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Investigation of the electron emission properties of Silver: from technical Ag surface to ion-cleaned Ag surface.

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INTRODUCTION

When a solid is hit by incident electrons, the energy transfer can result in the emission of secondary electrons (SE) and backscattered electrons (BSE). Electron emission (EE) is at the origin of Multipactor effect that can occur in several rf devices under vacuum. To improve the modelling of this effect and the estimation of its threshold, it is capital to know accurately some properties of the emitted electrons such as (i) the secondary electron emission yield (SEY), (ii) the electron backscattered yield (BSEY) and (iii) the energy distribution $N(E)$. These properties are ordinarily extracted from measurements performed on materials of high purity evaporated [1] or ion cleaned [2] under ultra-high vacuum conditions (UHV). However, the used materials in rf devices are technical and are usually exposed days and months to ambient atmosphere. Thus, their surface properties are extremely different from that of the bulk of pure metals. Since the emitted secondary electrons have a low energy (a few eV) and are generated along a few nanometers depth; obviously, the tabulated EE properties of pure materials are far from being representative of technical materials. For instance, the maximum of the electron emission yield (EEY) of pure aluminium is lower than 1 [1], while that of technical aluminium is higher than 2.8. The purpose of this paper is to study experimentally electron emission of technical silver and to establish the relation to the EE properties of pure technical silver. Technical Ag surface (exposed to atmosphere) is mainly composed by Ag_2S and other deposited compounds, like water and carbon compounds. Indeed, Ag is widely used as coating material in waveguides. Measurements are performed in an UHV experimental facility named CELESTE and located at ONERA. A special experimental protocol was developed to extract relevant quantities. The electron emission yield EEY is investigated from very low incidence energy (few eV) to 2000eV. The energy distribution of the emitted electrons was monitored with means of an electron analyser. A step by step Ar ion “cleaning” was performed in situ. The surface composition is monitored by Auger electron spectroscopy (AES) during cleaning process and EEY as well as the energy distribution of the emitted electrons were measured at each step. The effect of incidence angle on the EEY was also investigated. An overall drop of the EEY was observed during the ion cleaning process. The maximum of the EEY decreases from 2.26 to 1.67 and the first crossover energy increases from 20 eV to 125 eV during the ion cleaning process. The effect of the ion-cleaning on the EEY tends to be suppressed after venting of the vacuum chamber.

PRINCIPLE

The principle of the experimental protocol is represented in figure 1. EEY measurements, AES and electron emission spectra were performed before and after each erosion step. Similar protocol has been used by Contini *et al* [3]. All the measurements were performed in the CELESTE facility. This facility is entirely dedicated and designed to the study of electron emission. A dry turbo-molecular pump associated with an oil-free primary pump allows the system to be maintained at a vacuum level down to 5×10^{-9} mbar. The tank is grounded. The sample holder allows the variation of the electron incidence angle from 0° (normal incidence angle) to 60° . An ELG-2 electron gun from Kimball Instrument was used. The electron beam was pulsed during EEY measurements to limit conditioning effect and was continuous during spectra acquisition. The Tectra ion gun used has an energy range of 50eV to 5000eV. The Omicron electron analyser can record spectra from 0 to 2000eV with an accuracy of 0.5meV. The sample was negatively biased to -9V during EEY and AES measurements.

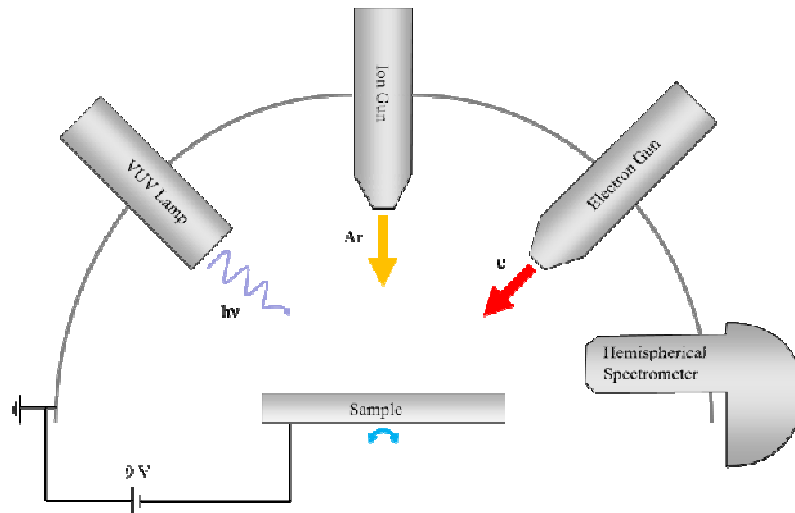


Fig.1.Schematic representation of experimental setup CELESTE

RESULTS

Sample

The sample was Ag (Ag00470/31) of high purity (99.99%) provided by Goodfellow Company. It was exposed for more than 3 years to ambient atmosphere. It has a shape of a 0.5 mm thick square plaque (32×32 mm²). Roughness measurements by Zygo interferometry performed on the sample prior to the experiments revealed an average roughness of 160 nm. The sample has been washed by ethanol before mounting in the measurement system, where it was outgassed in Ultra High Vacuum for 10 days before the first measurement.

Erosion parameters

The sample was sputtered with Argon ions in several steps. The same parameters (1 keV, normal incidence) for each erosion step were applied, only the erosion duration of each step was varied. The ion current, measured using a Faraday cup was adjusted to 3.5 μA/cm². The results presented in this paper are focused on the technical sample (before erosion), (b) the sample at an intermediate state corresponding to an erosion time of 62.5 min and (c) the sample considered as pure after 132 min of erosion (final state). The final state is considered reached when both the AES spectra of contaminants and EEY have reached a steady state.

Surface composition

The AES microanalysis technique was used to monitor the surface and near surface chemical composition (few nanometres in depth). After each erosion step, several AES peaks (as Ag, C, O, S) were recorded under 2 keV electron excitation. The evolution of Ag, C and O peaks at 3 main steps (a, b and c) are represented in figures 2, 3 and 4. On the 'as received' sample, the silver peak (figure 2) is weak in comparison with the intermediate and final states (b and c). This feature implies that the mean contamination layer thickness is comparable to the mean AES escape depth (few nm). This is supported by the large carbon contamination peak observed on the silver surface exposed to air. It should be noted that this peak is broadened to the higher energy range at the intermediate state. This broadening implies that a chemical valance shift occurred during the cleaning process. Indeed, the carbon compounds were most probably fragmented by ion bombardment resulting in a statically increase of the number of different chemical bounding for carbon. Oxygen was also observed on the as received Ag surface. The intensity of oxygen peak is weaker than that of carbon and decreases quickly. There is no more oxygen from the 3rd cleaning step, corresponding to 1.5 min of erosion. This oxygen was probably contained in deposited water layer on the sample, and probably not significantly in the carbon compounds since the carbon peak is still important after oxygen peak has disappeared during erosion. The Ag AES peak increases during the cleaning process. The ion etching removes the contamination layer resulting in a progressive increase of the Ag MNN AES transition. A peak shift was not observed in the case of Ag.

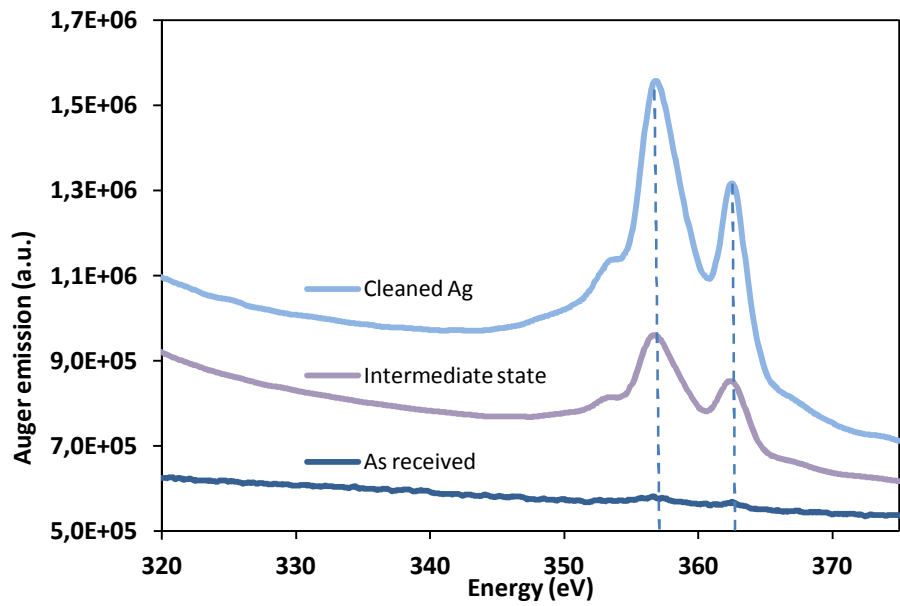


Fig.2. Auger peak of Ag (biased-9V)

Carbon is still detected even after the final state was reached (c). Possible reasons for that is important surface roughness that prevents evacuation of contamination stuck in asperities or carbon diffusion within silver.

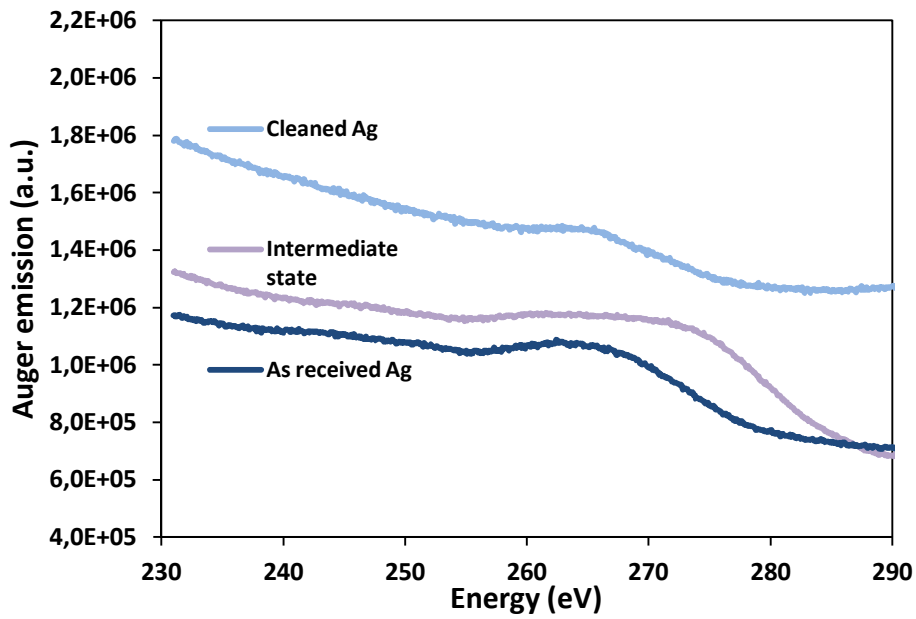


Fig.3. Auger peak of carbon on Ag (biased -9V).

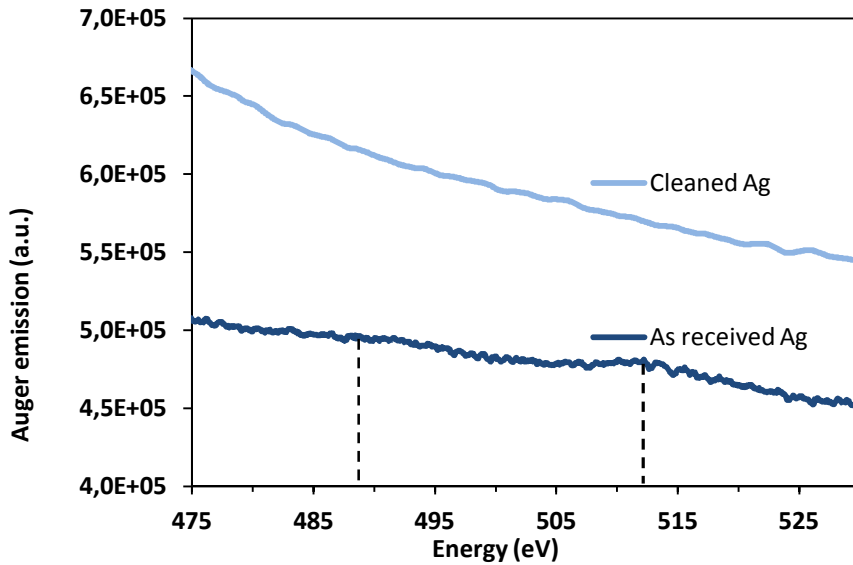


Fig.4. Auger peak of oxygen on Ag (biased -9V).

Energy distributions

Electron emission spectra of Ag measured under 20 eV electron irradiation are represented on figure 5 at three previously described states (a, b and c). The elastic backscattered peaks of the three spectra are very close in intensity. For clarity, the three spectra were normalized with respect to their elastic peak. Two major qualitative variations must be highlighted.

- The secondary electron peak decreases as a function of the erosion time. This trend is in good agreement with the EEY evolution presented in figures 6 and 7.

- The inelastic backscattered electrons quantity increases. Note that a characteristic backscattered peak corresponding to plasmon loss appears on pure Ag. This difference of Backscattered Electron Yield (BSEY) between pure and technical silver had already been observed for Ag in [4] in the energy range 100 to 2000 eV. The increase of the inelastic BSE contribution can be explained by the fact that contaminant layer has lower mean atomic number (carbon) than that of the bulk (silver). Indeed, the BSEY increases as the mean atomic number of the target increases.

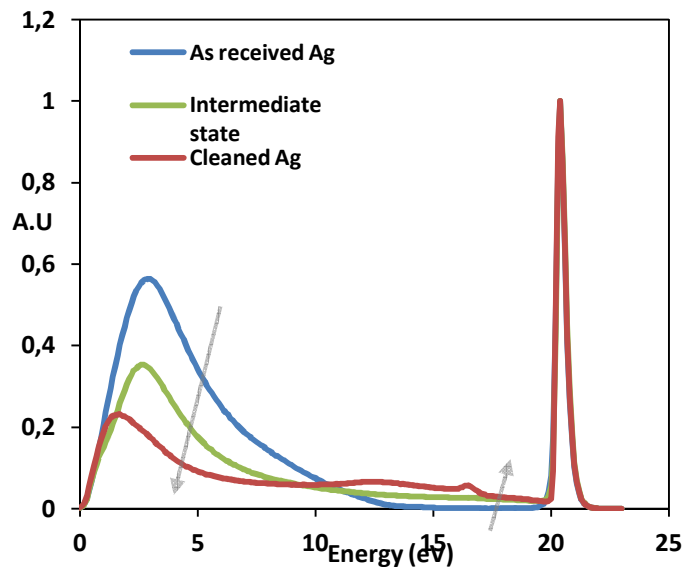


Fig.5. Electron emission spectra of Ag. $E_{incident}=20.4\text{eV}$

Total electron emission yields

The experimental method used for EEY measurements is described in [2]. The EEY is plotted in figure 6 as a function of the incidence angle for air exposed Ag sample. The energy of first crossover (E_1), the energy at EEY maximum (E_{max}) and the EEY_{max} for 'as received' and 'cleaned' sample are given in Table 1.

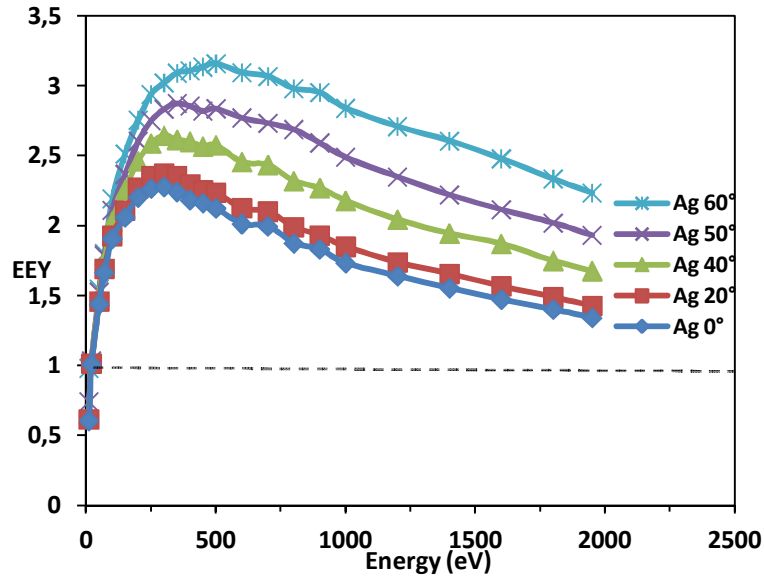


Fig.6. EEY of Ag for several incidence angles.

E_1 at normal incidence increases from 20eV for the as-received sample as technical Ag (a) to 125eV at the state (c) (cleaned sample). The shape of the EEY curve also changes with a huge shift of the EEY_{max} from 250eV for 'as received' sample to 700eV for 'pure' Ag. EEY measurements are compared to that of literature for pure Ag (evaporated under UHV) at normal incidence from Bruining *et al.* [5] and Brönstein *et al.* [1]. Results are in very good agreement, particularly with those of Brönstein *et al.*, even if there is a small divergence over 1500 eV. EEY values of Bruining *et al.* are lower but the trend is quite similar. This confirms that the contamination layer was well removed with the experimental protocol.

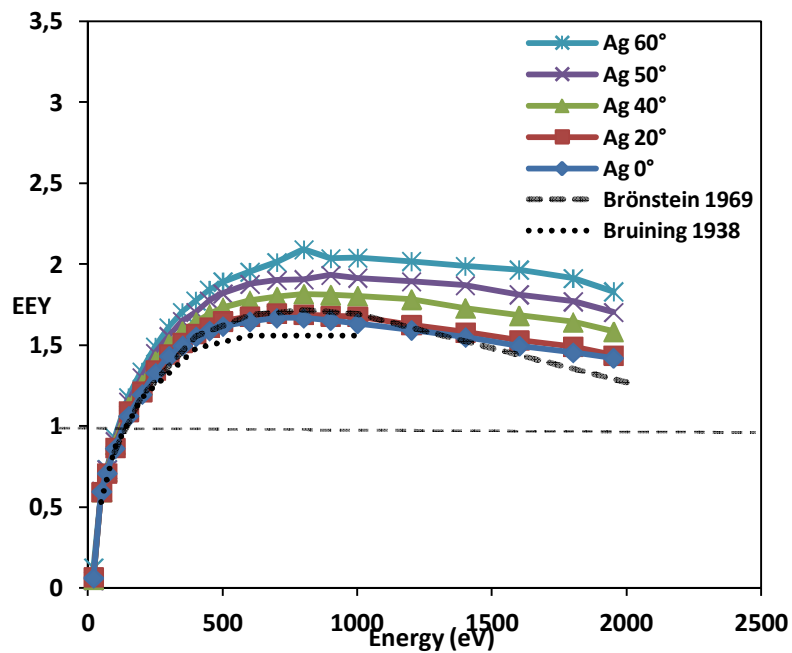


Fig.7. EEY on pure Ag

Table 1. E_1 , E_{\max} and EEY_{\max} of ‘as received’ and ‘cleaned’ Ag

Incidence angle (°)	0		20		40		50		60	
	As received	Cleaned	As received	Cleaned	As received	Cleaned	As received	Cleaned	As received	Cleaned
E_1	20	125	20	125	20	120	20	115	20	110
E_{\max}	250	700	250	700	300	800	350	900	450	1000
EEY_{\max}	2.26	1.67	2.35	1.67	2.64	1.82	2.87	1.81	3.13	2.03

In order to provide an overview of cleaning protocol effects on EEY, figure 8 shows the evolution of EEY (also called TEEY for total electron emission yield) at 2 particular incident energies; 300 and 1200eV. The figure is divided in 3 parts.

- i. In the first one, the sample is contaminated. After each erosion step, the TEEY decreases below the previous value. Thereafter, between two steps (of erosion), the EEY increases again. This implies that despite the fact that the sample was under UHV, some contamination quickly redepot on the surface. In figure 9 a simplistic chemical composition profile of the sample is represented based on the Auger spectra. The silver sample is probably covered by a carbon compounds layer and a thin water layer. In the same figure an estimation of eroded depth calculated on the basis of erosion rate of Ag tabulated in [6] and the experimentally measured ion current. It should be noted that the erosion rate of contaminant is certainly different from that of silver, which is not taken into account in our calculation.
- ii. In the second one, the TEEY at 1200 eV becomes higher than that at 300eV. This is in agreement with the shift of $TEEY_{\max}$ to high energies for pure silver (see table 1). Thereafter the TEEY becomes stable in spite of two successive erosion steps (at 500h and at 615h). This feature implies that a steady state is reached, the sample being considered as “pure”.

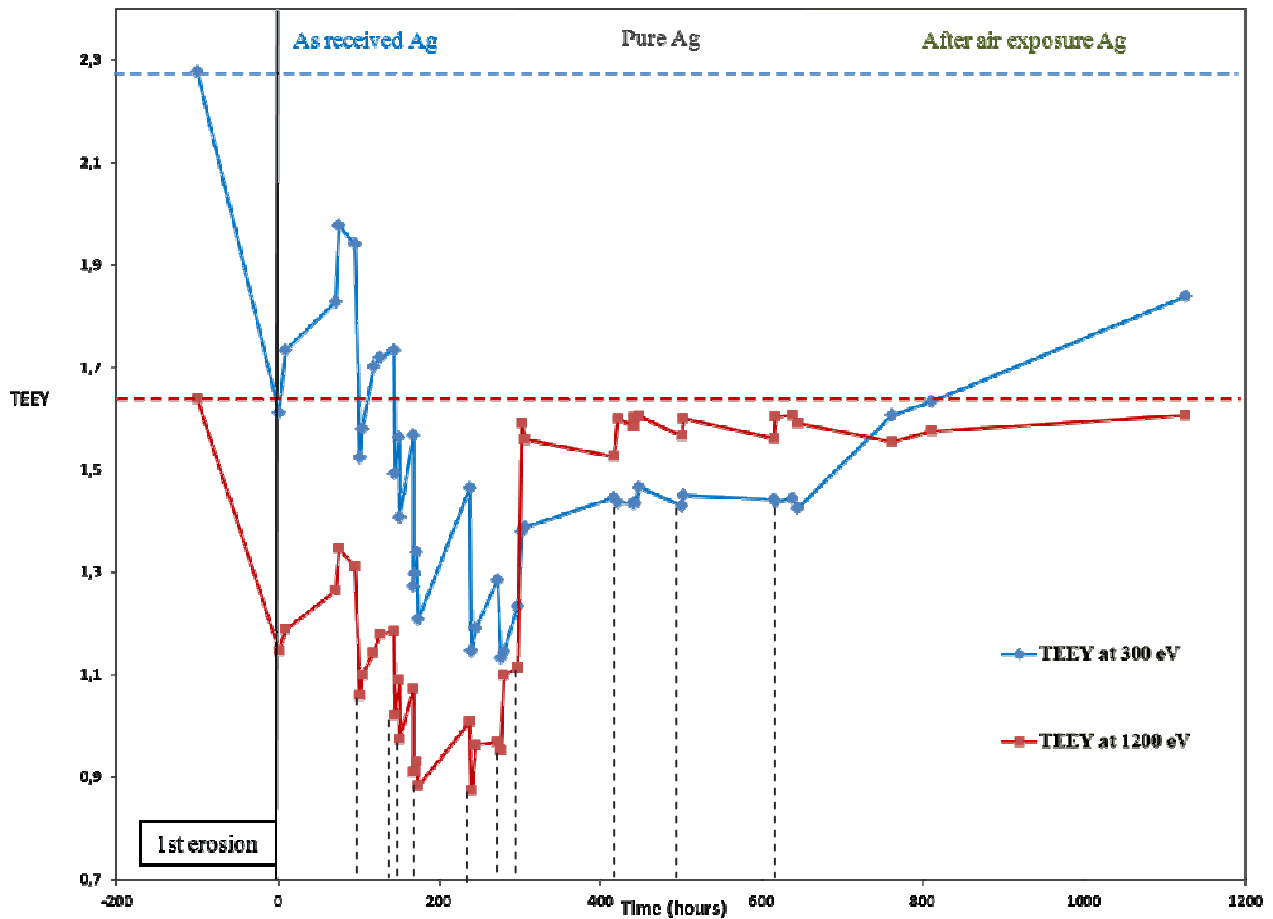


Fig.8. Evolution of TEEY at 300 and 1200eV as a function of time.

- iii. In the third part, the sample have been exposed to air for 15 min, and then evacuated to UHV. Two measurements have been performed (at 760h and 810h). A crossover between the TEEY at 300 and 1200eV is observed. The last measurements (1130h) were performed after an additional exposure of the sample to air for 24h. The TEEY converges to initial values due to the deposition of a new contamination layer.

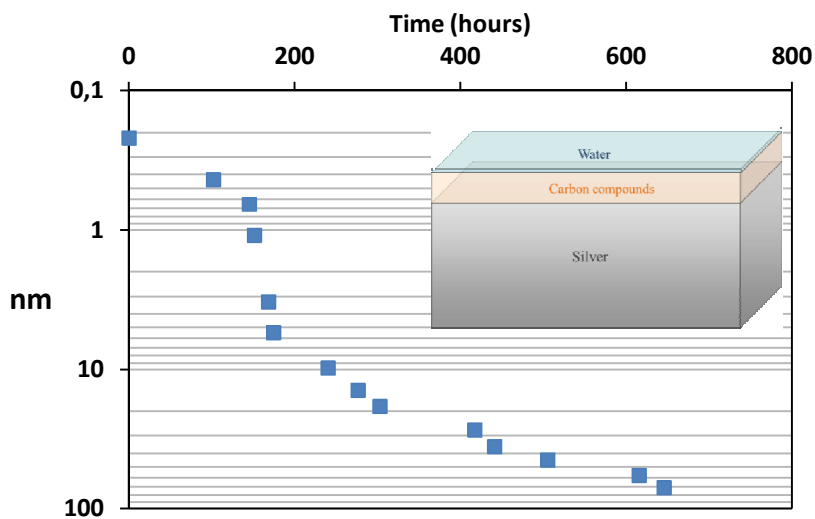


Fig.9. Theoretical eroded thickness and simplistic sample representation.

DISCUSSION

We have investigated in details the step by step evolution of the EE properties from as received silver sample (technical sample) to sample considered as pure Ag. Important evolutions of TEEY spectrum shape are observed during cleaning process. An overall decrease of the yield was observed and in particular the first crossover energy shifts from 20 eV (technical sample) to 125 eV (pure sample). The measured energy distributions show that the cleaning process leads to an increase of the inelastic BSE yield. The electron energy loss spectra (EELS), not presented here, clearly reveal an important increase of the characteristic energy loss frequency (surface and volume plasmon losses) when the sample was cleaned. This observation may explain the increase of the inelastic BSE yield. When the sample is exposed to ambient atmosphere after the cleaning process, the sample recovers progressively its initial state properties, in a relatively short time. This last observation may explain the fact that the EEY measured by us on many technical silver or silver plate samples over more than 5 years are extremely stable. The contamination layer built within a few days after sample processing plays the role of stable “passivation layer” whose properties replace those of the silver.

The presented results highlight the fact that the use of tabulated electron emission data measured or modelled very often on pure and clean materials for fundamental investigations purpose, must be used with great caution in context of applications (rf devices exposed to atmosphere).

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