

## Auger electron spectroscopy study of the interface between bulk aluminum and bulk aluminum oxide

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An extensive Auger electron spectroscopy study of the aluminum–aluminum oxide interface is presented, with the aim of identifying the behaviour of the contact zone between bulk metal and bulk oxide. Restored oxygen KLL and aluminum LVV spectra have been derived and analysed as a function of the depth of a thick aluminum sample evaporated onto an aluminum oxide crystal. The capability of the Auger electron spectroscopy to derive rather unique information on the nature of the contact zone is used to infer that the metal and oxide form small isles or domains in the interface region, so that the transition from the metal to the oxide is not characterized by a sharp surface.

### 1. Introduction

The study of *bulk* metal–*bulk* metal oxide interfaces is extremely interesting because, apart from the obvious applicative importance of this sort of interfaces, the presence of a metal and an insulator makes the electron states in the contact region very complex. The different organization of the electron states in metal and metal oxide affects both the valence or conduction states and the core states, so that it is important to study all of them. Moreover, it is now quite clear that the study of the electron states at the interface has to be performed employing electron spectroscopy to enhance the effect of the sample volume involved in the transition from the metal to the insulator

with respect to the bulk of the sample itself [1]. Nonetheless, a well defined method to identify univocally the transition between the metal and the oxide is still lacking because of the complexity of the results obtained in composite systems. In this paper we show that Auger electron spectroscopy (AES) is a rather unique technique to get spatial as well as spectral information in such systems.

To the purpose of studying the transition from the metallic state to the insulating one, we have considered the aluminum–aluminum oxide interface as the prototype of this sort of interface, because aluminum is a simple metal having almost free conduction electrons [2] and its oxide has a well defined stoichiometry with a very small

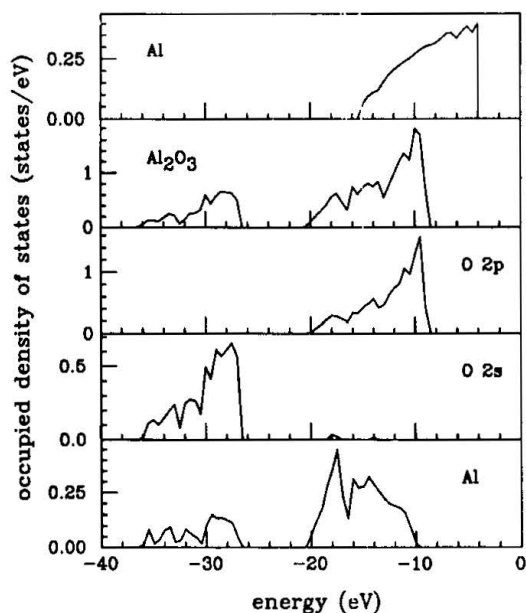


Fig. 1. Occupied total density of states of Al and  $\text{Al}_2\text{O}_3$ . In the case of  $\text{Al}_2\text{O}_3$  the contributions of 2s and 2p states of O and that of Al are also shown. The zero of the energy scale corresponds to vacuum level.

tendency to form oxides different from  $\text{Al}_2\text{O}_3$  [3]. The strong difference between the occupied densities of states of bulk Al [2] and bulk  $\text{Al}_2\text{O}_3$  [4,5] shown in fig. 1 suggests a complex electronic behaviour at the Al– $\text{Al}_2\text{O}_3$  interface. From fig. 1 we can expect some mixing of the conduction states of the metal with the valence states of the oxide and such a mixing should play an important role in the cohesion between the two systems. To identify whether this mixing is actually present a careful direct experimental study of the interface must be performed leaving the contact zone as unchanged as possible, in order to derive information on the interaction between the electron states of the two systems without introducing spurious features due to the measurement itself.

We chose to study the Al– $\text{Al}_2\text{O}_3$  interface employing AES. It is clear that AES, being intrinsically based at least on a two-body process, is more complex than photoelectron spectroscopy (PS) which allows also for much better energy resolution. However, one can exploit the intrinsic characteristics of the AES to the purpose of

identifying the features related to the contact zone between metal and oxide at the atomic scale. In fact, AES can be used to identify, in a single interaction process, *two electron states* having a total binding energy smaller than that of the hole. Moreover, thanks to the localized nature of the core-hole wavefunction, the decay process can take place only in a rather small spatial region. As a consequence AES does not give spectral information only, but it allows for the identification of two rather localized states that develop in a spatial region whose size is at the atomic scale. This fact can be exploited to identify unambiguously the mixing of the metal and oxide electron states through the appearance of a new band in the Auger spectrum. When a core hole is created on an atom which belongs to a spatial region where metal and oxide are in contact, one can observe a new Auger transition whose rate is a direct measure of the *contact surface*, because such a transition is absent in the bulk. Moreover, the new band is identified also when the electrons escape from a region which is about one mean free path below the sample surface. In this way one can analyse Auger electrons which are excited within the bulk and carry some information about the contact zone between the two components, still in bulk form. On the other hand PS, which is due to a single particle interaction, can give the energy distribution of the electron states of Al and  $\text{Al}_2\text{O}_3$ , but it cannot give any information about the spatial mixture of Al and  $\text{Al}_2\text{O}_3$  wavefunctions. The PS transition rate is governed by the number of atoms involved and any spatial information has to be inferred from the spectral changes by controlling directly the place where the transition occurs. However, this is possible only when the clean surface of one component is covered by the other one at the sub-monolayer level, i.e., not within the bulk. In this sense AES is superior to PS in order to study the contact zone between bulk metal and bulk metal oxide.

An accurate interpretation of the AES experimental results needs some care because, due to the effects of the energy losses encountered by the escaping electron, the measured spectrum cannot be considered as a true Auger spectrum.

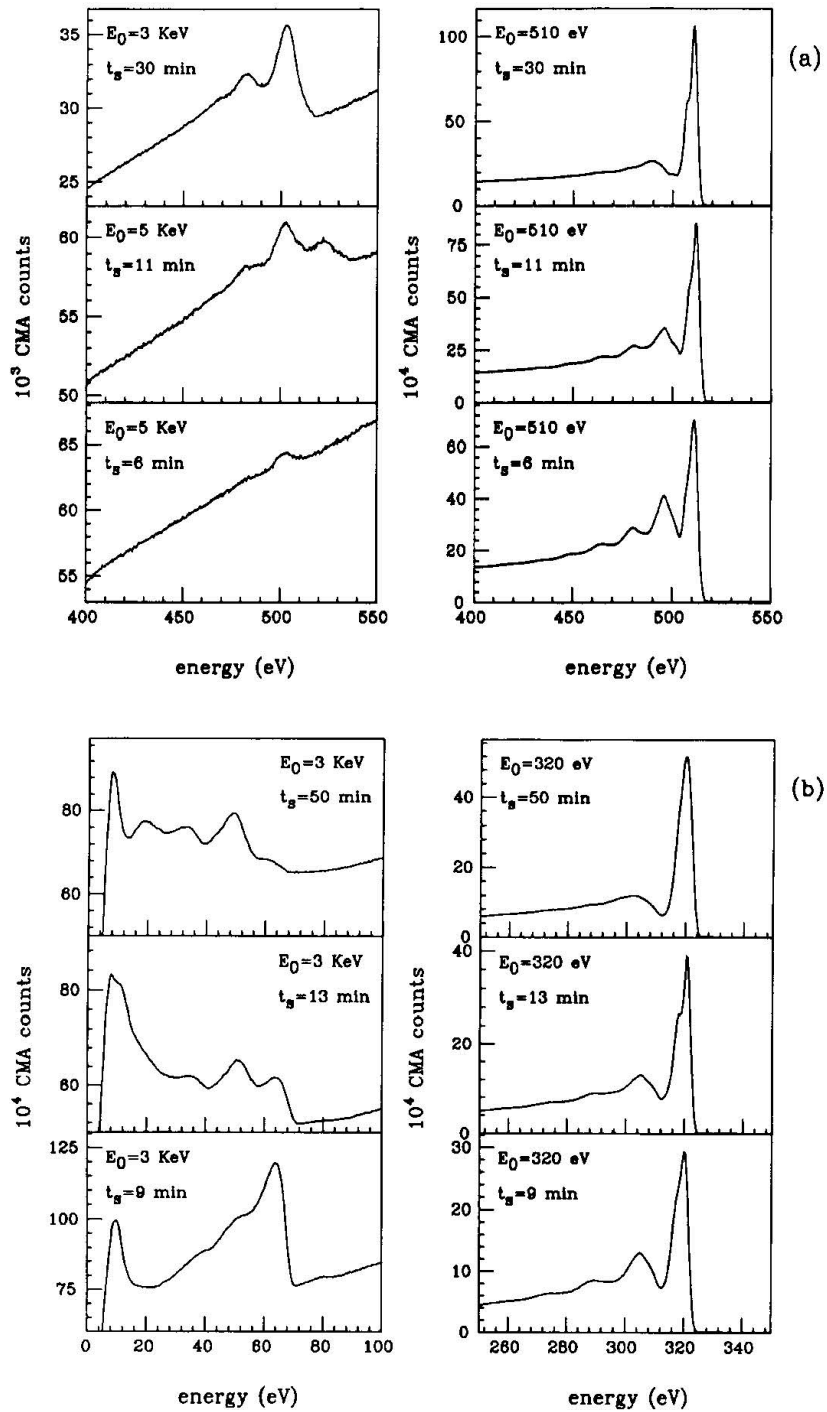


Fig. 2. Raw data (CMA counts) as a function of the sputtering time  $t_s$  and at two excitation energies  $E_0$ . (a) O KLL and energy loss at 510 eV. Charging effects are evident when  $E_0 = 5 \text{ keV}$  and  $t_s = 11 \text{ min}$ . (b) Al LVV and energy loss at 320 eV.

In a recent paper [6] we have introduced a reliable method to derive the actual Auger spectrum within the usual three-step model. The key point of the restoration procedure is always the determination of the energy loss function which must be employed to determine the loss-free spectrum. In the case of a uniform sample the loss function is reasonably modeled by the electron energy loss function obtained from the backscattering of a monochromatic electron beam [6]. When the sample is composite the situation is more complex [7,8] and a general method to deduce the clean information is not available so that one has to adapt the procedure to identify the most reliable information in a proper way. In the case of the Al–Al<sub>2</sub>O<sub>3</sub> sample we measured at *the same time* the aluminum and oxygen KLL spectra and the aluminum LVV spectrum together with the corresponding energy loss functions at a beam energy just lower than the Auger excitation energy. Using all these experimental data we have been able to deduce rather good clean Auger spectra and a systematic behaviour of the electron states has been identified.

## 2. Experiment

We performed an extensive investigation of a thick layer of Al metal, covering the surface of an Al<sub>2</sub>O<sub>3</sub> bulk sample, by progressively removing the metal layer by argon sputtering at a rate of about 20 Å min<sup>-1</sup>. The use of sputtering to analyse the structure of the sample along its depth, though customary, has the disadvantage of a considerable damage of the sample itself, possibly producing a less defined interface [9]. Although, using a deposition technique controlled at the monolayer level, the growth of the interface could produce a better sample, we do not consider a monolayer of Al on Al<sub>2</sub>O<sub>3</sub> as representative of the interface between *bulk* Al and *bulk* Al<sub>2</sub>O<sub>3</sub>. As a consequence we preferred to proceed using relatively thick samples, i.e., thicker than 1000 Å, analysing them by removing the outermost layers by sputtering.

The Auger measurements have been performed using a cylindrical mirror analyser (CMA)

spectrometer having a base pressure of 10<sup>-10</sup> Torr, employing electron excitation. The energy resolution was changed accordingly to a good compromise between intensity and accuracy in identifying the sharp features possibly present and considering also that the measuring time had to be short enough to avoid the contamination of the sample surface.

Two sets of data have been obtained evaporating Al metal on a single crystal of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> under a moderate vacuum (10<sup>-6</sup> Torr, during growing), holding the substrate at room temperature. After growing, the samples were held in a high-vacuum chamber for several days and were thick enough so that the major contaminants could be removed, using argon sputtering, before the investigation of the interface at different depths, i.e., different sputtering time. Carbon and nitrogen were checked. Neither carbon nor nitrogen were observed within the metal bulk, while a small amount of carbon was observed in the grown sample. The growing procedure outlined has the disadvantage of producing some contamination of the sample, but it allowed for a very high growing rate. Due to the poor vacuum of the growing chamber, all the samples had the external surface contaminated by about 50% aluminum oxide, which we could identify thanks to the fact that the oxygen KLL spectrum was exactly the same as that of the bulk Al<sub>2</sub>O<sub>3</sub>. However, we observed that the oxide contamination involved mainly the outer part of the sample and could be removed by appropriate sputtering, thus reaching a region thicker than 1000 Å, where the oxygen signal was almost negligible and indicating the presence of no more than 2–3% of Al<sub>2</sub>O<sub>3</sub> in the worst cases, as can be seen in fig. 2. Actually in this region the oxygen signal was so weak that we could not examine its shape, but we never observed an oxygen signal different from that of aluminum oxide. It should be also observed that the aluminum LVV signal obtained in the region where the oxygen signal was vanishing was identical to that obtained from a clean bulk aluminum sample.

On a first sample the measurement of the AlKLL as well as of the OKLL Auger spectra was performed together with the electron energy

loss at 1400 and 510 eV beam energy as a function of the sputtering time. It is important to note that the two Auger spectra were recorded during the *same* period by repeating several times the two scans at a rate of 10 Hz. In this way the Al and O spectra are representative of the *same* structural situation. The energy loss spectra were recorded in the whole energy range so that we could check the possible contamination from light elements between two sputtering operations. After several checks we selected a measurement time such that no contamination (carbon signal less than the noise level) could be detected between two sputtering operations. A second sample was analysed following the same procedure. In this case we measured the OKLL and AlLVV Auger spectra and the energy loss spectra were taken at 320, 510 and 1005 eV beam energy. As an example, the raw data for both samples are shown in fig. 2. We note that in all cases we determined the oxygen spectrum so that we could evaluate the amount of oxygen present within the Al metal.

All the data have been obtained by exciting the Auger process using a 3 keV electron beam. However, some data on the first sample were obtained using a beam energy of 5 keV. In this last case quite clear charging effects have been observed as a strong deformation of the OKLL spectrum. This effect is shown in fig. 2a, where the OKLL raw spectra measured at 3 and 5 keV are reported. In order to check the nature of the depicted effect, a third sample of pure aluminum, covered by an aluminum oxide layer, obtained by exposing the clean surface to an oxygen atmosphere for several months, was also studied. In this case, due to the good overall conductivity of the sample, no charging effect was observed. We want to note the fact that this last sample was covered by a rather thick layer of  $\text{Al}_2\text{O}_3$ , generally exceeding 100 Å. Such a sample gave essentially the same results we got on the evaporated ones, though the bad uniformity of the oxide layer prevented a well controlled and systematic study along the depth. However, the concurrence between the two procedures made us confident that the data we obtained were not affected by contamination or other spurious effects. Finally,

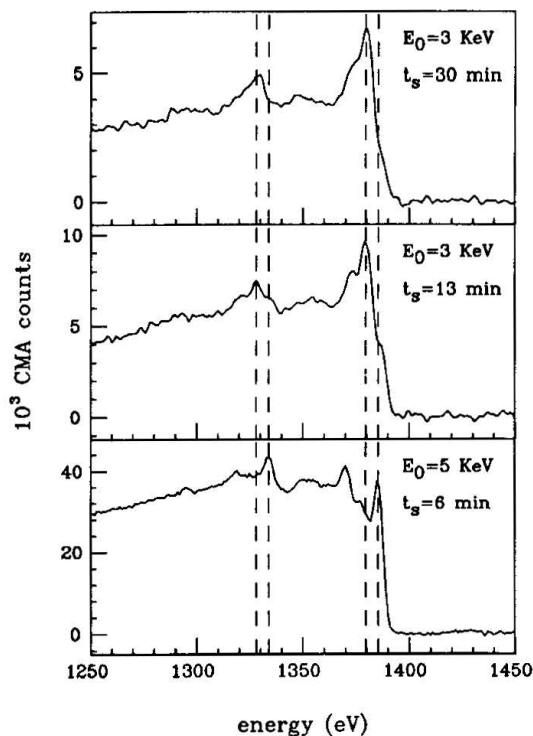


Fig. 3. AlKLL raw data after the subtraction of a linear background (see text). The dashed lines are eye guides to identify the contributions from Al in metal and oxide as observed at  $t_s = 13$  min, where pure Al ( $t_s = 6$  min) and pure  $\text{Al}_2\text{O}_3$  ( $t_s = 30$  min) coexist.

we note that the identification of metal and oxide contributions can be seen on the KLL spectrum of Al at the same time. A typical result is reproduced in fig. 3, where we see that the KLL spectrum of the pure oxide is shifted by about 6 eV at lower energy with respect to the metal. At intermediate sputtering time, i.e., at  $t_s = 13$  min, when the metal layer is only partly removed, this spectrum is a mixture of the metal and oxide spectra. This behaviour does not mean that the two phases coexist in the same region, because the mean free path at 1400 eV exceeds 100 Å, so that when the metal layer is thinner than 100 Å, the contribution from the underlying oxide is also seen in the KLL spectrum.

3. Data analysis

To derive the actual electron current per energy unit from the CMA counts, it is necessary to measure the energy window  $\Delta E$  of the apparatus defined by

$$\Phi(E) = \Delta E J(E), \tag{1}$$

where  $\Phi(E)$  is the flux measured by the CMA and  $J(E)$  is the electron current per unit energy flowing from the sample at the kinetic energy  $E$ . It can be measured as the broadening of the elastic scattering peak obtained from a monochromatic electron beam. We found that the resolution width changes linearly with the kinetic energy and in all cases a *non-zero* width is found on extrapolating to zero energy. This residual width ranged from 1.5 to 3.5 eV, depending on the assumed nominal resolution. A typical example is shown in fig. 4 for two nominal resolutions ( $\Delta E/E = 0.004$  and  $\Delta E/E = 0.005$ ) employed in the present experiment.

To derive the clean Auger rate from the electron current  $J(E)$ , we adapt the procedure [6] previously shown to be very effective in analysing AES data in uniform samples.

First of all, we concentrate on the OKLL data, because such a spectrum is relatively simple and its shape is almost independent of the sputtering

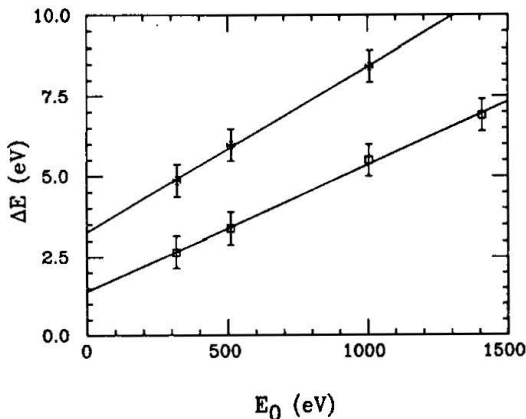


Fig. 4. Experimental energy window  $\Delta E$  of present CMA at two different nominal resolutions and at various energies as deduced from the broadening of the elastic peak produced by the backscattering of a monochromatic electron beam.

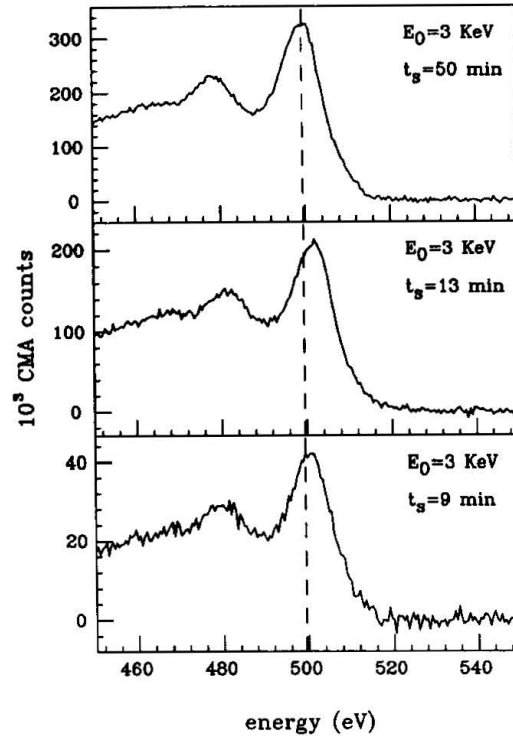


Fig. 5. Raw data for the OKLL spectrum after the subtraction of a linear background (see text). The dashed line is an eye guide to identify the uniform shift of the OK hole.

time. This is shown in fig. 5 where we report the raw OKLL data, i.e.,  $\Phi(E)$ , after the subtraction of a linear background obtained by fitting the high-energy side of  $\Phi(E)$  just above the Auger peak [10]. Apart from a shift of the order of 2–3 eV, no evident change is seen among the various curves shown in fig. 5. Such a shift cannot be ascribed to charging effects, because it was evident also in the spectra measured on the sample obtained by oxidizing bulk aluminum metal. On the other hand, because quite appreciable changes can be seen in fig. 2a in the corresponding energy loss spectra, the use of these loss spectra in the restoration procedure cannot give good results. This behaviour is quite expected as the energy loss spectrum measured by analysing the back-scattered electrons is not representative of the losses suffered by the Auger electrons escaping from a composite system. Ideally the Auger electrons cross the interface only once, while the

injected electrons have to cross the interface twice. As a consequence there is no way to determine experimentally a good approximation for the true energy loss. However, in the present case we can reverse the problem to get some information on the actual energy loss on assuming that the shape of the oxygen Auger spectrum is independent of the sputtering time. In fact, fig. 5 shows no evidence of different stoichiometries for the aluminum oxide, which is in accordance with ref. [3] as well. None of the spectra of fig. 5 presents a double Auger peak, or at least a complex structure, as could be expected if two or more stoichiometries were present.

As a consequence of the assumption that the OKLL spectrum is always the same, we infer that the loss function which affects these spectra is essentially that of bulk aluminum oxide. In order to check this behaviour, following ref. [6], we can write

$$J(E) = B(E) + \int L(E - E')W(E') dE' + n(E), \quad (2)$$

where  $B(E)$  is the primary electron background,  $L(E)$  is the energy loss function at the energy of the Auger peak,  $W(E)$  is the true Auger rate and  $n(E)$  is the noise introduced by the statistical fluctuations as well as other possible sources of noise. Eq. (2) and the restoration procedure described in ref. [6] can be easily applied to the data obtained at long sputtering time, where only  $\text{Al}_2\text{O}_3$  contributes. If, according to the previous discussion, the OKLL Auger rate is assumed to be independent of the sputtering time, we can derive the effective loss function at different depth, using eq. (2), by assuming  $W(E)$  and  $J(E)$  as known, and deriving  $L(E)$ . The same optimum linear filter technique employed in ref. [6] can be used in this case also and the results of this procedure are reported in fig. 6. The effective loss function deduced by means of the present method is almost independent of the sputtering time and is significantly different from the energy loss directly measured in the same condition. On the other hand, it compares closely, apart from a small shift, with that measured relative to pure

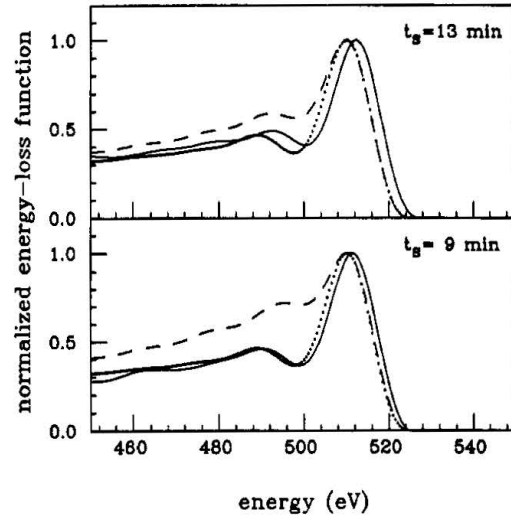


Fig. 6. Normalized loss function obtained by assuming that the Auger rate of the OKLL is independent of the sputtering time (solid line); loss function measured at the same sputtering time of the restored spectrum (dashed line); loss function measured at  $t_s = 50$  min (dotted line), which corresponds to the pure  $\text{Al}_2\text{O}_3$ . For comparison purposes all the experimental data have been convoluted with the same filter employed in the restoration procedure.

$\text{Al}_2\text{O}_3$  at the maximum sputtering time. As discussed before, this behaviour can be interpreted considering that when the oxygen signal is observed, the sample surface is close enough to the oxide layer so that the energy loss processes suffered by the escaping Auger electrons are those relative to the oxide, possibly modified by the presence of aluminum metal in the nearby region.

Let us now look at the AILVV spectrum. From fig. 2b we see that a very complex situation occurs. An evident evolution of the spectrum as a function of the sputtering time is present in the raw data. To analyse these data we employed the procedure of ref. [6] and eqs. (1) and (2) to derive the correct Auger rate. To model the loss function, we used that deduced from the energy distribution of the backscattered electrons at about 65 eV beam energy, at each sputtering time. This is justified by the fact that the loss function does not depend appreciably on the sputtering time in this energy range and, hence, on the actual composition of the sample at the corresponding depth.

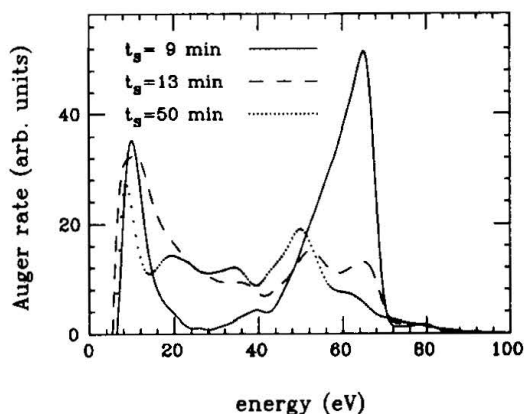


Fig. 7. Restored ALLVV Auger spectrum. Arbitrary units are employed, but the comparison among different spectra is meaningful.

The primary electron background has been assumed to be described by a linear extrapolation of the data between 85 and 120 eV. The restored spectra corresponding to the raw data of fig. 2b, are reported in fig. 7. A very good spectrum is obtained down to 6 eV, which is essentially the minimum energy which can be reasonably studied by means of the present apparatus.

#### 4. Discussion and conclusion

The nature of the present system and the set of data we collected suggest two kinds of conclusions. First of all we concentrate on the oxygen spectra. The systematic shift of the restored loss functions shown in fig. 6 compares with the shift of the raw data of fig. 5 and has some relevance. The energy shift of the restored loss function indicates a shift of the OKLL spectrum with respect to that used as a reference, namely the spectrum of pure  $\text{Al}_2\text{O}_3$ . Such a uniform shift suggests a change of the energy of the oxygen K hole. However, at each depth only a single K hole energy is present and the aluminum oxide behaves in all cases as a homogeneous sample having a well defined electronic distribution. This behaviour could be explained by the presence of a remaining small amount of aluminum metal which screens the oxygen K hole when the sput-

tering time is between 13 and 19 min. Considering that the sputtering time interval corresponds to a layer thicker than 100 Å and taking into account that the mean free paths of the electrons at 500 eV are 11 and 8 Å in Al and  $\text{Al}_2\text{O}_3$ , respectively [11], we deduce that there is no sharp interface between metal and oxide. In other words, the sample behaves as if the contact surface were much more extended, for instance due to the formation of domains, than in the case of a flat surface. Moreover, it should be remarked that within the spatial resolution of the present instrument (300–500 Å) the sample was always uniform, then the size of the domains of the contact zone can be expected at a lower scale. The shift of the oxygen K hole can be due to screening effects connected to the metallic aluminum nearby, only if the size of the aluminum oxide domains is comparable to the screening length in the metal.

A second kind of conclusion can be derived from the ALLVV spectra of fig. 7. At low sputtering time, an Auger spectrum characteristic of aluminum metal is obtained, in good agreement with that obtained, using an identical restoration procedure, on bulk aluminum with a negligible oxygen signal. The general features of the pure metal and pure oxide spectra are those expected from the theoretical band structure reported in fig. 1. The rise of the spectrum around 10 eV can be quantitatively attributed to an Auger process involving valence states only (VVV process). An interesting feature is seen when the sputtering time is between 13 and 19 min. Above 30 eV the spectrum is a mixture of those in relation to metal and oxide. However, in the energy range between 15 and 30 eV the observed spectrum exceeds both metal and oxide spectra: apparently a new band develops. This new band is easily interpreted as an Auger transition due to a localized hole, belonging to the  $\text{Al}_2\text{O}_3$  band, centered around  $-30$  eV and involving one valence state of Al and one valence state of  $\text{Al}_2\text{O}_3$ . This transition is observed in a sputtering time interval of about 6 min, which again corresponds to a thickness, in excess of 100 Å, that is much more than the 3–4 Å which is the mean free path of 50 eV electrons in Al and  $\text{Al}_2\text{O}_3$  [11]. As previously



observed, an Auger transition can take place only in a small volume around the atom where the hole is created, therefore the mixture between the metal and oxide electron states involves tens of atomic layers. Because the new band carries an appreciable fraction of the total intensity and considering that the transition rate of the mixing band is proportional to the contact surface, one has to expect that small oxide and metal domains develop to increase the surface to volume ratio. This hypothesis is reinforced by considering that the new band is observed in the same depth range where the uniform shift of the oxygen K hole is observed.

In conclusion, all the results of our AES investigation of bulk aluminum–bulk aluminum oxide interface show the utility of AES in performing this sort of studies. The results are coherent with a complex metal–oxide interface according to recent indications obtained from different experimental techniques [1,12]. The presence of small isles or domains in the interface zone, whose thickness is of the order of 100 Å, is also extremely plausible from a thermodynamical point of view, as the present samples were grown at room temperature. Further studies about the effect of the growing procedure, namely growing rate and substrate temperature, as well as the possible damage of the interface roughness by the sputtering operation are presently in progress.

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