Surface Science Letters

Quantitative modeling of electron spectroscopy intensities for supported nanoparticles: The hemispherical cap model for non-normal detection

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ARTICLE INFO

ABSTRACT

Nanoparticles of one element or compound dispersed across the surface of another substrate element or compound form the basis for many materials of great technological importance, such as heterogeneous catalysts, fuel cells and other electrocatalysts, photocatalysts, chemical sensors and biomaterials. They also form during film growth by deposition in many fabrication processes. The average size and number density of such nanoparticles are often very important, and these can be estimated with electron microscopy or scanning tunneling microscopy. However, this is very time consuming and often unavailable with sufficient resolution when the particle size is ~1 nm. Because the probe depth of electron spectroscopies like X-Ray Photoelectron Spectroscopy (XPS) or Auger Electron Spectroscopy (AES) is ~1 nm, these provide quantitative information on both the total amount of adsorbed material when it is in the form of such small nanoparticles, and the particle thickness. For electron spectroscopy conducted with electron detection normal to the surface, Diebold et al. (1993) derived analytical relationships between the signal intensities for the adsorbate and substrate and the particles' average size and number density, under the assumption that all the particles have hemispherical shape and the same radius. In this paper, we report a simple angle- and particle-size-dependent correction factor that can be applied to these analytical expressions so that they can also be extended to measurements made at other detection angles away from the surface normal. This correction factor is computed using numerical integration and presented for use in future modeling. This correction factor is large (>2) for angles beyond 60°, so comparing model predictions to measurements at both 0° and ≥60° will also provide a new means for testing the model's assumptions (hemispherical shape and fixed size particles). The ability to compare the hemispherical cap model at several angles simultaneously also should enable more accurate estimates of surface structural parameters when elastic diffraction effects cause strong peaks in the angular distributions of emitted electrons.

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A very common structural motif in materials science involves nanoparticles of one material dispersed across the surface of another. Such structures are commonly encountered when making and/or studying catalysts, microelectronics, plasmonic and optical devices, nanoelectrode arrays, sensors, coatings and thin film growth by vapor deposition or other condensation processes. For example, metal nanoparticles dispersed across the surfaces of oxides and carbon supports are key ingredients in many heterogeneous catalysts, fuel cells, other electrocatalysts and photocatalysts, all of which are crucial for energy, fuel and environmental technologies and chemical processing. One of the three growth modes that occur during thin film growth by vapor deposition is the Volmer–Weber mode, whereby clusters of the deposited material first nucleate and then grow as 3-D nanoparticles on the substrate. [1–8] A very common method to estimate the size and number density of such nanoparticles is based upon measurements of the intensities of peaks associated with substrate and adsorbate elements

using an electron spectroscopy, typically either XPS or AES. A model that has been very widely applied for analyzing these intensities is the hemispherical cap model introduced by Diebold et al. [1], which assumes that the nanoparticles all have the shape of hemispheres with the same diameter. It is often applied to cases where the intensities of substrate and adsorbate peaks have been measured versus the amount of adsorbate deposited on the flat substrate surface, in which case the further assumption is made that the number of particles per unit area remains constant. This number density is estimated from a fit to these plots of intensities versus coverage (or the intensities at any one coverage) to the resulting equations of this hemispherical cap model, which also gives the average diameter of the particles at each coverage [1,6]. Unfortunately, these equations for the hemispherical cap model only apply when the electron intensities have been measured for a take-off angle normal to the substrate surface. Here, we present an extension of that model that allows it to be applied at other angles of electron detection, which are often demanded by the constraints on sample mounting or manipulation imposed by the particular vacuum chamber being used. This ability to model measurements at several different

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angles should also mitigate the complications associated with strong peaks in the angular distributions of electrons due to diffraction effects.

In either XPS or AES, electrons are emitted from a material due to interaction with either X-Ray photons or high energy electrons. The intensity of the electrons emitted at given kinetic energies is element specific. These electrons can interact with matter prior to escaping vacuum and lose energy. The probability for an electron to traverse through matter without significant loss of energy, or its escape probability, p_{escape}, is given by the equation:

$$p_{escape} = e^{-d/\lambda}, \tag{1}$$

where d is the distance the electron transverses through matter and λ is the characteristic attenuation length for the measured electron. The value of λ depends on its kinetic energy and the material through which it is passing. It is usually approximated as equal to the inelastic-mean-free-path (IMFP), which has been tabulated in detail as a function of kinetic energy and material [9]. However, that approximation neglects elastic scattering effects like those that give rise to forward-focusing peaks is photoelectron diffraction. Therefore, it has been shown that a better approximation is to use the so-called "effective-attenuation-length" (EAL) for λ instead [10,11], which has also been tabulated as a function of kinetic energy, material and other parameters [12]. Those tables show that the EAL can differ by up to 35% from the IMFP for common XPS and AES measurement conditions, but they are usually closer.

Using Eq. 1 for a simple flat overlayer of an adsorbate of uniform thickness, t, on a substrate, the ratio of the intensity of electrons from an element of the substrate, $I_{sub, normal}$, to its intensity with no overlayer, $I_{sub, 0}$, for normal detection is given by [13]:

$$I_{sub, normal}/I_{sub, normal, 0} = e^{-t/\lambda_{sub}}, \tag{2}$$

where λ_{sub} is the IMFP or EAL of electrons from the substrate element's peak through the adsorbate material. Similarly, the ratio of the intensity of electrons from an overlayer, $I_{ads, normal}$, to the intensity of electron from an infinitely thick adsorbate overlayer, $I_{ads, normal, \infty}$, at normal detection is [13]:

$$I_{ads, normal}/I_{ads, normal, \infty} = 1 - e^{-t/\lambda_{ads}}, \tag{3}$$

where λ_{ads} is the IMFP or EAL of electrons from the adsorbate element's peak through the adsorbate material. When the angle of detection is instead at some angle θ from normal to the surface, the thickness, t, is replaced with $t/\cos \theta$ in these equations [13].

When the adsorbate is in the form of uniform-size hemispherical nanoparticles instead of a uniformly thick layer, the analysis is much more complex, since the distance any electron travels through the solids is dependent upon where the electron originated from within the plane of the substrate surface (e.g., how thick the particle is at that location). In the hemispherical cap model mentioned above, the ratio of the intensity of emitted electrons from adsorbed hemispherical particles to the intensity of emitted electrons from an infinitely thick film of the same adsorbate for the case of normal detection was calculated by Diebold et al. by averaging (integrating) over the total surface area, and found to be [1]:

$$\frac{I_{ads, normal}}{I_{ads, normal, \infty}} = n\pi R^2 - 2\pi n\lambda_{ads}^2\left[1 - \left[1 + \frac{R}{\lambda_{ads}}\right]e^{-R/\lambda_{ads}}\right], \tag{4}$$

where n is the particle density, and R is the radius of the hemispherical caps. For the signal from the substrate relative to its signal at zero adsorbate coverage, they found that [1]:

$$\frac{I_{sub, normal}}{I_{sub, normal, 0}} = 1 - n\pi R^2 - 2\pi n\lambda_{sub}^2\left[1 - \left[1 + \frac{R}{\lambda_{sub}}\right]e^{-R/\lambda_{sub}}\right]. \tag{5}$$

These equations are only valid for electrons detected normal to the surface.

In order to determine the relationship between particle geometry and signal intensity of electron spectroscopies using non-normal detection methods, equations similar to Equations 4 and 5 can be derived for other angles by properly integrating the escape probability given in Eq. 1. Consider a hemispherical adsorbate particle centered at $(0, 0, 0)$, where its interface with the support substrate surface is defined as the $z = 0$ plane, as shown in Fig. 1. For detection at some angle θ from the surface normal as shown, the distance an electron travels through the adsorbate from a single coordinate is no longer simply related to the z-coordinate, or the z-coordinate divided by $\cos \theta$. Fig. 1 illustrates, for example, how a simple $R/\cos \theta$ correction would misrepresent the distance the electrons travel through the adsorbate material. Next we describe how one can solve for signal intensities using a simple numerical integration over the surface and sample volume.

The substrate surface is divided up into tiny increments (i.e., differential area elements $dxdy$), each located at some x,y coordinate in the $z = 0$ plane. For a single area increment on the substrate surface located at point $(x_0,y_0,0)$, the distance that an electron emitted from that point would travel through the hemispherical cap in the direction of the detector is calculated. For any point on the surface directly underneath the hemispherical cap, this distance is simply the length of the line originating from that point $(x_0,y_0,0)$, aiming toward the detector, and stopping at the point where it intersects the top surface of the hemispherical cap, which is defined by the equation for the sphere: $x^2 + y^2 + z^2 = R^2$. For each such starting point on the substrate surface, the (x,y,z) values of this point on the hemisphere's surface is calculated for the chosen values of R/λ, and θ. (To generalize, this was actually done for a given value of R/λ, treating x, y and z in "reduced length" units, x/λ, y/λ and z/λ.) Since $y = y_0$, this simply requires solving for the only two unknowns (x and z) using two equations: the equation for the sphere and the equation for the line that goes from $(x_0,y_0,0)$ to the detector. The distance the electron travels is then simply the distance between

these two points $(x_0,y_0,0)$ and (x,y_0,z), $d = \sqrt{(x-x_0)^2 + (z-0)^2}$. For points on the substrate in the "shadow" of the particle (as viewed from the detector, see Fig. 1), the line originating from that point to the detector intercepts the top surface of the hemisphere twice, so there are two solutions to these equations. The distance between
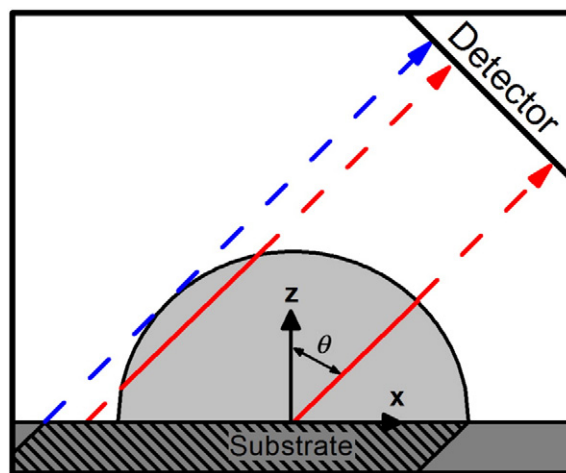

Fig. 1. Coordinate system used for derivation of electron intensities from a hemispherical cap of adsorbate and from the underlying substrate when the detector is at the angle shown but infinitely far away compared to the particle size. The y axis (not shown) is out of plane. Electrons emitted from the substrate will be attenuated by the hemispherical cap if they originate from either the area under the cap or from the shadow created by the cap as indicated by the hashed area. The hashed area of the substrate therefore represents the effective spectroscopic footprint of the particle at this particular angle of detection (θ, from normal to the substrate surface).