Pt nanoparticle and the carbon surface for various energies of the incident electrons. Number of electron trajectories: 30,000 [38].

Fig. 11: High-angle annular dark-field image (a) and Pd MNN Auger map of a PdM/zeolite supported bimetallic catalyst (M: second metal, in commercial catalyst) [41].