# NEW INSTRUMENTS AND MEASUREMENT METHODS

# Assessment of the feasibility of appearance potential spectroscopy

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The investigation and utilization of surface properties of solids is of tremendous interest both from the theoretical point of view and from the point of view of solving many practical problems that are encountered, for example, in the production of semiconductor and electronic vacuum devices, in the production of microelectronic devices and functional units, and in the study of the processes of adhesion, catalysis, chemisorption, and diffusion.

In the connection with the feasibility of obtaining a vacuum of $\sim 10^{-10}$–$10^{-11}$ Torr, at which the analyzed surface layer of the material is not significantly altered by interaction with the surrounding medium, many methods have been developed which made it possible to determine the elemental composition of the surface and the relative arrangement of the atoms on the surface, and to establish the energy distribution of the valence electrons and the effective charge of the ions (in particular, using x-ray photoelectronic spectra by means of the "chemical" shifts of the internal levels of the atoms[1]). From among the most widely used methods, notice should be taken of the local x-ray spectral analysis, photoelectronic spectroscopy, Auger spectroscopy, the diffraction of slow electrons, and the diffraction of fast electrons with glancing incidence of the beam, secondary ion emission, and scattering of primary ions[2,3].

The foregoing methods, however, do not make it possible to study the density of the states of the unfilled level above the Fermi surface, knowledge of which makes it possible to predict many physical properties of condensed systems. The methods produced for this purpose, those of the isochromates of bremsstrahlung[12] and characteristic[5] x radiation have a low sensitivity when it comes to investigations of surface layers of thickness on the order of several Angstroms. The reason is that for this purpose it is necessary to work with electrons of low energy, 50–100 eV, which do not penetrate more than 5–10 Å into the material. The x rays produced at these energies lie in the range 12–250 Å, for which there are no monochromators with sufficiently large aperture. Therefore great importance should be attacned to the appearance of the method of appearance potential spectroscopy (APS), which makes it possible to establish the same physical parameters which are determined also from the isochromates of the characteristic x radiation. The APS method is more sensitive because nonmonochromator is needed and because the x rays can be registered in a solid angle larger by one or two orders of magnitude then in the isochromate method.

The APS method consists in the following: A slowly and linearly varying electron-accelerating voltage V is applied between the cathode, which is an incandescent tungsten filament, and the anode, which is the investigated sample. The resultant x rays are registered with a vacuum electron multiplier (VEM) or with some other detector. With increasing accelerating voltage V, the number of bremsstrahlung photons $I_b$ increases. When the threshold potential $V_q$ for the excitation of some series of characteristic spectrum is reached, the VEM

registers the additional number of photons $I_c$ of the characteristic spectrum. The total number of photons $I = I_b + I_c$ will increase by a small amount, but with a rather large derivative with respect to V (Fig. 1, upper curve). In practice, however, it is very difficult to register the increase of I due to $I_c$, owing to the large intensity of the bremsstrahlung spectrum $I_b$, the fluctuations of which are comparable with the value of $I_c$. In APS one measures not I itself, but the derivative $dI/dV$, and this leads to a much better signal to background ratio $(dI_c/dV)(dI_b/dV)^{-1}$ (Fig. 1, lower curve). The reason for this is that a sinusoidal component of high frequency and small amplitude is superimposed on the slowly-varying accelerating voltage. As a result the number of photons measured by the VEM is also modulated at this frequency. If a synchronous detector tuned to the modulating frequency is connected in the VEM circuit, the synchronous detector can deliver a signal proportional to $dI/dV$. The use of a synchronous detector makes it possible not only to improve the signal to background ratio, as a result of taking the derivative, but also to improve significantly the signal/noise ratio, since the synchronous detector is insensitive to noise having frequencies and phases different from the frequency and phase of the modulating voltage. The APS resolution is 1–1.5 V.

The structure of the appearance-potential spectra is connected with the density of states over the Fermi surface by the following relation[7]

$$\frac{dI_c}{dE} = C \int_0^{E-E_i} N(\varepsilon)\left[\frac{d}{dE}(E - E_c - \varepsilon)\right]d\varepsilon + CN(0)N(E - E_i), \quad (1)$$

where $N(0)$ is the density of states on the Fermi surface, $E_i$ is the energy of the internal level of the atom, $E = eV$ is the energy of the incident electrons, and C is a quantity that depends little on the electron energy. Formula (1) affords, in principle, a possibility of predicting the shape of the appearance-potential spectra from the calculated density of state $N(\varepsilon)$, and thus verify the calculations of the band structure of solids. By measuring the heights of the peaks and the widths from the appearance-potential spectra, it is possible to determine the relative values of the density of states on the Fermi surface and the width of the conduction band.

The appearance-potential spectra were calculated so far only for the simplified band model of transition 3d metals[8], although the spectra of Mg, Be, and Al[7,9], Th[10], Au[11], Ba[12], B[13], C[14], Cu[15], and O[16] have also been plotted.
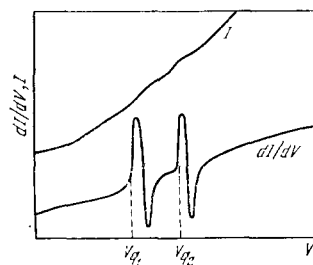


FIG. 1. Dependence of I and $dI/dV$ on V near the threshold potentials $V_{q1}$ and $V_{q2}$.
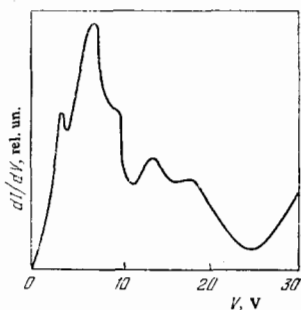
FIG. 2. K spectrum of appearance potential of beryllium (the voltage V is reckoned from the threshold potential 112 V).

In the analysis of the experimental results it must be borne in mind that the smallest contamination can greatly change the shape of the appearance of the potential spectrum. This is the main reason why the spectrum of aluminum obtained in[7] differs from that given in[11], while the appearance potential spectra of Be, obtained by Nilsson[7] and by us (Fig. 2), while similar from the point of view of the positions of the extrema, differ from each other in shape.

Of great importance for the development of the theory of alloys (in the one-electron approximation) is the choice of a physical model based on the experimental data for the electron structure. The experimental data make it possible to estimate, albeit qualitatively, the degree of the collectivization of the states of different components in the valence band and in the conduction band.

The large amount of experimental data obtained from measurements of the fine structure of x-ray and x-ray-photoelectronic spectra have shown that the Mott rigid band model is justified only in rare cases; more general is the Friedel-Anderson tight-binding approximation[18, 19].

An examination of the appearance-potential spectra of Ti-Ni[20] and Cu-Ni[21] alloys also leads to the conclusion that for the alloys of the first of these systems the rigid band model is valid only at a component ratio 1:1, while for the second the 3d conduction band of Ni turns out to be unfilled even at a copper concentration 60%.

From the appearance potentials $V_q$ we can determine the binding energy of the electrons on the core levels of the atoms, and from these we can establish the elemental composition of a surface layer 5–10 Å thick. The sensitivity with which the elemental composition can be determined in the APS is high enough for elements with large density of the free states near the Fermi surface; it depends also on the fluorescence yield of the corresponding series of the x-ray spectrum.

As shown by direct comparison of Auger spectroscopy and APS, the sensitivity of both methods when it comes to determining transition 3d metals is of the same order ($\sim 10^{-10}$ g/cm$^2$), and for such elements as O, S, Cu and 4d metals, the sensitivity of the Auger spectroscopy is larger by one or two orders[22]. Among the advantages of APS, when it comes to determining the elemental composition, is the simplicity of the interpretation of the spectra of multicomponent systems.

Just as in the x-ray photoelectron spectroscopy, the APS can determine the change of the energy of the core levels of the atoms when they interact with other atoms[17].

By comparing the appearance-potential spectra excited by electric impact and by a photon beam, it was possible to establish that the binding energy of the electrons with the core $2p_{3/2;1/2}$ levels of the atoms Ti, Tr, and Ni in the surface layer in the volume differ by 0.7, 1.1, and 0.9 eV, respectively[23].

The unique results obtained in the study of the structure of the conduction bands, the large group of solved problems, and the exceptional simplicity of the apparatus give grounds for assuming that APS will play an important role in the surface layers of Angstrom thickness.

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