The oxidation process of the K/GaAs(110) interface

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Abstract. The K-promoted oxidation of GaAs(110) has been studied using Auger electron spectroscopy and principal component analysis. We found that the oxidation process of the interface is not a properly catalytic mechanism, as the alkali metal reacts forming compounds that become mixed with the substrate oxidation products. The substrate oxidation process starts, as well as that for the adsorbate, from the beginning of the oxygen exposure without showing an adsorption stage like that observed during the oxidation process of the clean GaAs surface. The alkali-promoted oxidation of GaAs involves the simultaneous oxidation of all the elements present, K, As and Ga, and neither induction nor adsorption stages are observed.

1. Introduction

The oxidation process of semiconductors is probably one of the most studied issues in surface science, owing to both its basic interest [1–14] and technological potential applications. Perhaps the greater impact of semiconductor oxides occur in MIS (metal–insulator–semiconductor) devices [15–18]. Since electronic technologies are continuously evolving, the demands on the improvements of the oxidation processes are sustained. For instance, in order to achieve superscaled MOS (metal–oxide–semiconductor) devices [15] it is necessary to obtain ultra-thin oxide films of 50–100 Å. This demand is incompatible with the normal oxidation processes that, being performed under high temperatures and pressures, enhance the diffusion of dopants degrading the quality of the oxide films. The natural solution for this problem is the oxidation at lower temperatures and the forced use of catalysts. A great variety of elements has been tested to this purpose, including noble metals, transition metals, rare earths and alkali metals [19–26]. All of them enhance the semiconductor oxidation rate although the effects on the final product are quite different. Except for the alkali metals, all of them react with the substrate and the oxygen forming stable compounds. While alkaline elements exhibit a clear promotion effect and are easily removed from the surface, their poisoning effect on the semiconductor properties makes their use as oxidizing catalyst a very hard task. On the other hand, the study of alkali-promoted oxidation processes raises additional interest through the development of photocathodes, image intensifiers, infrared sensitive detectors and night vision devices [27–29].

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The action of adsorbed alkali metals on the oxidation process of the semiconductor is so complex that even after several years of work ([30] and references therein [31, 32]) there are several points under discussion. A clear example is the interpretation of the mechanisms of the Si and GaAs alkali-promoted oxidation. In both cases, the oxidation mechanism has a different behaviour depending on whether the pre-deposited alkali coverage is either below or beyond one monolayer (1 ML).

In this work we study the promoted oxidation of a III–V semiconductor (GaAs) through the pre-adsorption of an alkali metal (K). We limit our study to coverages below the saturation one at room temperature, i.e. 1 ML. The history of the understanding of the GaAs oxidation process has not been free from errors and misinterpretations. In fact, the first models suggested, based on the large chemical shift observed in the As XPS peak, the preferential oxidation of As [1, 3]. After improvements in the XPS sensitivity, the observation of an earlier shift of the Ga peak led to the adoption of a different point of view, i.e. an earlier oxidation of Ga was suggested [2, 4, 6–9]. The simultaneous oxidation of both elements has also been proposed [10, 11]. In a recent work [33], we have shown by means of Auger electron spectroscopy (AES) and principal component analysis (PCA) that the first stages of GaAs oxidation process are characterized by the simultaneous oxidation of both constituents, i.e. As and Ga. All these controversies arise again when referring to the oxidation process of alkali/GaAs interfaces. For instance, an induction period, where the adsorbate oxidation is observed without detecting changes in the substrate, has been reported for a variety of alkali/GaAs systems: Cs/GaAs(100) [34] and Cs(K)/GaAs(110) [35]. After this period, earlier Ga oxidation via the formation of Ga_2O_3 has been reported [34]. Also, the primary oxidation of As has been reported [35], as indicated by the formation of As_2O_3 for the K-covered surface, while for the Cs-covered one the simultaneous presence of As species with different oxidation states has also been found [35].

In spite of its high sensitivity, Auger electron spectroscopy (AES) has been only scarcely used to study the growth and further oxidation of the alkali/GaAs interface. Moreover, owing to the difficulties in interpreting the Auger lineshapes, AES studies have been almost exclusively confined to the basic peak-to-peak intensity analysis of the Auger differentiated spectra. The Auger transitions $As_{M_{4,5}VV}$, $Ga_{M_3M_{4,5}M_{4,5}}$, $Ga_{M_2M_{4,5}M_{4,5}}$, $Ga_{L_3M_{4,5}M_{4,5}}$, K_{LMM} and O_{KLL} have been used to verify the interface growth mode [26, 36], the kinetics of the K/GaAs(110) oxidation process [26] and, through the ratio between $Ga_{M_2M_{4,5}M_{4,5}}$ and $Ga_{M_3M_{4,5}M_{4,5}}$, the Ga oxidation state [26]. However, the power of the information contained in the Auger line shape for this system has been proved through the detection of the existence of a reaction occurring between K and Ga or As atoms during the interface growth [36].

2. Experiment

2.1. Experimental set-up

All measurements were performed in a commercial ultra-high-vacuum (UHV) surface analysis system (PHI 590A) with a base pressure in the 10^{-10} Torr range. The Auger spectra were acquired in the differentiated way with a single-pass cylindrical mirror analyser (SCMA) having an energy resolution of 0.6% and 2 eV modulation amplitude. The sample was excited with a 2 keV primary electron beam. In order to maintain the electron-stimulated oxidation as low as possible, the electron gun was turned on only during the Auger spectra acquisition periods and always after the oxygen was evacuated from the chamber.

The sample was an n-type GaAs(110) crystal doped with Te (3.0×10^{17} atoms cm^{-3}). We prepared the surface by means of ion bombardment and annealing (IBA) cycles, using Ar$^+$ ions of 1.5 keV and an annealing temperature of 850 K. The sample was heated by backward electron

bombardment and the temperature measured by a chromel–alumel thermocouple attached to the edge of the sample. No traces of contamination were detected within the sensitivity of AES after this treatment. Through these processes the (1×1) low energy electron diffraction (LEED) pattern, typically found on III–V(110) surfaces, with sharp and intense spots were obtained.

K atoms were deposited onto the GaAs(110) surface at room temperature (300 K) by direct heating of a K dispenser (SAES-Getters, Italy). During the K deposition, the pressure never rose above the 10^{-10} Torr range. After each interface growth no contamination peaks were detected by means of AES. The oxygen exposures were carried out with the sample at room temperature and under a constant pressure of high-purity oxygen (>99.997%) in the UHV chamber.

2.2. Measurement procedure

It is well known that the presence of excited oxygen molecules (ion gauge, ion pump, light, electron bombardment) strongly affects the kinetics of the GaAs oxidation process [7, 9, 33, 37, 38]. It is also accepted that only the kinetics of the process is affected, i.e. the chemisorption and oxidation depend only on the amount of oxygen at the surface [7, 9, 33, 37]. As we are mainly interested in the Ga, As and K oxidation and the formation of different oxide phases, the presence of excited oxygen is not assumed to play an important role in our experiment. Nevertheless, we have performed the K/GaAs interface oxidation measurements with the same conditions as our electron stimulated oxidation experiment (EBS) [37, 39], i.e. on the same spot and with the ion pumps switched on. The primary beam current density was 2.5 mA cm^{-2}.

2.3. Data treatment method

The method of principal component analysis (PCA) [40] has been successfully applied to different analysis techniques including AES [33, 36, 41–45]. The sequential method, as well as the criteria applied to determine the number of independent components, has been detailed in a previous work [43]. Therefore, we will limit ourselves to give here a brief description of the method.

In AES, the aim of PCA, together with the target transformation (TT) approach [40], is to decompose the data matrix **D**, formed by n Auger spectra (acquired in a certain sequence) of m energy channels, into two matrices as follows:

$$\mathbf{D} = \mathbf{RC} \tag{1}$$

where **D** is an $m \times n$ matrix, **R** is an $m \times c$ matrix whose columns are formed by the Auger spectra of the c pure components and **C** is a $c \times n$ matrix whose rows are formed by the weights of each pure component. The first step in the PCA treatment is the construction of the covariance matrix

$$\mathbf{A} = \mathbf{D}^{\mathrm{T}}\mathbf{D}. \tag{2}$$

If the number of independent chemical components of **D** is c, the rank of **A** will be also c. Therefore, for a perfectly noise-free set of spectra, the determination of the number of independent chemical components is reduced to the determination of the number of non-zero eigenvalues of **A**. However in a real experiment, noise is always present and all eigenvalues will be different from zero. Then the key point in PCA is to determine those eigenvalues that have physical meaning, i.e. those eigenvalues that statistically are different from zero.

The second step in PCA analysis requires diagonalizing **A**

$$\mathbf{Q}^{\mathrm{T}}\mathbf{A}\mathbf{Q} = (\lambda_{ii}\delta_{ij})$$
$$\mathbf{A}(Qj) = \lambda_j(Qj) \tag{3}$$

where the columns of $\mathbf{Q}(Qj)$ are the eigenvectors of **A**. One of the possible decompositions of **D** can be achieved by associating the diagonalizing matrix **Q** with the component matrix **C** in equation (3). Obviously, this is just one of all the possible abstract decompositions of **D** into two matrices. Its physical significance is achieved in the third and last step, known as TT [40]. Using the complete rotation matrix **Q** one should reproduce the data matrix **D**, even including the statistical errors. The goal of PCA is just to lower the dimension of **Q** to that corresponding to physical meaningful values, i.e. the use of the minimum number of eigenvectors (eigenvalues) to reproduce **D** within the experimental error. In addition, the simplest criteria behind the sequential method [43–45] is to fix the number of eigenvalues and to study the evolution of the error. This is defined as that generated in reproducing the data matrix **D**, as more spectra are added to this matrix. The last step of factor analysis (FA) consists in performing a suitable rotation of the abstract matrices **R′** and **C′** in order to obtain the physically meaningful composition matrix **C** and pure component matrix **R**

$$\mathbf{D} = \mathbf{R}\mathbf{C} = \mathbf{R}'\mathbf{T}^{-1}\mathbf{T}\mathbf{C}'. \tag{4}$$

In the TT [40–42], extra information is required. In the conventional TT, one needs to know the concentration of $c-1$ components at least in c (the rank of the data matrix) points of the profile. In the current case, we know that our starting compounds are GaAs and K, depending on what we are looking at; then the TT can be performed if PCA reveals up to two independent compounds along the profile. On the other hand, the condition to apply the sequential PCA is less restrictive: it can be used for any number of independent components under the requirement of having at least a portion of the profile showing the coexistence of no more than two components.

3. Results and discussion

In figure 1 we show the oxidation kinetics of the K/GaAs interface for different coverages of K, through the evolution of the O_{KLL} Auger yield. For comparison purposes, we present the O_{KLL} yield normalized to the clean $Ga_{M_2M_{4,5}M_{4,5}}$ Auger signal acquired before each experiment was done, i.e. different K coverage and further oxidation. Beyond, we have divided all values to that of the oxygen saturation obtained on the experiment with a K coverage of 1 ML (this was done for comparison purposes with Si experiments not presented here). In order to evaluate the extent of the effect of the K coverage on the oxidation kinetics, we have included in figure 1 our previous results on the oxidation of GaAs with minimum external excitation (MEE) [33, 37] and under electron bombardment stimulation (EBS) [37, 39]. Through these results we can clearly state that, as it is already known [26], the presence of even minute amounts of K strongly enhances the oxygen uptake kinetics. From the results of this figure it is also evident that, as long as we are mainly concerned with oxidation purposes, the addition of minimum amounts of alkali is largely more effective than performing electron stimulation.

Through this section we will analyse the chemical behaviour of the K/GaAs interface based on the changes observed in the Auger line shape produced by the oxidizing process. In figure 2 we show the evolution of the As, Ga (a) and K (b) Auger transitions obtained at different oxygen exposures during the oxidation process of a 1 ML alkali-covered GaAs(110) surface. We can observe changes in the Auger line shape suggesting that both the substrate and the adsorbate react in the presence of oxygen, in disagreement with previous reports [34, 35].
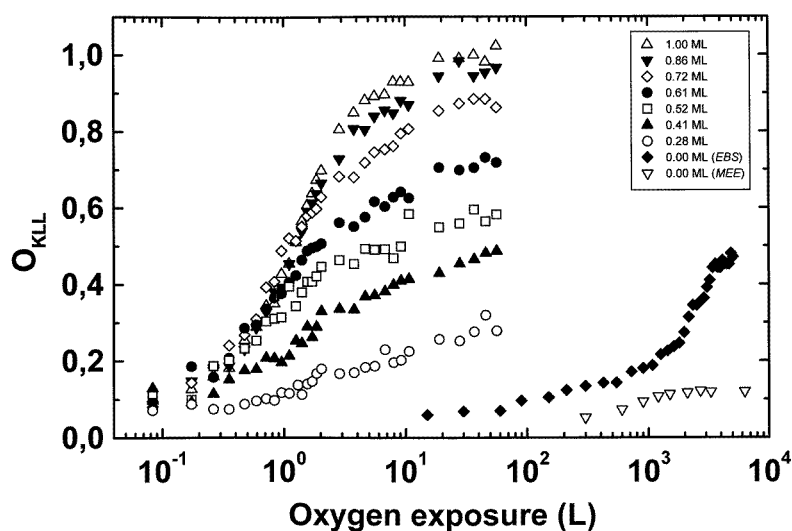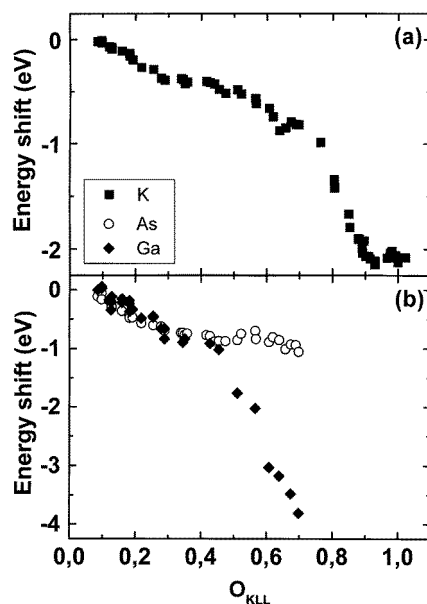
Figure 1. Oxidation kinetics of the K/GaAs(110) interface at 300 K. Oxygen evolution against exposure for different coverages of K. The results are compared with those of the oxidation of clean GaAs under electron bombardment stimulation (EBS) and minimizing the external excitation (MEE).
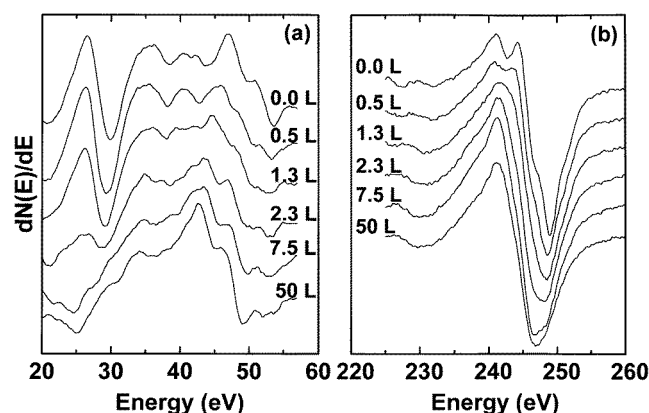
Figure 2. Evolution of the Auger transitions for different oxygen exposures on the K/GaAs(110) interface with a K coverage of 1 ML. (a) As, Ga and (b) K.

The $As_{M_{4,5}VV}$ (30 eV) Auger transition is strongly attenuated and shifted to lower energies up to its disappearance. The $Ga_{M_3M_{4,5}M_{4,5}}$, $Ga_{M_2M_{4,5}M_{4,5}}$ (50–54 eV) transitions shift towards lower kinetic energies. This shift suggests the partial replacement of the Ga double peak (50–54 eV) by that characteristic of Ga in Ga oxide occurring at 45–49 eV [9]. On the other hand, the K_{LMM} spectra show the disappearance of the double peak (240–245 eV) corresponding to the non-reacted K/GaAs interface, and also a noticeable shift to lower kinetic energies.

In figure 3 we exhibit in a more quantitative way the results previously shown in figure 2: we summarize the energy shifts of the negative extreme in the derivative K_{LMM} (a), $Ga_{M_2M_{4,5}M_{4,5}}$ and $As_{M_{4,5}VV}$ (b) Auger peak, as a function of the oxygen uptake. Through the analysis of the evolution of these energy shifts, one can identify two different stages of oxidation for the

Figure 3. Energy shift of the K (■) (a), As (○) and Ga (◆) (b) Auger peaks as a function of the oxygen uptake over the adlayer of K atoms, obtained during the oxidation process of the K/GaAs(110) interface.

adsorbate as well as for the substrate. In fact, in the first stage the K peak shifts slowly towards lower kinetic energies (0.5 eV approximately). This stage lasts up to around half of the oxygen saturation value. Beyond this value the second stage appears showing a larger slope for the K chemical energy shift variation against oxygen coverage. This last stage ends with a final energy shift for the K Auger line larger than 2 eV. On the other hand, the energy shifts of Ga and As Auger peaks show a less clear behaviour, mainly due to the attenuation of the signal and the strong changes taking place in their Auger lineshapes. Nevertheless, up to the point where we still observe each peak, the evolution of the energy shifts is in the same sense as in the K case, i.e. we can identify two stages which are distinguished by the slope in the energy change against oxygen at the surface, at least for the case of Ga.

In figure 4 we show the evolution of the error in reproducing the data matrix **D** as a function of the oxygen uptake for the K (a) and GaAs (b) Auger spectra. These plots were obtained by considering an increasing number of independent factors, as explained in section 2.3. These results show that, in order to reproduce the data matrix **D** with an error lower than the experimental one along the whole oxidation process, three independent components including the O-free structure are needed for K and GaAs Auger transition lines. In both cases, the first phase is detected from the beginning of the oxidation process. The second phase arises, in coincidence with the second stage observed through the energy shifts (figure 3), for an oxygen yield close to half its saturation value. A similar but not shown sequential analysis performed on both individual Ga and As Auger transition lines exhibits the same behaviour, i.e. three independent components appearing at the same oxygen coverages. This analysis points out a couple of startling results, concerning the behaviour of the GaAs substrate during the first step of the promoted oxidation process. First of all, the GaAs oxidation occurs in phase, i.e. the simultaneous oxidation of both constituents. Thus, the process takes place as if the K promoting layer were absent [33, 37]. Another remarkable point is that the adsorbate and the substrate
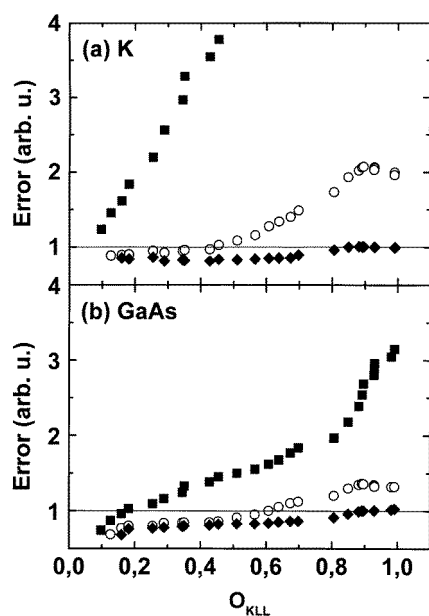
Figure 4. Evolution of the error in reproducing the data matrix **D** as a function of the oxygen uptake over 1 ML of K adatoms. The sequential PCA method was performed on the K (a) and GaAs (b) spectra measured during the oxidation process of the K/GaAs(110) interface, considering one (■), two (○) and three (◆) factors. The horizontal line corresponds to the experimental error (the errors in reproducing **D** are normalized to this value).

react simultaneously with oxygen. This result is in disagreement with the existent current assumption referring to the existence of an induction stage [34, 35], supposedly consisting of an initial alkali layer oxidation followed by the oxidation of the substrate, just after some amount of oxygen is incorporated. Finally, the substrate and the adsorbate oxidize from the very beginning of the oxygen exposure. This fact points out a difference with reference to the oxidation of a clean GaAs surface, where a non-reactive oxygen adsorption stage is detected [33, 39].

In figures 5(a) to 5(d), we summarize our findings concerning with the oxidation of the K/GaAs interface, as obtained through the TT method. In these figures we show the Auger line shape corresponding to the pure components involved in the oxidation of both GaAs (a) and K (b). These components, as well as their weights (5(c) and 5(d), respectively) characterize completely the evolution of the oxidation process. This is characterized by the presence of two new compounds for both the adsorbate and the substrate. The adsorbate is totally consumed in the process (figure 5(d)); i.e. a complete transformation of K into a chemically different compound is produced. In fact, K has been already consumed while the oxygen adsorption stage is still proceeding. On the other hand, the line shape of the unreacted GaAs is still observable after the oxygen saturation is reached. This is clearly observed in figure 5(c), through the non-vanishing weight of component 1 (associated with GaAs covered with 1 ML of K) at oxygen saturation. Based on this fact and on the low value of the Auger electron escape depth of Ga and As [46], we can infer that the substrate oxidation process stops and that the formed GaAs oxide film is extremely thin.

Let us consider the evolution of the K compounds in detail. The whole oxidation process is characterized by three different K-associated Auger lineshapes. The first one corresponds
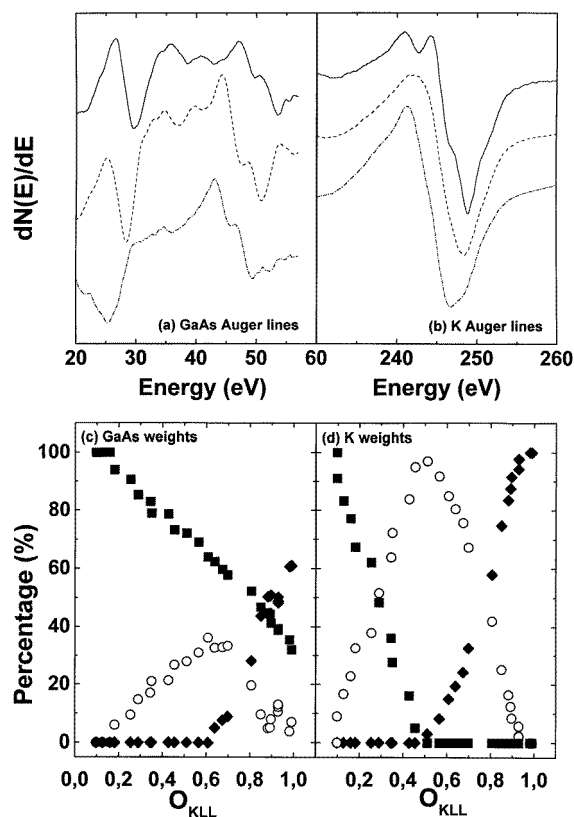
Figure 5. Auger spectra of the pure independent components obtained after performing the TT approach to the GaAs (a) and K (b) spectra, and the corresponding weights ((c) and (d), respectively) as a function of the oxygen uptake over 1 ML of K adatoms, during the oxidation process of the K/GaAs(110) interface (Auger spectra, solid line corresponds to component 1, dashed line to component 2 and dot–dashed line to component 3; weights, component 1 (■), component 2 (○) and component 3 (◆)).

to the non-oxidized K Auger line, although, as we have previously shown [36], this line is characteristic of one monolayer of K over GaAs and does not necessarily indicate the fingerprint of the K metallic Auger line. The new K Auger lineshapes are very similar, i.e. both show the disappearance of the double positive peak and a broadening as well as a shift of the main peak towards lower energies. The difference rests just on the magnitude of the broadening and the chemical shift. The analysis of the appearing sequence of these K compounds reveals the origin of the two stages observed in the chemical shift of the K Auger lines (figure 3(a)). In fact, the shift of the third and last compound being the most important, it is important to notice that the appearance of this compound is responsible for the break in the evolution of the energy shift observed in figure 3(a). These results can be analysed following the proposal of García Michel [47]. Within his sequential exposure experiment, the two new K Auger peaks correspond to K_2O and K_2O_2. As KO_2 is not stable at room temperature [47], its presence may be discarded. Therefore, in order to test this model we have analysed the evolution of the oxidation process at coverages below those corresponding to one complete monolayer.

In figure 6 we show the evolution of the error in reproducing the data matrix **D** of the K spectra, by using one (a) and two (b) independent factors, as a function of the oxygen amount
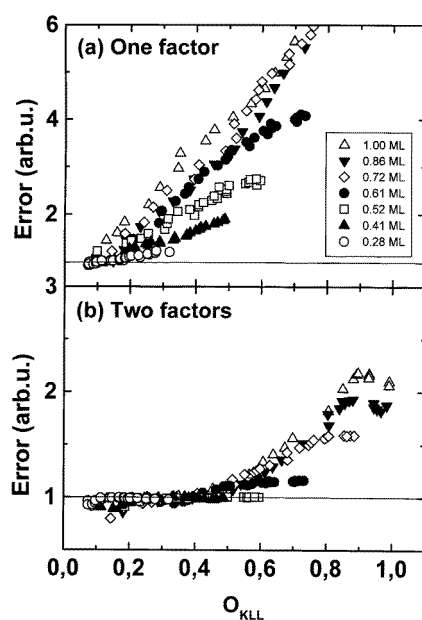
Figure 6. Evolution of the error in reproducing the data matrix **D** of the K spectra, by using one (a) and two (b) independent factors, as a function of the oxygen at the surface for different K coverages. These results were obtained by applying the sequential PCA analysis to the K spectra measured during the oxidation processes of the K/GaAs(110) interface with different K coverages.

at the surface for different K coverages. As in all our previous analysis, the appearance of a new compound is pointed out when the error overcomes the experimental one. From these results it is clear that K peroxide (K_2O_2) appears always for the same oxygen amount, and only at K coverages over a half of a monolayer. The analysis of the K Auger line shape performed in this section shows a couple of interesting results: (i) the way in which K deposited over GaAs reacts with oxygen depends on the coverage; (ii) the oxidation of K is sequential, i.e. K reacts with oxygen to form K_2O, and only when this transformation is completed does K_2O react to form K_2O_2. After this analysis we can also ascribe the Auger lineshapes presented in figure 5(b), obtained from the PCA and TT analysis, to particular K oxide compounds.

The analysis of the evolution of the GaAs Auger lineshapes shown in figure 5 also points out the presence of two different oxide phases along the oxidation process. A first difference with respect to the overlayer oxidation process rests on the fact that the final state is characterized by the presence of two compounds, the most oxidized one (component 3) and GaAs (component 1), the third and least oxidized one (component 2) being consumed along the process. This result shows that the oxidation of a GaAs surface is a passivating process, despite the presence of the oxidizing promoter. In fact, the results summarized in figure 5(c) exhibit the presence of the GaAs Auger signal from the bulk, below the K and GaAs oxide film. Since the escape depth of these electrons, of 60 eV and less, corresponding to the As and Ga transitions is rather below 1 nm [46, 48], it is clear that the oxide film is extremely thin.

The identification of oxides based on the Auger line shape, usually accomplished through a fingerprint procedure [49–51], is a hard task. This is even worse for low energy peaks as in the GaAs case. Nevertheless, we can analyse some general trends: (i) the increasing energy shift in going from component 1 to component 2 points out an increasing oxidation state, as

in the K case; (ii) in component 3 the As (30 eV) and the Ga (50–54 eV) peaks of GaAs have disappeared, being replaced by an As peak at 25 eV and the double peak of Ga at 45–49 eV. The As peak is associated with As oxides (As_2O_3) [6, 9, 52, 53], while the Ga double peak is well known to be characteristic of Ga in a Ga oxide (Ga_2O_3) [9, 52, 53], showing the features of a heavily oxidized GaAs.

As far as we know our lineshapes for K_2O and K_2O_2 are the first AES data found in the literature, so we do not have fingerprints with which these can be compared. However, the successful comparison of the GaAs third component with the heavily GaAs oxidized Auger lineshape obtained by Alonso and Soria [9] leads us to think that the K lineshapes reported actually correspond to real, well defined chemical species.

4. Conclusions

The alkali-promoted oxidation of the GaAs(110) surface is characterized by the following features: (i) there is no evidence of an induction stage: both the adsorbate and the substrate oxidize together from the beginning of the process; (ii) two oxide phases are detected for both the adsorbate and substrate, and within the substrate both constituents, i.e. Ga and As, oxidize in phase, as in the non-promoted case; (iii) for the adsorbate these phases are ascribed to potassium oxide (K_2O) and peroxide (K_2O_2), the oxide acting as a precursor of the peroxide and being consumed in the process; (iv) the peroxide is formed only for K coverages over half a monolayer; (v) the final stage of the substrate oxidation process is characterized by the presence of the most oxidized phase of GaAs and GaAs not oxidized at all. Since the intermediate oxide disappears in the process, this result suggests a sharp interface and a thin (of the order of the Auger electron escape depth) oxide film.

Acknowledgments

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