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Charge transfer and redistribution in the formation of the K/GaP(110) interface: a photoelectron spectroscopy study

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Abstract. We present the results of a photoelectron spectroscopy study of the K/GaP(110) interface grown at $T = 120$ K. We have investigated the system looking at the Ga 3d and P 2p core level spectra by analysing their lineshape. This analysis shows that the transferred charge in the adatom–substrate bonding formation affects the electronic and chemical environment of both surface Ga and P atoms. The results suggest relevant differences with the intuitive picture of strong ionic localized bonding between the alkali atom and surface Ga. They are instead more consistent with a delocalized redistributed valence charge between the adsorbate and the substrate. We also conclude that the system at $\Theta = 1$ ML is metallic, with an increasing disorder and inhomogeneity at the highest coverage studied. The similarities and differences with the Na/GaP(110) and the other alkali metal/GaAs(110) systems are discussed.

1. Introduction

The adsorption of alkali metals (AM) on cleaved III–V semiconductor surfaces is a subject that has been studied extensively [1, 2]. One of the main reasons which is often given to explain this interest is that it is a good model for the investigation of the formation of the Schottky barrier, because of the simple electronic configuration of the AM atoms (a single valence *s* electron) and the well known properties of the [110] surfaces of the III–V compounds. Despite this reasoning, it was found that the AM/III–V interfaces are not simple for a number of reasons. First, their high degree of surface reactivity is a well known problem that can hamper the experiments, because of possible surface contamination, even in good ultra-high-vacuum (UHV) conditions. Moreover, the electronic and structural properties exhibit a surprising variety of effects, depending strongly on the conditions in which the AM–semiconductor interfaces are grown (e.g. the substrate temperature [1–5]) and also on which AM is deposited at the surface. For instance, it was observed with scanning tunnelling microscopy that at very low coverages Cs on GaAs(110) forms zig-zag atomic chains along the [110] direction, while only sparse linear chains are formed in the Na/GaAs(110) interface [6, 7]. Another interesting example of this variety is the semiconducting nature of one monolayer (ML) of Cs deposited on GaAs(110) observed with scanning tunnelling spectroscopy [6], ascribed to a Mott–Hubbard insulating state of the system [6, 8–10]. This property was observed also with other spectroscopic techniques

like electron energy loss spectroscopy (EELS) [11, 12], but the excitation spectrum for Na deposited on GaAs(110) does not show the same sub-band losses observed in the case of Cs and of K. Recently the explanation of this experimental finding has been given in terms of the combination of the Mott–Hubbard effect and the presence of a bipolaron caused by a ‘negative- U ’ surface state resulting from a lattice local distortion [13, 14].

In order to characterize better the growth of the interface, some of the most essential pieces of information to be extracted are: the nature of the bonding of the adsorbed atom to the substrate, which electronic surface states are involved in the bonding, the amount of charge transfer from AM to the surface and where this charge is displaced.

The results of the many theoretical studies on this subject can be summarized in the following points:

(a) There is a very high amount of negative charge transferred to the substrate per K atom, estimated to be between 0.7 and 0.9 e [2].

(b) This charge is mainly displaced on the Ga dangling bond. According to these studies the nature of the bonding between the AM adatom and the Ga is very localized. The correlation effects and the Mott insulating state of the interface are consequences of this localization [2, 15, 16].

(c) For many recent studies, the charge distribution around As surface atoms seems to be affected little by the AM adsorption, at least at low coverage, although a paper by Fong *et al* [17] showed that there is also a polarization of the As dangling bond in the case of Na/GaAs(110).

Few experimental or theoretical studies have been extended to the adsorption of AM to the (110) surfaces of other III–V compounds, especially in the case of GaP. We believe that this extension is very important, in order to have a systematic knowledge of the role played by the different physical and chemical characteristics of the substrate atoms (like their electronegativity and their size) and the different size of the surface cell. To this purpose, we have performed an experimental study on the K/GaP(110). The technique that we used in this investigation is photoelectron spectroscopy (PES) from shallow core levels with synchrotron radiation, which is very powerful to obtain information about the properties of the interfaces at their early stages of formation, like the electronic environment of the photoemitting atoms and the nature of the electronic states induced by the overlayer. We have concentrated our attention on the analysis of the P 2p and Ga 3d core level lineshapes. Although there are similarities with other systems already studied, we obtain an indication that the K electronic charge donated to the substrate during the bond formation affects also the environment of the surface P atoms, contrasting with the intuitive and accepted view that only the surface Ga atoms are involved.

2. Experiment

All the experiments were performed at the beamline 6.1 of the Synchrotron Radiation Source, Daresbury Laboratory (UK), in a UHV chamber with a base pressure of 7×10^{-11} mbar. p-doped ($p = 3 \times 10^{18} \text{ cm}^{-3}$) GaP single-crystal bars were cleaved to obtain clean surfaces and kept at low temperature ($T = 120 \text{ K}$) with liquid nitrogen cooling. The temperature was monitored with a thermocouple. Although some large-scale steps were visible on the surface after the cleaving procedure, the quality of the surface was good enough for our core level analysis (see figures 2 and 3, table 1 and the related discussion in the next section). K layers were deposited from outgassed getter sources (SAES Getters, Italy). The amount of K dosage was determined from the shift of the sample work function measured

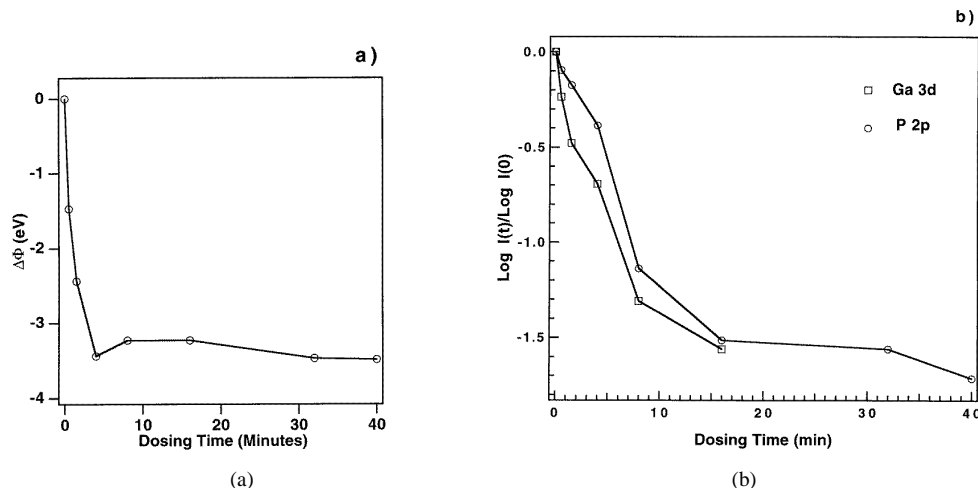


Figure 1. (a) Variation of the work function $\Delta\Phi$ plotted against the time of K evaporation. The experimental points are joined by line segments as a guide to the eye. (b) Attenuation curves of the total intensities of the Ga 3d and P 2p core level PE spectra (after background subtraction) against the dosing time.

by looking at the secondary electrons cut-off spectra, and from the attenuation of the P 2p and Ga 3d core level signals. The cleanliness of the surface was checked looking at the photoemission from the valence band (VB). The spectra were taken with a double-pass cylindrical mirror analyser. We took PE spectra from the Ga 3d core levels and from the VB with a photon energy $h\nu = 80$ eV, while the P 2p core level spectra were taken with $h\nu = 160$ eV. The experimental resolution and the Fermi energy position were measured from the VB spectrum of an Ag film deposited on the sample. The overall energy resolution was found to be $\Delta E = 0.24$ eV (full width at half maximum, FWHM) at $h\nu = 80$ eV and $\Delta E = 0.45$ eV at $h\nu = 160$ eV.

3. Results and discussion

In figure 1(a) the variation of work function $\Delta\Phi$ is reported as a function of the dosing time of K. The variation is similar to other AM/semiconductor interfaces, with a rapid decrease for low coverages, a minimum of $\Delta\Phi = -3.4$ eV after 4 min of K dosing and a slow increase due to the depolarization effect. The last two points of the data show again a slow decrease, probably due to some reactivity at the interface. It is also clear from figure 6 that at $t = 8$ min the surface core level shifted components in both Ga 3d and P 2p PE spectra have disappeared. We can deduce that the GaP(110) surface is completely covered by a layer of K atoms after this dosing time, and we define therefore this coverage as 1 ML of K on GaP(110). We calibrate in this way the amount of K deposited also on the basis of the attenuation curves of the total Ga 3d and P 2p intensity, which are shown in figure 1(b). There is some difference in the rate of decay of the Ga and P core levels, which can be caused by different effects, namely different values of the escape depths for the P 2p and Ga 3d photoelectrons or a preferential chemical reaction with some interdiffusion. We believe that the first hypothesis is more likely than the second one, as the surface component in the P 2p core level spectrum from the clean GaP(110) surface is more intense than the corresponding Ga 3d one. We cannot exclude, on the basis of our analysis, a modification

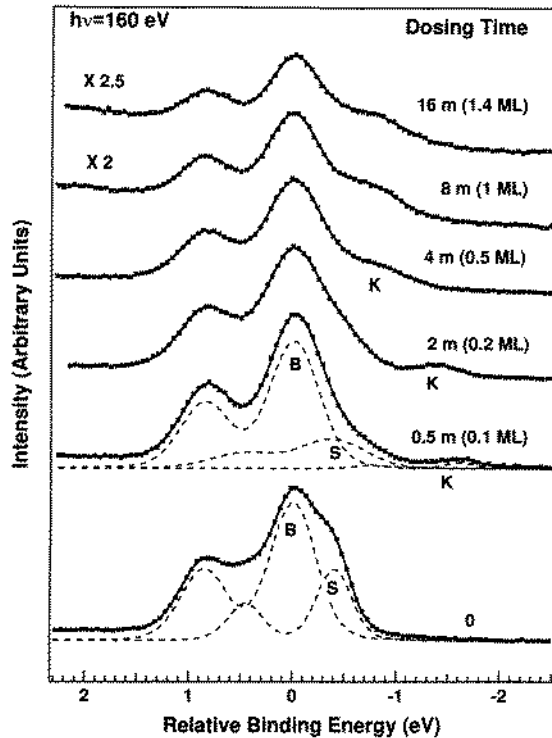


Figure 2. P 2p core level photoemission spectra taken after different K evaporation times (dots) and fitting results (continuous line). The energy scale of each spectrum is referred to the relative bulk P $2p_{3/2}$ component.

of the local geometry of the Ga and P surface atoms induced by the chemisorption process. At low coverage the analysis of both core level spectra shows a well defined K induced component (see figures 2–4) that allows the supposition of a well defined chemisorption site. We also see in figure 1 that there is a much slower decrease of the attenuation signals for $\Theta > 1$ ML, probably due to the formation of clusters on the surface, accompanied by an increasing disorder and inhomogeneity.

In figure 2 we plot the evolution of the P 2p (a) and Ga 3d (b) core level spectra, together with the result of a least-squares fitting (LSF) analysis. The behaviour is similar to the other similar systems already studied [3, 20, 21]. Band bending and surface photovoltage (SPV [22]) caused rigid energy shifts in the original spectra at different coverages. SPV was shown to be quite relevant at these values of temperature and with similar doping levels to the one of our samples [4, 20–22]. In order to make the *relative* energy shifts of the different components more evident, we chose to plot the spectra in a binding energy scale relative to the bulk $2p_{3/2}$ emission for the P 2p and bulk $3d_{5/2}$ emission for the Ga 3d spectra, respectively. In our VB spectra we could observe the emission from a gap state as in previous experiments on Na/GaP(110) [20, 21], but since its position was not very clear, it is difficult to correct the relative position in order to account for SPV, and therefore we could not estimate the value of the interface potential barrier.

We now concentrate on the evolution of the Ga 3d and P 2p lineshape: the clean surface spectra look similar to those reported in the literature [18], with the presence of

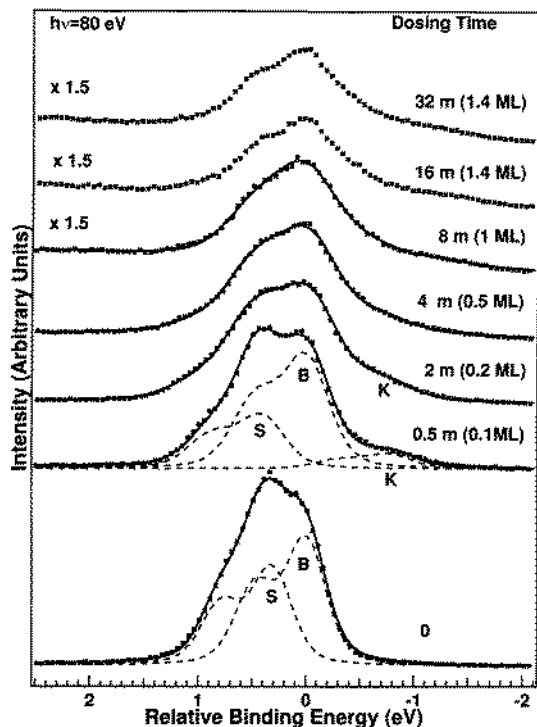


Figure 3. Ga 3d core level photoemission spectra taken after different K evaporation times (dots) and fitting results (continuous line). The energy scale of each spectrum is referred to the relative bulk Ga 3d_{5/2} component.

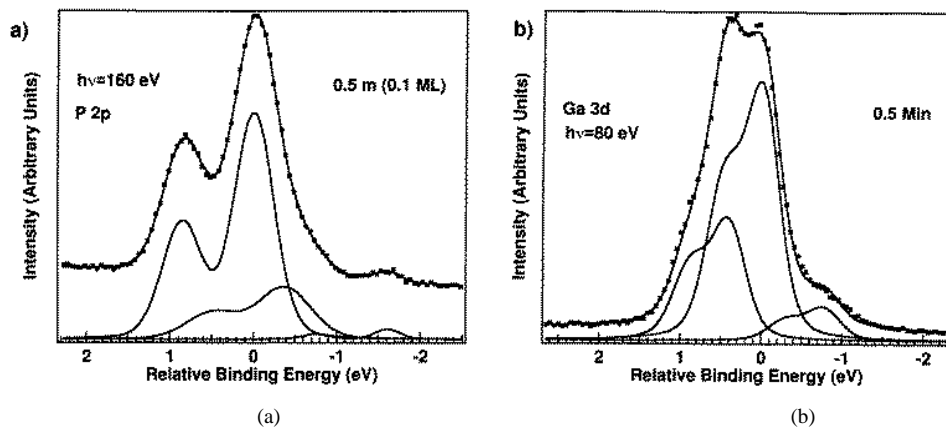


Figure 4. (a) P 2p core level spectrum taken after 0.5 min (0.1 ML) of K dosing (dots), plotted together with the LSF resulting lineshape, and the three different components (continuous line). (b) corresponding Ga 3d spectrum.

shoulders which can be assigned to the surface core level shifted (SCLS) components. At low coverage we observe a gradual reduction of the SCLS peak intensity and the growth of

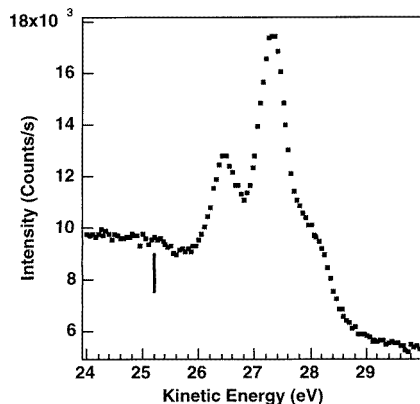


Figure 5. P 2p core level spectrum taken after 8 minutes of K dosing, corresponding to 1 ML of coverage. The vertical bar indicates the position of the plasmon feature.

a small peak at higher kinetic energies (i.e. lower binding energies). In the P 2p spectra, the energy shift of this peak is big ($\Delta E = -1.6$ eV). At increasing dosing times, this K induced component grows in intensity and shifts towards the bulk components. For $\Theta = 1$ ML and $\Theta = 1.2$ ML, the P 2p spectra look very similar each other, with a high-energy shoulder, a higher secondary-electron background and the appearance of satellite structures (visible in figure 5) which we attribute to plasmon losses. The Ga 3d core level spectrum has a similar behaviour, but we can observe the appearance of a new structure at lower binding energies for high coverages ($\Theta > 1$ ML). This structure was interpreted as a reacted component in a previous paper studying the evolution of the Na/GaAs(110) interface (see figure 1 in [21]).

In order to obtain further insight into the core level data set, we performed a LSF analysis of the spectra. The P 2p and Ga 3d core level spectra of the clean surface were fitted with two doublets, a SCLS and a bulk component, and a third-order polynomial approximating the secondary-electron background. Each doublet consists of two spin-orbit (SO) split Lorentzian peaks convoluted with Gaussians, to simulate the broadening due to inhomogeneity and experimental resolution. The most relevant fitting parameters obtained from the LSF of the clean surface spectra are shown in table 1 and they are in good agreement with previous experimental results [18]. The P 2p spectra at increasing coverage could be fitted with three components: the bulk (B) component, the clean SCLS component and the K induced (K) component. We could obtain the best and most consistent fitting results with the following constraints: the SO splitting, the SO branching ratio and the Lorentzian FWHM were kept fixed and they were the same for all the three components in all spectra, while the intensity, the energy position and the Gaussian width of each component were allowed to vary for the different spectra.

In figure 4(a) the P 2p spectrum is plotted together with the separate components. From figures 2 and 4(a) it is clear that the quality of the fit is generally very good. We performed also the fitting of the Ga 3d core level spectra with three components, the B, SCLS and K component (see figures 3 and 4(b)). Again, the SOS, BR and Lorentzian FWHM were kept fixed, equal to the values obtained for the clean surface, while the Gaussian FWHM, the energy positions and the intensities of the single components were allowed to vary.

For the highest-coverage Ga 3d spectrum studied (corresponding to $\Theta = 1$ ML), we fitted with one more component to take into account the additional feature probably caused by the surface reaction [3–5, 21].

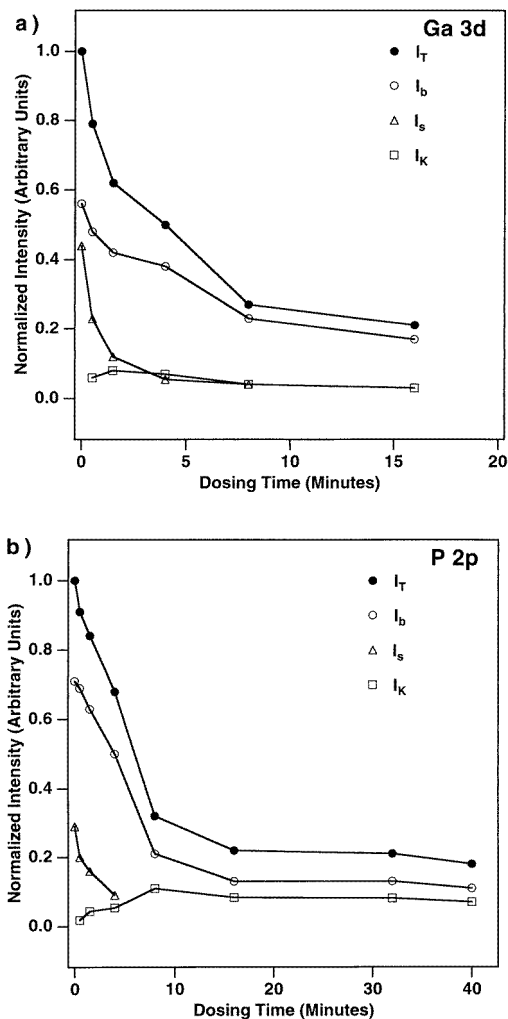


Figure 6. (a) Total intensity of the P 2p core level spectra, intensity of the surface component (triangles) and of the K induced component (squares) plotted against K dosing times. (b) The same as (a) for Ga 3d core level spectra. The values are joined by line segments as a guide to the eye.

It is known that the binding energy of the K 3p core level (BE = 18.3 eV for metallic K [3]) is very close to that of Ga 3d. Therefore, a decomposition of the Ga 3d spectrum with a LSF analysis similar to the one performed for the P 2p spectra is in principle hampered by the presence of an extra peak, i.e. the K 3p emission line.

Nevertheless, the Ga 3d spectra look similar to those reported for the growing Na/GaP(110) interface, especially at low coverages, and the LSF analysis remains good enough without taking into account the presence of the K 3p peak. This can be explained by the fact that the photoionization cross section (σ) of K 3p core levels at the photon energy used in this experiment ($h\nu = 80$ eV) is lower by a factor 6.5 than the corresponding σ of the Ga 3d [23]. If we assume that the number of emitting K atoms is at most of the order of a monolayer for high coverage, and with a value of the intensity ratio between the SCLS

Table 1. Fitting parameters for the P 2p and Ga 3d spectra of the clean surface. BR = branching ratio $I(2p_{3/2})/I(2p_{1/2})$ of the spin-orbit split components for P 2p and $I(3d_{5/2})/I(3d_{3/2})$ for Ga 3d core levels respectively. ΔE_{SO} = spin-orbit splitting value. γ = Lorentzian FWHM. σ_{B} , σ_{S} , Gaussian parameter for the bulk and surface component. ΔE_{s} = surface core level splitting.

	BR	ΔE_{SO} (eV)	γ (eV)	σ_{B} (eV)	σ_{S} (eV)	ΔE_{s} (eV)
P 2p	1.95	0.86	0.10	0.15	0.20	-0.40
Ga 3d	1.31	0.47	0.15	0.15	0.15	0.31

and the B components in the Ga 3d spectrum of about 0.44 for the clean surface, we can estimate that the intensity of the K 3p signal is at most 7% of the Ga 3d total intensity. The minimum component intensity that we could resolve in our LSF analysis was equal to 9% of the total signal, therefore the presence of the K 3p signal can be neglected in our fitting analysis from low coverages up to 1 ML. We also estimate an error in the energy position of the various fitted components of about 0.15 eV.

We should point out that the quality of the fit for the Ga 3d lineshape is slightly worse than the case of the P 2p, probably because we did not take into account the presence of the K 3p signal.

The total (I_t) and partial intensities of the different components normalized to I_t are plotted against the dosing time in figure 6. The SCLS component intensity diminishes gradually, and it is no longer detectable $t = 8$ min (1 ML), while the K induced component increases and tends to a constant value after $t = 8$ min, revealing the absence of large-scale interface reactivity. The behaviour of the SCLS components for Ga 3d and P 2p suggests that the surface relaxation changes gradually without a complete removal in the submonolayer coverages.

The K induced structures in P 2p and Ga 3d spectra can be interpreted in terms of initial components, as in previous studies on similar systems [3, 4, 19–21, 24]. Although the possibility of final-state effects, like the change of final-state screening caused by the formation of a metal overlayer, cannot be ruled out completely, theoretical calculations estimated energy shifts (caused by these effects) to be about 0.3 eV, smaller than those observed here [25].

On the basis of this interpretation, we can consider the following.

The K induced components in the core level spectra can be ascribed to charge transfer from the AM atom to the substrate, as in the case of the Na/GaP interface. We observe that the binding energies of the K components in the P 2p PE spectra increase with the K coverage, with a consequent gradual movement in energy towards the B component (see figure 7). This is due to a charge redistribution caused by the growing adatom–adatom interaction, reflected also in the behaviour of $\Delta\Phi$. The surface atoms not directly involved in the bonding formation, i.e. the ones still giving rise to the SCLS component in the spectra, are also affected, as there are small variation in the relative energy positions. The Gaussian FWHM values used to perform the LSF also increase continuously, as a result of increasing disorder and inhomogeneity in the surface.

At $\Theta = 1$ ML $\Delta\Phi$ increases again after the occurrence of a minimum and, correspondingly, we observe the appearance of a plasmon-like feature in both core level spectra. This behaviour can be ascribed to the metallicity of the interface at this coverage.

The attenuation curves in figure 1(b) show that there is a tendency to the formation of K clusters after the completion of the first monolayer. There is also an indication of a

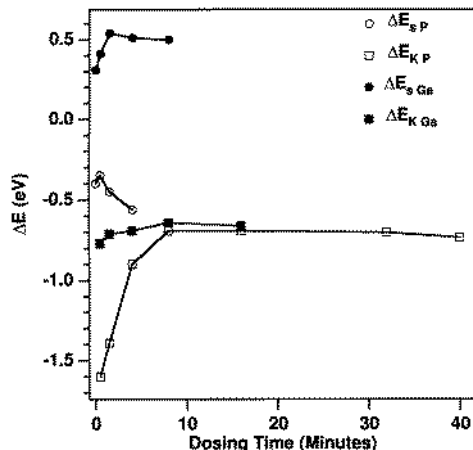


Figure 7. Relative binding energy shift values of the different components (K and SCLS) plotted against the dosing time for the P 2p and Ga 3d core level spectra. See figures 2, 3 and the discussion for the choice of the energy scale. The values are joined by line segments as a guide to the eye.

low degree of reaction at the interface. Previous studies on the Na/GaP(110) reveal that in the temperature range between 120 and 140 K the interface formation mode changes: at $T = 120$ K the adatom is adsorbed on a chemically undisrupted state, while at $T = 140$ K there is occurrence of reactivity and interaction between the Na and the bulk GaP atoms [5].

In earlier PES studies of AM on GaAs(110) an AM induced shifted component was observed only in Ga 3d core level spectra [3]. This result was seen as a confirmation of the strong local character of the bonding between the AM and the surface Ga atom. In this picture, the AM valence *s* electron is donated to the Ga derived empty DB state, and a simple estimation of the Ga 3d AM induced core level shift was made in terms of the presence of a surface dipole potential [2]. But some more recent experimental results of Na/GaAs(110) show the presence of an AM induced component also in the As 3d core levels [21]. This component is even more evident in the case of the Na/GaP(110) interface and in the system that is the object of our study. We believe that the surface As and P atom electronic environments are both affected by this charge redistribution between the adatom and the substrate. Some reasons why this effect is more evident in the AM/GaP(110) interface can be a smaller surface unit cell or a higher degree of delocalization of the empty DB state occupied by the valence electron.

A comparison with the Na/GaP(110) system reveals that the absolute value of the energy shift of the K peak in our P 2p spectra is much higher at low coverage than the Na component, while the absolute value of the shift in the Ga 3d is slightly lower. If the AM induced component is explained only as due to charge transfer, the shift of both sets of spectra should show the same behaviour. In fact, with K being less electronegative than Na, there should be a larger amount of charge transfer to the substrate, and the core level energy shifts should go to the same direction.

We then deduce that there are some differences in the adsorption process and interface formation. The main reason for these differences would be the bigger size of the K atom than the Na atom, the ionic radius of the former being around 35% larger than the latter.

We cannot also exclude a different adsorption site, or even a change in the local geometry of Ga and P atoms in the presence of the chemisorbed K, but unfortunately no explicit measurement of the K adsorption site is reported in the literature. A less ionic bonding than anticipated is more unlikely, since the energy shifts of K induced components in Ga 3d and P 2p are very high.

4. Conclusions

We have shown the results of a PES experiment on the formation at low temperatures ($T = 120$ K) of the K/GaP(110) interface. At low coverage in the P 2p and Ga 3d core level photoelectron spectra there is a shifted component which we assign to charge transfer from the adatom to the substrate. This K induced component is present on both sets of core level spectra, revealing that there is a valence charge redistribution in the whole surface, contrary to the conclusions deduced from earlier results on the AM/GaAs(110) interface. The intensity of the SCLS component in both core level spectra diminishes gradually down to 1 ML, suggesting that surface relaxation is still present in the submonolayer coverage, although varying continuously. Our PES data are consistent also with the onset of interface metallization at $\Theta = 1$ ML, and with an increasing inhomogeneity and disorder of the interface, with some degree of reaction at the highest coverage studied. A comparison with the results obtained from the Na/GaP interface shows an overall similarity, but there are some differences, which we suggest are due to the larger size of the K atom or, to some extent, to different adsorption site and to a modification of the local surface atomic geometry.

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