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ELECTRON ENERGY LOSSES AND ASSOCIATED SECONDARY ELECTRON
EMISSION OF CARBON, OXYGEN, HYDROGEN ON METALS

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A B S T R A C T

Elements of low atomic number can be studied by electron energy loss, secondary electron emission and Auger emission. Auger electron spectroscopy is correlated with the inner shell ionization mechanism and atomic relaxation. Electron energy loss spectrometry is related either to collective phenomena like plasmon excitations, or to the excitation of molecular electronic states. The secondary electron emission of contaminated layers results from the desexcitation of these excited states. Using these results, we characterized graphite, Carbon segregated on Aluminium and organic layers, by excitation of π (6 eV) and σ (25 eV) orbitals. Molecular Hydrogen, adsorbed on Pt, Ta and Al, produces a 13 eV electron energy loss which is attributed to the excitation of the transitions $1\Sigma_g^+ \rightarrow 1\Sigma_u^+$, $1\Pi_u$. Adsorbed Oxygen on clean Aluminium produces an electron energy loss at 7 eV which has been reported as due to the 2p 0 level ionization. The cross section of $\sigma \rightarrow \sigma^*$ orbital excitation is $\sim 10^2$ times higher than the inner K-level Carbon ionization cross section. Molecular electronic level desexcitation produces a secondary electron emission at an energy equivalent to that of the electron energy loss value.

INTRODUCTION

After separate developments, S.E.M. and A.E.S. were combined, in ultrahigh vacuum apparatus. This evolution was necessary to enable analysis of light elements and thin films. However the interactions between the electron beam and the observed samples, limit the capabilities of A.E.S. to studying the trace elements because on one hand, the Auger cross section is very low and on the other hand radiation effects appear since the current density is higher than 10^{-3} A.cm⁻². [1] .

On technological samples, the study of the electron energy losses and secondary emission spectra shows clearly several peaks at 6, 7, 13, 20 eV. The purpose of this work is to identify one origin of these peaks and to apply it to the elementary microanalysis.

EXPERIMENTAL

We use a C.M.A electron spectrometer mounted on an ultrahigh vacuum apparatus with a Tungsten hairpin electron gun. The signal detection is based on beam brightness modulation. The F W H M of the primary electron beam is 750 meV.

The analyser energy window width was measured between 12 eV and a few keV on a Carbon layer. A post acceleration (~ 300 V) was applied between the C.M.A outlet slit and the first dynode of the electron multiplier in order to avoid a drop of the gain below 100 eV. Figure 1 presents a typical spectrum recorded with $E_p \sim 30$ eV, $I_p \sim 10^{-10}$ A, on a clean polycrystalline Aluminium sample [2] . This spectrum which must be taken as a test for a correct use of the C.M.A spectrometer is characterized as follows :

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1. a lack of secondary electrons between 0 and about 4 eV ; this energy range measures the work function, ϕ , of Aluminium, as no electron can be emitted with an initial energy below ϕ . In this experiment, the energy zero of the electron spectrometer is adjusted at the Fermi level [3].

2. a symmetrical elastic peak of F W H M about 1 eV which represents mainly the energy spread of the incident beam.

3. an energy loss peak at $\Delta E \sim 4$ eV, attributed [1] to the Aluminium interband transition. No loss peaks relative to surface and volume plasmon does exist at this accelerating voltage.

These three features correspond to a good spectrometer reliability.

RESULTS

Our main results are relative to electron energy losses and secondary electron emission of Carbon Oxygen and Hydrogen on metals.

1. Carbon

1.1. When a clean polycrystalline Aluminium sample becomes gradually contaminated with C, the electron energy loss peak corresponding to the Al surface plasmon excitation ($\Delta E \sim 10$ eV) decreases very quickly and disappears for a low coverage [2] ($\theta \lesssim 0,01$) while electron energy losses appear at 6 and 20 eV, and secondary emission increases at 20 eV.

1.2. Graphite and organic monolayer (Allyl Cyanid) with both samples, we observed peaks of secondary emission at 6 and 20 eV, whereas the electron energy loss peaks are observed at 6 and 24 eV for graphite and 6 and 25 eV for the organic layer.

2. Oxygen

Table I summarizes the results obtained on a clean polycrystalline sample exposed to oxygen.

E_p (eV)	Al		Al + O ₂	
	S.E.	E.L.S.	S.E.	E.L.S.
50	11	4,10,15	7,11	4,7,15
250	11	4,10,15	7,11	4,7,15
30	11	4	7,11	4,7

3. Hydrogen

Electron energy loss spectra recorded at increasing pressures of H₂ on various metals show the development of a peak at 13 eV (Figure 2).

DISCUSSION

Electron energy losses on a clean metallic substrate have been reported previously by other authors. In contrast with their results, when a clean metal becomes contaminated with C, O, H, the first noteworthy feature is the fast decrease of the electron energy loss intensity peak corresponding to the surface plasmon excitation. Furthermore, the energy value of the electron energy loss which is developed during the contamination, seems to be essentially dependent on the adsorbed element, without correlation with the electronic structure of the material.

The electron energy loss observed with C has been attributed previously either to transition between high density of state zones in the band structure of

graphite [4, 5] or to excitation of π and σ bonds [6]. As the electron energy loss values are roughly the same for Carbon contaminated metal, Graphite and organic layer, we prefer the molecular electronic excitation model.

The electron energy loss due to Oxygen contamination has been attributed to excitation of a resonance level of chemisorbed Oxygen ($2p\ 0$ level) [7]. Then we do not understand why this loss is developed at the same value for every studied case.

With regard to the Hydrogen contamination, studies have been conducted on silicon and rare earth hydrides [8]. No loss was observed at 13 eV. Then we assign the 13 eV observed electron energy loss on Pt, Ta, Al to the excitation of Hydrogen molecular electronic levels $^1\Sigma_g^+ \rightarrow ^1\Sigma_u^+, ^1\Pi_u$.

As this process is not fully reversible with pressure (we had to heat the sample at 300° C to return to the initial state), we consider that the contribution of gas molecules to the 13 eV loss peak, is negligible. On the other hand, the physically adsorbed Hydrogen molecules or the molecules trapped in clusters of vacancies, could produce this loss peak.

In every case, the secondary electron emission developed was at the same energy value as the characteristic electron energy loss, and could be the result either of ion neutralization near the surface, or of molecules desexcitation by an Auger like mechanism. The intensity of the electron energy loss and that of the secondary electron emission have the same value.

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For Carbon, comparison between the electron energy loss intensity and that of KLL Carbon Auger transition, shows that these processes have a cross section greater than the inner shell ionization cross sections.

CONCLUSION

Segregated and adsorbed elements can be characterized by electron energy losses at 6 and 25 eV for Carbon, 7 eV for Oxygen, 13 eV for Hydrogen. These electron energy losses for C and H₂ are attributed to molecular electronic level excitations. This desexcitation results in secondary electron emission. These emissions are used to make secondary electron micromappings of the adsorbates on a surface.

R E F E R E N C E S

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FIGURE CAPTION

Fig. 1 - $-En(E)$ energy distributions at $E_p = 30$ eV

Fig. 2 - electron energy loss spectrum on :
a, clean Ta ; b. c. d., under various partial
pressures of H_2 .

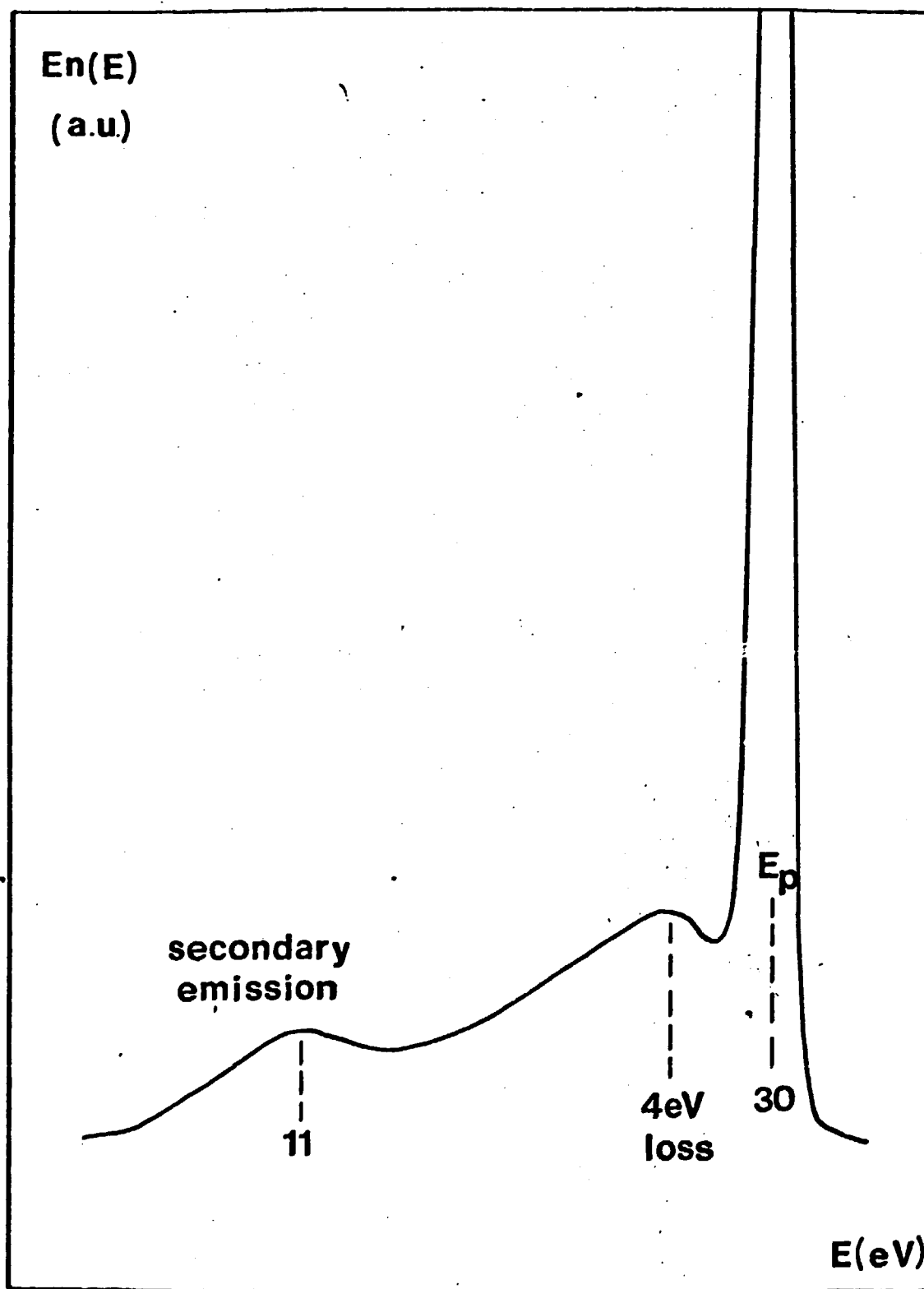


FIG 1

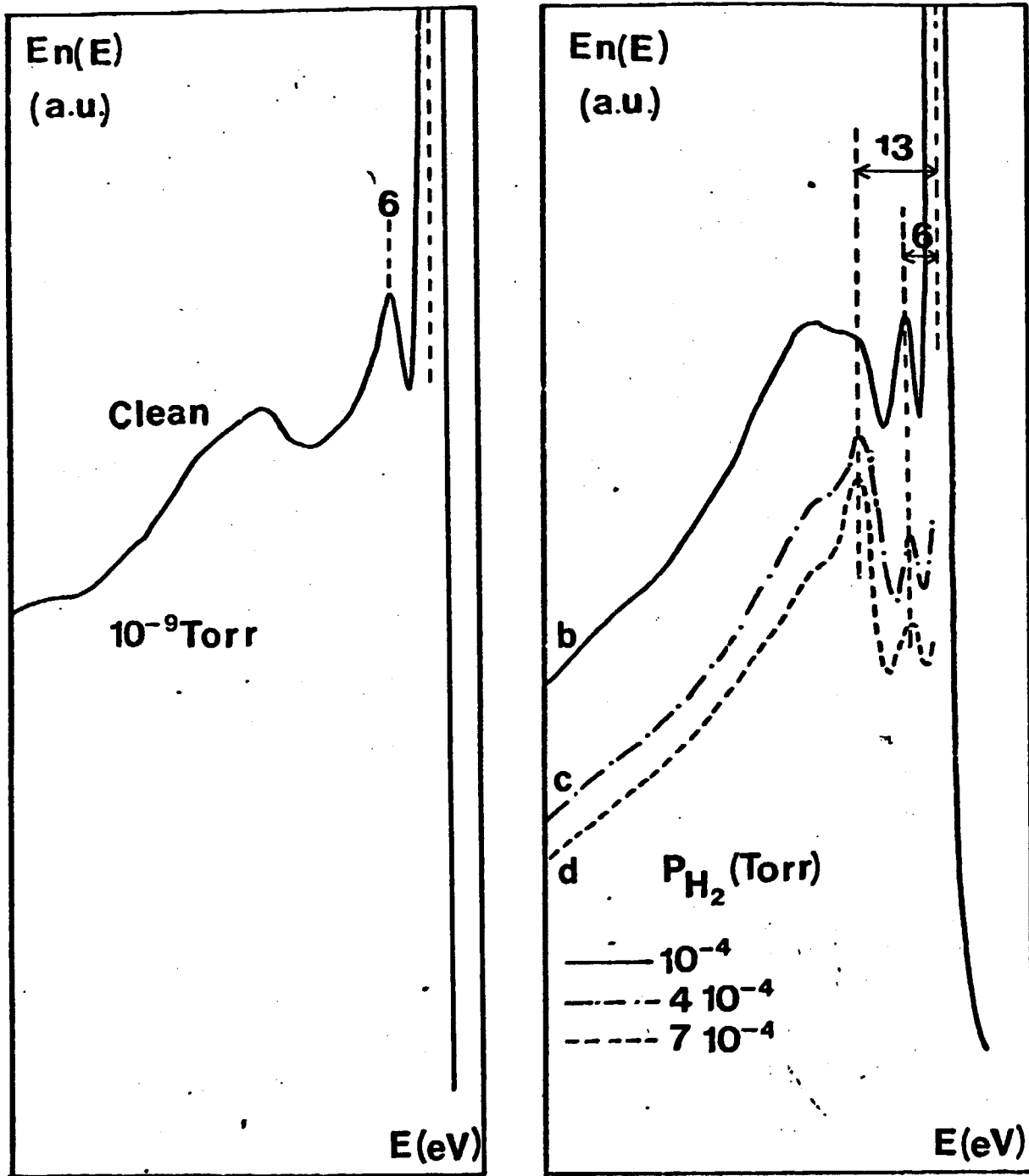


FIG 2