Historical Auger Electron Spectroscopy. II

Keisuke Goto

Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555

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This review continues from the part I (J. Surface Anal. **1**, 328 (1995)) and describes applications and techniques in AES.

2.1. Auger electron spectroscopy (AES)----Application to the surface analysis

In the previous sections (1.1. and 1.2.), all samples of metals and gases had been investigated under very poor vacuum conditions, for example 2×10^{-3} Torr in the magnetic energy analyzer [1] and 100 Torr at best in the cloud chamber. No one had taken precaution against surface contamination because they were concerned about the far greater energy region where the contamination could not affect the results and where there was no problem in the experiments of the gases. In these circumstances, however, Robinson and Young did suggest an application of the Auger process to the determination of elements [2], i.e., AES.

Haworth (1935) [3] studied an energy distribution of secondary electrons from Mo-foil by a primary electron beam of 37-147eV using a magnetic energy analyzer (Fig.1) with a pair of Helmholtz coils. The energy resolution of the analyzer was 0.6%. The apparatus was evacuated by a mercury diffusion pump with a series of two liquid air traps and the whole system was baked at 500℃ for 50hr. The sample was outgases for 3500hr at 2100 K in the chamber at 3-4 $\times 10^{-8}$ Torr. These procedures must yield
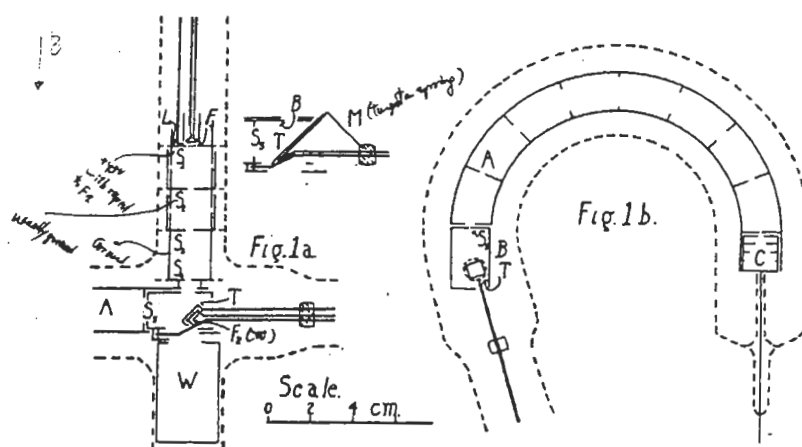

Fig. 1 Experimental apparatus of magnetic energy analyzer constructed in Pyrex glass by Haworth (1935) (Ref. 3).

a condition compatible with UHV. Moreover, it should be noted in the technique (Fig.1) that (1) the energy analyzer (A) had an effective shield against the scattered electrons in the path of magnetic field, which made the observation very reliable particularly in the lower energy range, (2) the collector (C) had many plates to realize an ideal blackbody for the electrons collected, (3) the electrons collected by the collector were amplified by an electrometer with a maximum sensitivity of 2.5×10^{-16}A/mm and an electron multiplier was never used. Thus, this allowed Haworth to make quantitative measurements. Obtained results for the lower energy are shown in Fig.2. The ordinate was corrected for the electron energy to be equal sensitivity. The figure shows three "humps" at 11, 24 and 35eV, which were independent of the primary energy. Among them, the hump at 24eV was interpreted as the external photoelectric effect due to the $N_{2, 3} N_{4, 5}$ X-rays of Mo (Fig.4 (b) in part Ⅰ). Although Haworth did not referred to Auger's work Haworth's results (at least the hump at 24eV) should be interpreted as $N_{2, 3} N_{4, 5} N_{4, 5}$ Auger electrons of Mo.

Haworth (1936) [4] also reported similar results for Columbium (Cb, which is now called Nb), in which a "hump" at 21eV was also interpreted as a result from the photoelectric action of soft X-rays ($N_{2, 3} N_{4, 5}$) of Cb. This should be, however, due to the Auger process like the above case for the Mo.

Lander (1953) [5], who is believed to be a pioneer of AES, was the first scientist that really showed the possibility of using AES for studying solid surfaces because of the thin emission depths of Auger electrons. The apparatus made of Pyrex-glass is shown in Fig.3 and the whole system was evacuated by a series of two liquid nitrogen traps and a 2-stage mercury pump. The system combined with the backout might produce a vacuum of UHV compatible though it is not sure that the B-A gauge [6] was used or not. The secondary electrons emitted were deflected by a two dimentional focusing type 90 electrostatic electron energy analyzer and then collected by the collector. The collected electron current was amplified by an electrometer with sensitivity of 1×10^{-15}A, which was specially made for his experiment [7]. Bulk materials,
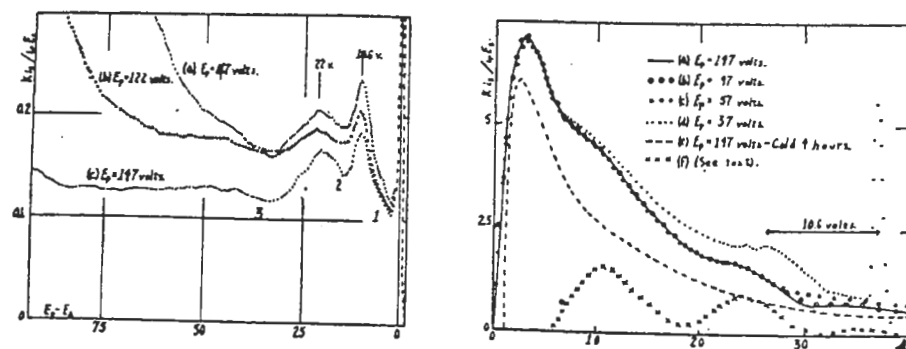

Fig. 2 The energy distribution of Mo in the low energy range by Haworth (1935) (Ref. 3).

evaporated *in situ* and then contaminated were used as samples. They included Be, C, O, Al, Ni, Cu, Ba and Pt. Two peaks at 152 and 185eV, which were observed in the Ni and Cu samples, respectively, might not be Auger signals for the Ni and Cu. Rather, the peaks may be attributed to sulphur and chlorine, respectively, according to recent data.

Lander has pointed out the following significant facts.

1. The Auger electron is not subject to the selection rules governing the emission of X-radiation, so that additional information can be obtained from the Auger electron spectrum.

2. The Auger spectrum will reflect the distribution of valence band electrons, such types as KVV, LVV, ..., but not in a simple manner.

3. The Auger spectrum will show much less detail than the soft X-ray spectrum.
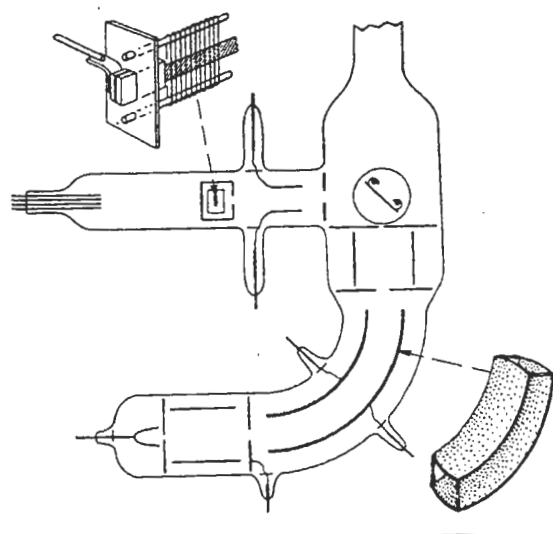
4. The long tail of the Auger peak on the

Fig. 3 Spherical electrostatic energy analyzer by Lander (1935) (Ref. 5). The spheres were cut out from glass spheres.

secondary electron background towards the lower energy side is probably the most serious problem for obtaining a very accurate spectrum. The exact form of the background is not readily determinable.

5. The light elements give the strongest peaks, as Auger's results and theoretical work have already suggested.

6. The emission depths are, on the average, of the order of ten atomic layers and thicker for atoms of low atomic number.

7. The method has some experimental advantages over the soft X-ray emission technique: The measurement can be accomplished very rapidly (e.g., can be displayed on an oscilloscope in a small fraction of a second) and the experimental tube is comparatively simple (e.g., no precision gratings are needed).

8. In many problems of applied physics and chemistry, identification of surface composition will become of considerable importance.

9. The emission depth can be determined by evaporation method.

Harrower (1956) [8] carried out extensive experiments on fairly clean Mo and W in UHV conditions. An electrostatic 127 type energy analyzer was used with 1% energy resolution, and the energy range of 10-5000eV was observed. Many subsidiary maxima or "humps" were obtained and these structures were distributed at fixed energy positions for the various primary energies 100-2000eV. These structures were interpreted as being due to the

electrons by the Auger process. It was possible to predict the energies, with which Auger electrons expected to be emitted, using the data available from X-ray studies. The general prediction of the peak position of Auger electrons, however, has been left unknown.

Tharp and Scheibner (1967) [9] studied an energy distribution of secondary electrons from the W (100) for primary energies of 50-350eV using a three-grid LEED apparatus. Here, the apparatus was used as a normal LEED display and as an energy analyzer, which is a retarding field energy analyzer with an AC differentiation scheme [10] using a phase-sensitive detector (lock-in amplifier) [11]. The Auger spectra between 10-50eV, similar to those obtained by Harrower [8], were reported. They emphasized that the combination of the LEED and AES would give additional information about the state of surface cleanliness. This system has been used extensively in laboratories since then.

Harris (1968) [12] has introduced a revolutionary technique in AES, i.e., a spectrum differentiation method. In this method, the energy distribution is differentiated by the energy. This differentiated energy distribution can then effectively reveal many details that are usually within the background. A typical example for contaminated Be is shown in Fig. 4. This example shows how convenient this method is. Today, in most cases, the Auger spectrum is defined using this differentiated energy

distribution. This was the start of the recent AES. Harris used an 127 type electrostatic energy analyzer with an energy resolution of 0.3%, which was quite similar to that of Harrower [8] but with an electron multiplier. Various kinds of elements have been measured from the atomic number 3 (Li) to that about 80. Although his paper was not published until 1968 [34], Harris started this method following the suggestion of Stout in 1964 [13].

Weber and Peria (1967) [14] have introduced a technique to obtain a differentiated energy distribution of

$dN(E)/dE$ in the LEED-AES system after Harris [12]. They noticed that the modulated collector current should include the higher order harmonics of the modulation frequency and the coefficient of the second harmonics must correspond to the first derivative of the energy distribution. The validity of the method
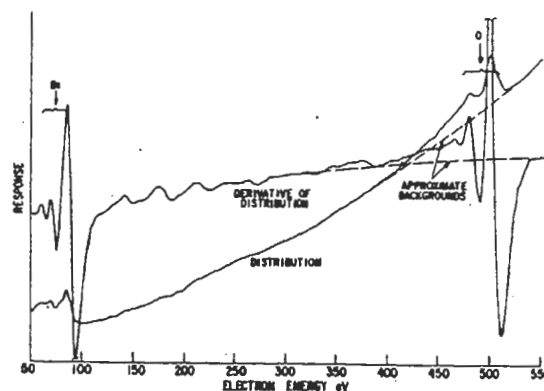

Fig. 4 The Auger spectra of Be in a form of energy distribution ($EN(E)$)* and derivative of the energy distribution ($dNE(E)/dE$)* by Harris (1968) (Ref. 12). *Designated by the author.

was confirmed for contaminants such as Na, K and Cs on Ge (111), (100), and Si (111), (100) using an apparatus as shown in Fig.5. The Cs of 0.1 monolayer was detected on the sharply changing background. This method has been employed in the LEED-AES system after this demonstration.

Palmberg and Rhodin (1968) [15] showed an epoch-making experiment, which determined the escape depths of Auger electrons in Ag using the method mentioned above [14]. The escape depths of 4 and 8 were obtained for energies of 72 and 362eV, respectively, evaporating Ag on Au at room temperature. The reversed process, i.e., Au on Ag, however, yielded a formation of islands of several monolayers thick. The other clean surfaces of Cu, Pd and Ni were also measured and a deposition on a substrate at lower temperature of -195℃ was also tried using a cold stage [16].

Palmberg et al. (1969) [17] introduced a superior cylindrical mirror electron energy analyzer (CMA) in AES (Fig.6).

CMA was first designed by Blauth (1957) [18] (Fig.7) to obtain an energy distribution of secondary electrons ejected from the gas target by proton bombardment, though, it was not designed to be optimum. Zashkvara et al. (1966) [19] and Sarel (1967) [20] have published improved designs and both authors determined the same optimum design. The former was also predicting the merits of using a double-pass CMA (Fig.8); the distortion of the image caused by non-axial rays can be eliminated to a considerable degree and the resolving power can be increased. Palmberg (1975) [21] demonstrated the double-pass CMA for use with a large-diameter X-ray beam in an AES-ESCA system.

CMA has the following advantages over the 4 (or 3)-grid LEED-AES optics and thus make the CMA reliable, quick and sensitive.

1. The shot noise is greatly improved by one or two orders of magnitude because CMA is basically a band pass type energy analyzer while LEED-AES is that of a
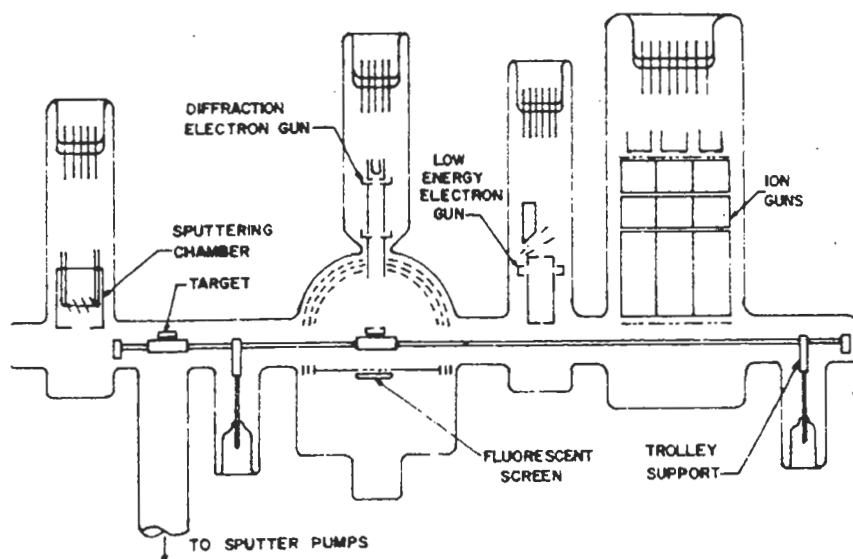

Fig. 5 LEED tube for overlayer studies by Weber and Peria (1967) (Ref. 14).
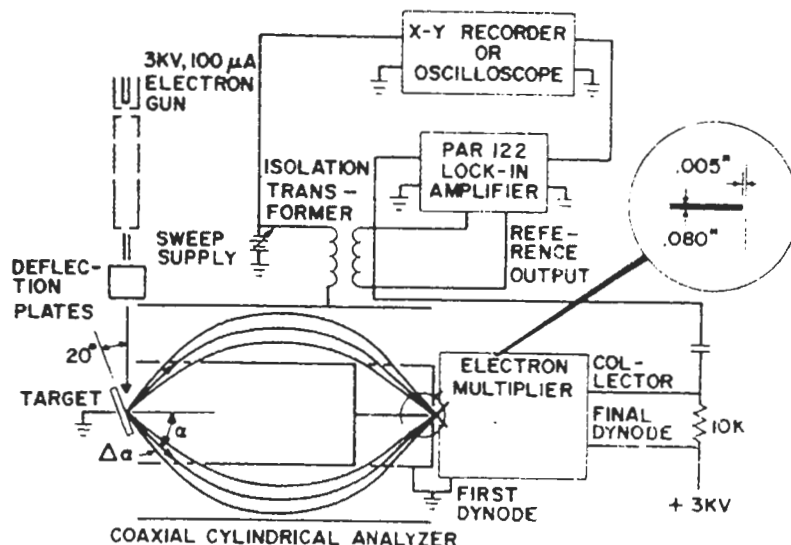
Fig. 6 The cylindrical mirror analyzer (CMA) used for AES by Palmberg et al. (1969) (Ref. 17).

high pass.

2. The transmission of CMA is about 10% and this large value is near that of LEED-AES.

3. The typical energy resolution of 0.3-0.6% is obtained and this is high enough for the surface analysis.

4. The design allows the use of an electron multiplier, which the LEED-AES system is not allowed for.

5. The design is rather free from the electrons scattered in the analyzers. On the contrary, however, LEED-AES greatly suffers the trouble caused by the electrons scattered and those ejected at the grids [22].

6. Most parts of CMA are axially symmetrically arranged so that its machining and alignment are quite reliable.

MacDonald and Waldrop (1971) [23] introduced scanning electron microscope into AES and obtained Auger electron images (Fig.9). This was the birth of micro-beam analysis by AES. It was quite natural that the CMA system was utilized. The sample used was Fe wires (25 m diam.) buried in Cu. The primary
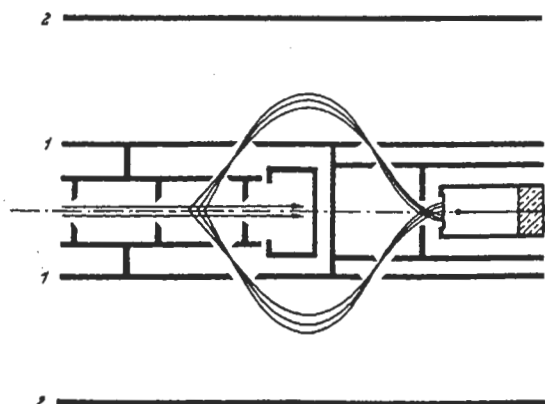
Fig. 7 The first CMA used for SE energy analysis from gas, not to scale, by Blauth (1957) (Ref. 18).
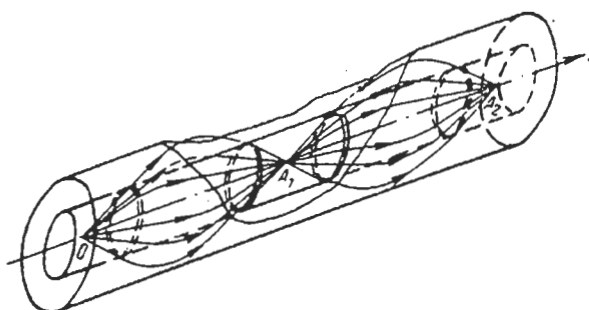
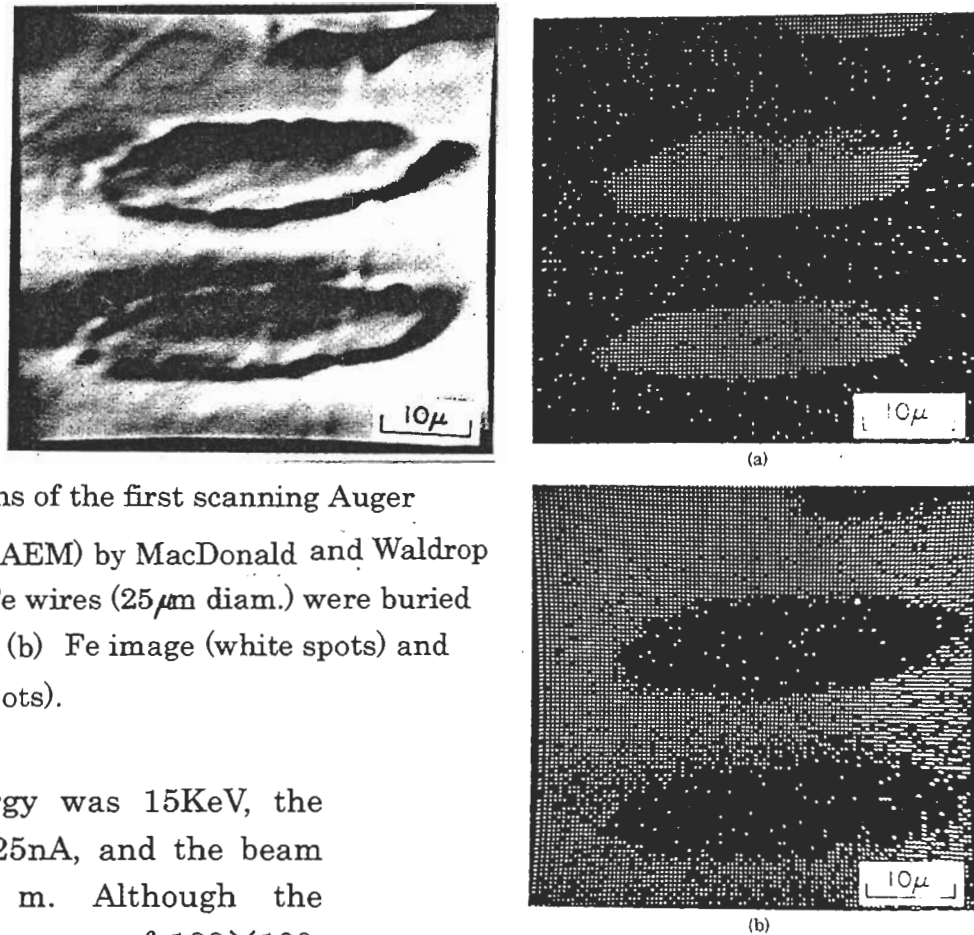Fig. 8 Double-pass CMA by Zashkvara et al. (1966) (Ref. 19).

(a)

(b)

Fig. 9 The photographs of the first scanning Auger electron microscope (SAEM) by MacDonald and Waldrop (1971) (Ref. 23). Two Fe wires (25 μm diam.) were buried in Cu; (a) SEM image, (b) Fe image (white spots) and (c) Cu image (white spots).

electron beam energy was 15KeV, the beam current was 25nA, and the beam diameter was 0.3 m. Although the picture elements, an array of 100×100, were immediately stored in the computer memory, the actual picture was only produced after 1.7hr of signal accumulation.

2.2. Specific techniques developed for quantitative AES

The energy analyzer for AES has already been described in the preceding section (1.3.). Hence, the other specific techniques needed for AES are described here.

2.2.1 Modulation technique

Energy modulation in AES is very important to obtain spectra of either $dN(E)/dE$ with CMA and $N(E)$ and $dN(E)/dE$ with LEED-AES, or to obtain further high order derivatives. This technique was mathematically calculated for arbitrary input functions (shape) and an example was demonstrated for a Lorentzian function by Houston and Park (1972) [24], while those for Gaussian, Lorentzian (in phase and out of phase), and series RLC resonance functions were also reported by Hanisch et al. (1975) [25].

Gerlach et al. (1970) [26] introduced an interesting modulation technique in the retarding field energy analyzer: Modulations both on the retarding grid and the primary energy produce a spectrum originating from zero energy such as Auger and secondary electrons. The modulation only on the primary energy produces a spectrum originating from primary energy (e.g., elastically and
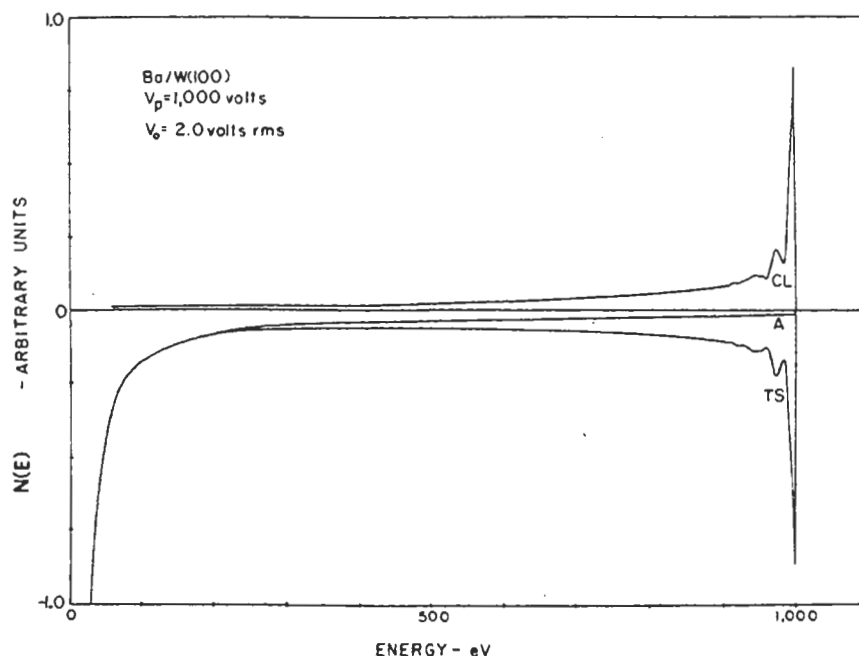
Fig. 10 The energy distribution was experimentally separated into two parts with special modulations: the energy distributions originating from zero and the primary enegies.

inelastically backscattered primary electrons and primary electrons which lose characteristic energy). This experiment was the only result that separated the energy distribution into the two parts. These results is shown in Fig.10.

The mesh effect [22] in LEED-AES was greatly reduced by adding a modulation on the sample. This experiment was carried out by Everhart et al. (1976) [27].

These modulations can be also applied to CMA. In general, however, attention must be paid to the properties of the secondary electron yield vs primary energy and to the deflection of the tracks of electrons emitted (in the sample modulation).

The tailored modulation, owing to the wave form, was introduced by Springer et al. to obtain $N(E)$ and $N(E)dE$ directly

with an automatic background subtraction (1975) [28]. This technique was applied to the depth-profile measurement of Al_2O_3-Al interface by Grant et al. (1976) [29] and it provided superior quantitative results as compared with the ordinal peak-to-peak value of the derivative spectrum. Various tailored modulations were mathematically calculated by Pocker (1977) [30].

The square wave modulation by Goto et al. (1977) was also one kind of tailored modulation. This modulation allows for the maximum intensity in a scanning Auger electron microscope (SAEM) when using a modulation method, i.e., simultaneous signal detection and background subtraction (see Chap. VI).

In the tailored modulation, however, rather larger modulation amplitude such as 10-100eV$_{p-p}$ can be used as compared

to that of the ordinary 1-10eV$_{p-p}$. When this method is used in practice the caution must be taken for the spectrum consisting of complicating peaks, otherwise the result will be meaningless.

2.2.2 Spectrum subtraction

The Auger spectrum is, in general, quite complicated and thus a sample consisting of multi-elements is sometimes quite difficult to analyze due to overlapping spectra.

Grant et al. introduced a spectrum subtraction technique using a computer in AES for electron bombardment (1975) [31] and for ion bombardment (1975) [32]. In this technique, the standard spectrum of the matrix was subtracted from the spectrum of the sample under observation. The technique allowed them to reveal an Auger signal of a low concentration of Mn in steel [33]. This concentration was only 1.4%. One can hardly detect this amount of concentration by conventional methods. Therefore, the author would like to emphasize that the subtraction method is very useful and can lead to substantial improvement in practical analysis.

In addition to subtraction, the technique can also be used synthesize the spectra of standard elements so as to reconstruct the spectrum of a sample under observation. This method becomes important particularly in making quantitative analysis of surface composition by AES.

2.2.3. Background (secondary electrons) subtraction

In AES, the large amount of background for the Auger signal has been a substantial problem when determining the Auger signal intensity correctly [2][5][55]. However, no one has succeeded in developing a conclusive method to determine the background as yet. The differentiation technique [12][14], the tailored modulation [28] and the dynamic background subtraction [34] are convenient but not comprehensive enough to be satisfactory in practice. The most conventional method to subtract the background in the Auger peak has been carried out by extrapolation of the background in higher energy towards a lower energy range or by interpolation of the background between the higher and considerably lower energy regions (see, for example, Fig.12). Within this method, there still remains some arbitrary choice for the curve. Powell and Stein [35] considered that the background level determined by the above method (extrapolation) might allow a region, extrapolated to about 15eV, to be accurately analyzed to within ±5%. This leads to the considerably accurate determination of the signal intensity by peak height and by integration of a peak area over the higher energy edge to the top of the peak position [36][37].

Sickafus (1971) [38] proposed a mathematical model of the background, which mainly consisted of the energy distribution of the secondary electrons after Wolff (1954) [39] and Seah (1969)

[40]. The model functioned through an analog computer, which subtracted the background from the results experimentally obtained, and then producing an Auger spectrum with the background removed.

Sickafus further attempted to linearize the secondary electron cascades from the metal surfaces of clean and homogeneous concentrations (1977) [41] and of surface and subsurface concentrations (considering impurities and contaminations) (1977) [31] (see refs.41 and 42 for practical analysis). background was assessed using transport theory and was then removed to obtain a retrieved Auger spectrum. The band structure of Si was investigated by an analysis of the fine structure, which appeared in the Auger spectrum. Similar methods have also been used by Musket and Fortner (1971) [46] for Be (KVV), Salmer n (1974) [47] for Cu ($M_{2,3}$VV) and (M_1VV), Alli et al. (1975) [48] for Al ($L_{2,3}$VV) and Onsgaard et al. (1978) [49] for Si ($L_{2,3}$VV).

Mularie and Peria (1971) [50] studied the Auger spectra of In (MNN), Cd (MNN), from CdS and O (KLL) from TiO_2 and Mo-oxide using the deconvolution technique in which the energy distribution of nearly elastically-backscattered primary electrons were used. The energy distribution contained information of energy loss and analyzer resolution. This demonstrated that the application of the deconvolution technique to AES yielded spectra, which were in good agreement

with those obtained with a high resolution spectrometer (such as ESCA). In addition to increasing resolution, this technique also eliminated much extraneous structure, which arises from inelastic interactions of Auger electrons within the solid, such as plasma excitation. Similar methods have also been used by Madden and Houston (1977) [51] for Li (KVV), Smith and Levenson (1977) [52] for C (KVV) from TiC, VC and Cr_3C_2, Tagle et al. (1978) [53] and (1979) [54] for C (KVV) and L_2,

Hesse et al. (1976) [43] developed a method to automatically determine a structureless background in a measured spectrum. The method was based on a third order smoothing Spline algorithm model. However, a severe limitation of the model is that it must be three times differentiable with the first and third derivatives to be negative and the second derivative to be positive for the energies range of interest. This method was applied to an UHV cleaved mica and the results were satisfactory.

2.2.4. Deconvolution and convolution of the spectrum

The main purpose of the deconvolution and convolution is to obtain real signal intensities of Auger electrons. This may be made by removing the background, instrumental spectrum broadening and removing the tailing, which accompanies a main peak towards the lower energy side. The Auger spectrum can be composed theoretically or by employing experimental data from

the convolution technique [28]. Thus those processes should reflect the fundamental considerations involved in Auger transition.

Amelio and Scheibner (1968) [44] obtained a retrieved Auger spectrum of C (KVV) utilizing the entire spectrum with aid of the Laplace transformalism. The result was reported to be satisfactory.

Amelio (1970) [45] also obtained a retrieved Auger spectrum of Si (LVV) from that as measured. The effect of $_3$VV's from Al, Al_2O_3, Mg, MgO, Si and SiO_2.

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