The Absolute AES is Coming; Work Functions and Transmission of CMA

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The feasibility of an absolute energy and intensity calibration in Auger electron spectroscopy (AES) has been studied, in which the work functions of the analyzer and sample, and transmission of the analyzer shall be known. We need a stable surface in an electron analyzer even for frequent introduction of air, gases and any vacuum. Some types of carbons and metals have been studied. Presently, soot and aquadag®are the most suitable candidate and have been satisfactorily used in our CMA. Transmission of the CMA is scheduled to be measured by using a mini-electron gun consisting of a tungsten hair pin cathode set at the sample position. This electron beam current can be measured by an electrometer before entering into the CMA by movable Faraday cup. The electrons which pass through the CMA are detected by another electrometer normally to detect the spectra. The ratio of the two measured values will give the transmission.

INTRODUCTION

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) are popular in surface analysis and the metrological standards for their calibration references (energy and intensity) have been published as ISO15472 for XPS [1], ISO 17974 for high resolution AES [2-5]. Further NPL has supplied a software [6]. This calibration is available for the energy range 20eV to 2500eV which covers the energy range required for quantitative AES analysis. These works by NPL should be appreciated.

We have been studying another absolute AES in a calculable way for the medium energy resolution, which measures the whole energy range of 1eV to 5000eV and the range is useful for the theory and simulation. In an actual experiment, we usually pay no attention for the work function, then an ambiguous value will be resulted in the spectrum. It is a quite common problem in AES and any other energy analyses as well. To obtain a reference spectrum to calibrate the analyzer and to offer the standard [7], we have to find method to correct the work function of the analyzer (CMA) [8-10]. Now we need a stable surface in the electron analyzer even for the frequent introduction of air and gases, any vacuum, and bombardment of electrons and ions, which shall be required for the absolute AES for its standardization. Low secondary electron yield is also required for the material in the coating of the analyzer to reduce the electron scattering, which would result in a improved signal to noise ratio and ghost feature [11] in the spectra. It has been believed that carbons are the most stable material [12, 13]. It is interesting how atomic scales of structure would present macroscopic characteristics of work function. Our main concern is the work function, *i.e*., contact potential difference and the secondary electron yield.

On the other hand, the transmission of the CMA should be calculable for the reference. We have examined it in an optical method to simulate the transmission. Though the actually transmission must be confirmed by experiments. Transmission of the CMA is going to be measured by using a mini-electron gun consisting of a tungsten hair pin cathode set at the sample position in conjunction with a mini-Faraday cup.

Table 1. Experimentally obtained work functions.

	As evacuated (eV)	After ion Sputtering (250-1000eV)	Comments
soot (butane)	4.41(4)	4.34→4.40(3)	superior
soot (benzene)	4.53(4)	4.47→4.45(4)	superior but rather bulky (wooly)
Soot (naphthalene)	4.85(5)	4.74→4.55(5)	stable but considerable change after ion sputtering
aquadag®	4.65(5)	4.57→4.73(7)	stable but the secondary electron yield is higher than soots
graphite	4.73(4)	4.37→4.63	stable but torn by ions
glassy carbon	4.92(5)	4.61→4.34(5)	stable but torn by ions
charcoal activated	4.58(8)	4.67→4.82(5)	not stable
carbon black	4.89(4)	4.62 4.75	not stable
C_{60}	6.16	5.65 6.12	stable but broken and agglomerated by the ions
C_{70}	4.75	4.49 4.80	visual size of the piece scattered away from the sample holder
CNT	4.35 4.77	4.2 4.4	difficult to prepare and easily emits FE
Au (100)	4.48→5.05	5.08(4)	as evacuated surfaces were not stable but would be saturated and stable in the vacuum after UVs irradiation and ion sputtering, adsorbed residual gases for a day of exposure in UHV
Au (110)	4.54→4.97	5.04(5)	
Au (111)	4.67→5.12	5.12(6)	
Au(poly)	4.83	4.62→4.80(11)	
Cu(100)	4.76	4.81→4.24 (11)	unstable even in UHV
Al(111)	3.57	4.10→3.90/200min	changed in minites in UHV and other Al(100), (110) changed similary.

COATING MATERIALS FOR AN ABSOLUTE ELECTRON ENERGY ANALYZER (CMA)

To find a suitable material, we used a special PEEM which was modified from the commercial PEEM of Staib Instrument Model 350 [14] and measured work functions of carbons (soots, aquadag®, graphite, glassy carbon, activated carbon, carbon black, C_{60}, C_{70} and CNTs), golds, copper(100) and aluminums. The obtained results are tabulated in Table1.

The soots were made by burning a fuel butane gas, liquid benzene, solid naphthalene and directly coated on a sample holder in the flame. The work function has been determined at the threshold of the photoemission characteristic in the PEEM. The threshold of the soot which was made from a butane flame, as received and after ion sputtering were determined to be 4.41(4)eV and 4.40(3)eV, respectively. The latter value was obtained after saturation of the characteristic with enough sputtering of more than 10 atomic layers. The difference of 0.01eV was very small as within the standard

deviation, so the work function in this particular case did not practically change even after the ion sputtering. The other soots made from a benzene flame and naphthalene, their difference before and after the adsorption were considerably rather larger than that of butane gas. These soots were observed by TEM. The soot consisted of coral like aggregate of small (20-50nm) structure block. The fractal-like and projected aggregate structure properties would give the durable characteristics that were relatively independent of fuel type and flame conditions [15]. The structure of the soot depends on the materials and correspondingly the work functions. Some perceptible geometrical shape on the ion sputtering was observed by TEM. In the critical study, such as metrological measurements, the coating shall not be exposed to the ions and energetic neutrals. The latter can also sputter the surface and change the structure. The coating of the analyzer must be kept free from the ion bombardment, because of which surface cannot be retouched after the construction of the analyzer. Our CMA was provided for the ions by shutter between the CMA and ion gun. In addition to
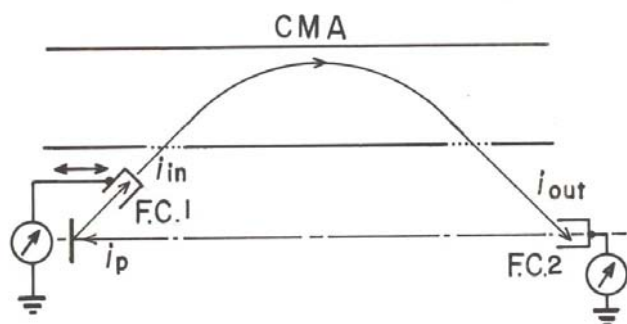
Fig.1 The schematic of CMA system for the measurement of transmission; total system with movable Faraday Cup (left) and e-gun for the virtual sample.
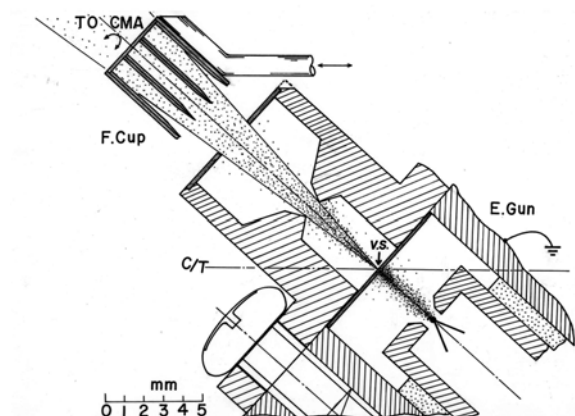

Fig.2 Details of mini e-gun with a small (50μm) aperture at the virtual sample position and mini movable Faraday cup with small bundle of pipes.

these properties the low secondary electron yield characteristic of broad yield of δ=0.30-0.50 for primary electron energies 200-700eV, correspondingly. It increased to be about 0.7, when the sample was settled in an alcohol suspension by the agglomeration [16]. It should be considered for the use in an energy analyzer. The soot is a good conductor and also has durable property. Thus, we can say that the soot is the most suitable material.

The work functions of aquadag®(Hitachi, AB-1 for vacuum tubes) before and after ion sputtering were 4.65(5)eV and 4.73(7)eV (4.57eV at the begining), respectively. The difference was 0.08eV and it also seemed as a suitable material. The secondary electron yield of aquadag ®is 0.75 [17] and the value is rather higher than the soots.

From these experimental results, the soots and aquadag®were found to be a suitable candidate and have been satisfactorily used in CMA. Though for the complex material of aquadag®, we need further confirmation. It can be applicable to other electron analyzers and apparatus. The graphite and glassy carbon were easily torn by ions. The other carbons of the charcoal activated and carbon black showed similar properties. The changes of the fullerenes were enormous in the geometrical property by the ion sputtering. Correspondingly, the work functions were changed. The CNT also showed the changes for the vacuum and ion bombardment, however, the detail was not analyzed because of the nano fiber structure. Golds as precious metal would seem to be stable only after the cleaning by the irradiation of UV and ion

sputtering. We found gold may be unsuitable in the commonly used Kelvin probes and coating material for the critical applications. Further metals such as Al and Cu should be avoided for the coating and reference.

TRANSMISSION MEASUREMENTS OF CMA

The transmission of CMA, which would particularly arise from the design and meshes used, should be calculable. Ideally the calculated transmission of the CMA must be found in experiments. As an estimation of the transmission, we have examined an optical method to simulate the transmission and obtained an expected value from the geometrical structure, though it should be confirmed truly with an actual electron beam. Absolute measurements can be performed by using an electron source at the sample position and electrometers. The design of the experiment is schematically shown in Fig.1. The details of a mini electron gun as an virtual source and a mini Faraday cup for the monitor of the incident signal to the CMA are shown in Fig.2. The mini-electron gun as the virtual electron source(V.S.) consists of a tungsten hair pin cathode and the anode at ground potential set at the sample position with a small pin hole of 50 μm, as the actual beam diameter being used has beam as large as about 50μm in diameter. The electron beam is shaped by two apertures with sharp edge and enters into the CMA

with a circular cone incidence angle of ±6° around 42.3°. After the description of this paper, we examined the mini-electron gun and found that this design, however, did not worked out. The majour modification was satisfactorily introduced without an alteration of the external shape. This electron beam current is measured by an electrometer before entering into the CMA using a movable mini-Faraday cup being set between the CMA and the electron gun. The mini-Faraday cup is consisted of seven bundle of small copper pipes of 1.2mm outer diameter (0.9mm internal diameter) and 5mm in length coated with aquadag®and soot. The edge of each pipe is sharpened to be about 3μm. Collection efficacy of this Faraday cup may be better than 99%, since the aspect ratio of the pipe is about 5 [18]. The electrons pass through the CMA are detected by another electrometer being used normally to detect the spectra. The ratio of the two measured values will give the transmission. Results may not represent the whole transmission, but it can be a good measure.

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