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2001 J. Phys.: Condens. Matter 13 8725

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# The annealing behaviour of a Cs<sub>2</sub>O/GaAs(110) surface studied by electron spectroscopy

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Received 30 May 2001, in final form 30 July 2001

Published 13 September 2001

Online at [stacks.iop.org/JPhysCM/13/8725](http://stacks.iop.org/JPhysCM/13/8725)

## Abstract

A Cs<sub>2</sub>O overlayer was prepared by simultaneous oxygen–caesium adsorption on GaAs(110) at room temperature. Electron spectroscopy has been used to investigate the Cs<sub>2</sub>O/GaAs surface as a function of annealing temperature. The Cs<sub>2</sub>O-covered GaAs surface exhibits metallic behaviour. The results show that x-ray irradiation transforms Cs<sub>2</sub>O into an O<sup>-</sup> species on the top surface and facilitates the interfacial reaction forming the Cs–O–Ga bond. In the temperature range from 300 to 620 K, the decomposition of Cs<sub>2</sub>O caused by x-ray irradiation and annealing is accompanied by growth of the O<sup>-</sup>, Cs–O–Ga, Cs–O–As, As–O and Ga–O species as well as the desorption of Cs. For further annealing, oxygen bonded to caesium gradually transfers to Ga and As, leading to fast Cs desorption and the formation of Ga<sub>2</sub>O<sub>3</sub> and As<sub>2</sub>O<sub>3</sub>. Meanwhile, the evaporation of As<sub>2</sub>O<sub>3</sub> and the reaction between the As<sub>2</sub>O<sub>3</sub> species and substrate GaAs to form Ga<sub>2</sub>O<sub>3</sub> occur.

## 1. Introduction

The coadsorption of oxygen and alkali metal on GaAs surfaces has been studied intensively in the past because of its catalytic role in GaAs oxidation and its effect on reducing work function [1–7]. Most previous studies were carried out by investigating oxygen adsorption on alkali-covered GaAs surfaces. Alkali metals enhance the GaAs oxidation rate up to 10<sup>6</sup>-fold and can be easily desorbed from the GaAs surfaces in vacuum at modest temperatures, which has a technological application in modern microelectronics. On the other hand, the strong reduction of work function caused by both alkali metal and oxygen adsorption plays a crucial role in the preparation of negative electron affinity (NEA) photocathodes, where the bottom of the conduction band is brought above the vacuum level. A GaAs photocathode with NEA can be prepared by treating the surface with caesium and oxygen. It has been proposed that a Cs<sub>2</sub>O layer formed on GaAs after the treatment is a semiconductor with a work-function value of 0.6 eV [8]. However, there is no evidence of the formation of Cs<sub>2</sub>O during oxygen adsorption on the Cs/GaAs surfaces at room temperature.

According to the results of Su *et al* [2], a typical activated GaAs surface consists of both a layer of oxygen bonded to GaAs and a ( $\text{Cs}^+$ ,  $\text{O}^{2-}$ ) layer, and the better yield achieved by the two-step activated process is due to the presence of the O–GaAs layer. This study uses ultraviolet photoelectron spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS) to investigate the annealing behaviour of the  $\text{Cs}_2\text{O}/\text{GaAs}$  surface. The  $\text{Cs}_2\text{O}$  overlayer was prepared by alkali-metal deposition in an oxygen ambient [9–11]. The spectra of the valence band, O 1s, As  $2p_{3/2}$ , As 3d, Ga  $2p_{3/2}$ , Ga 3d and Cs  $3d_{5/2}$  core levels as well as As  $L_3M_{45}M_{45}$  and Ga  $L_3M_{45}M_{45}$  Auger transitions have been used to determine variations of the composition due to the coadsorption and annealing.

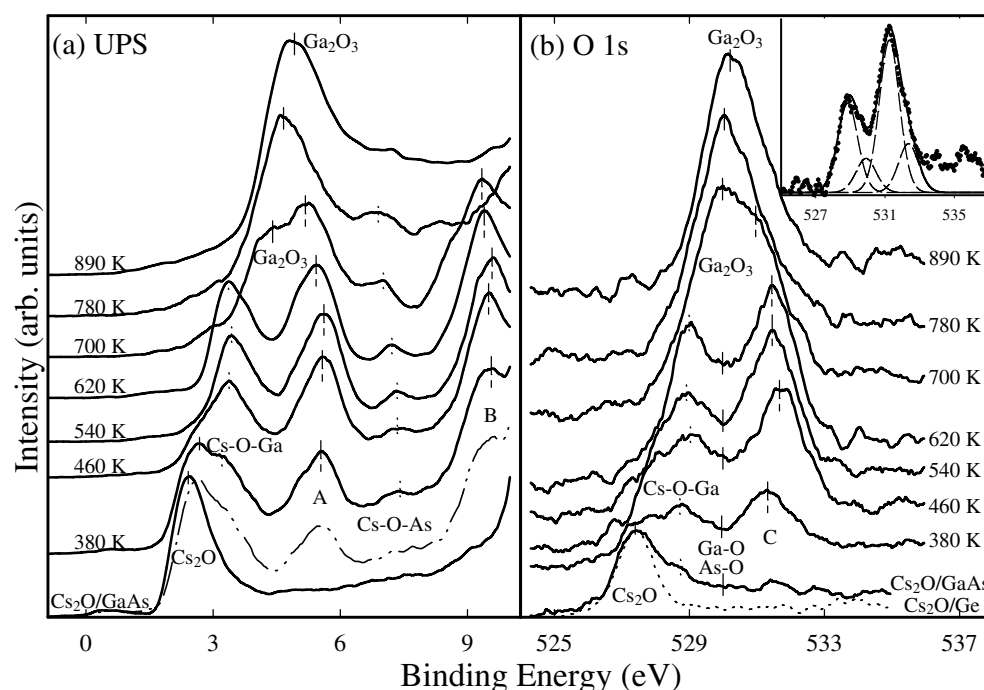
## 2. Experiment

The experiments were carried out in an Escalab mark II system with a base pressure of  $2 \times 10^{-10}$  mbar. UPS spectra were taken using a He I line ( $h\nu = 21.2$  eV) and an Al  $K\alpha$  radiation source ( $h\nu = 1486.6$  eV) was used in XPS measurements. The UPS and XPS spectra were collected at an emission angle of  $15^\circ$  with respect to the surface normal. The analyser is in the constant resolution mode, at a pass energy of 5 eV for UPS and 20 eV for XPS. The GaAs(110) sample (Te doped,  $n \approx 5 \times 10^{17} \text{ cm}^{-3}$ ) was cleaned by several cycles of Ar ion sputtering with an energy of 800 eV and annealing up to 900 K by resistive heating. The Ga/As atomic ratio of the clean surface was about 1.3, determined by the quantitative XPS analysis of the Ga  $2p_{3/2}$  and As  $2p_{3/2}$  core levels. This means that the clean surface studied was As deficient. The Cs adsorption was done by passing a current through a well outgassed commercial source (SAES Getters). The annealing temperature was estimated by the heating current according to a current–temperature calibration curve and the annealing time at each temperature was 7 min.

## 3. Results and discussion

The  $\text{Cs}_2\text{O}$  overlayer was prepared on the clean GaAs(110) surface by Cs deposition in an oxygen ambient of  $1.0 \times 10^{-8}$  mbar at room temperature. After Cs deposition, the intensities of the As  $2p_{3/2}$  and Ga  $2p_{3/2}$  levels were reduced to 0.06 and 0.14 times their values on the clean surface, respectively, which can be used to estimate the thickness of the overlayer. By assuming the mean free path of  $\sim 5$  Å for the As  $2p_{3/2}$  photoelectrons [7], the thickness of the overlayer was about 14 Å. Figures 1(a) and (b) display the spectral evolution of the valence band and O 1s core level, respectively, upon annealing temperature. The valence-band spectrum at the bottom of figure 1(a), taken after coadsorption, exhibits a feature at 2.4 eV. As can be seen in previous works [9, 12], there is emission at the Fermi edge. The corresponding O 1s core-level spectrum in figure 1(b) shows a peak at 527.4 eV and a long tail at higher binding energy. The O 1s curve (dotted line), taken from a  $\text{Cs}_2\text{O}/\text{Ge}(111)$  surface by using Al  $K\alpha$  radiation, is given in figure 1(b) for comparison. The peaks at 2.4 and 527.4 eV are typical of the O 2p and O 1s levels for  $\text{Cs}_2\text{O}$  [9, 11–14]. The dash-dotted spectrum in figure 1(a) was collected after the  $\text{Cs}_2\text{O}/\text{GaAs}$  surface was irradiated by the Al  $K\alpha$  line for 20 min at room temperature, showing that three extra structures emerge at 3.4, 5.5 and 9.4 eV. It is obvious that the  $\text{Cs}_2\text{O}/\text{GaAs}$  surface is sensitive to x-ray irradiation.

After annealing the sample at 380 K, the O 2p and O 1s features of  $\text{Cs}_2\text{O}$  decrease in intensity. In the valence-band spectrum, a structure at 7.3 eV emerges and the peaks at 3.4, 5.5 and 9.4 eV grow. Figure 1(b) demonstrates that the O 1s features on the high binding energy side of the  $\text{Cs}_2\text{O}$  peak become distinguishable. The inset of figure 1(b) gives the O 1s



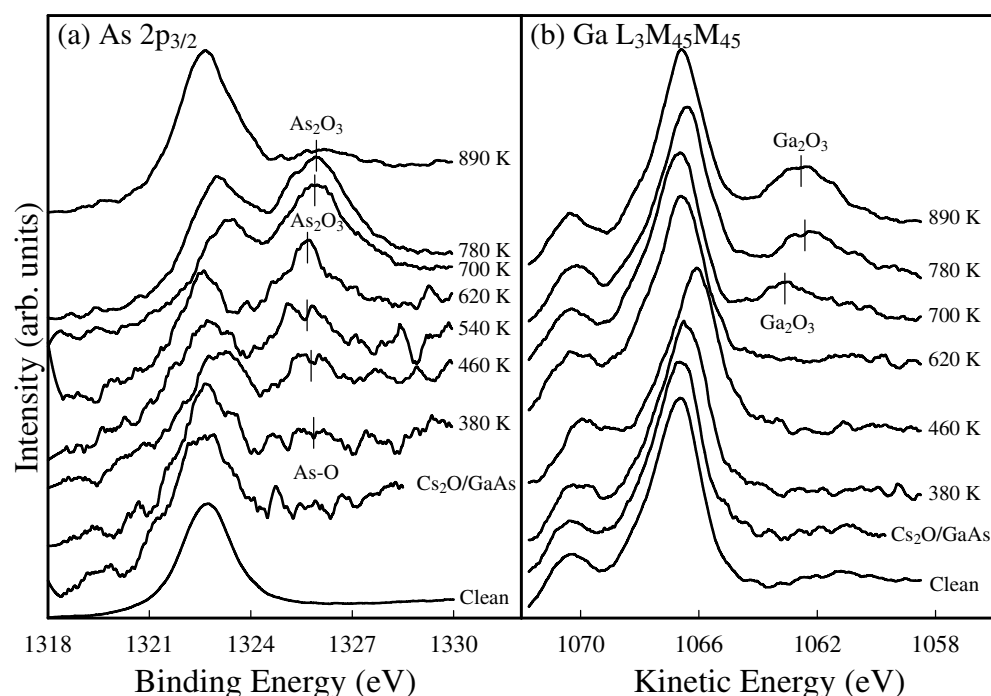
**Figure 1.** Evolution of the valence-band (a) and O 1s core-level (b) spectra for the Cs<sub>2</sub>O/GaAs(110) surface upon annealing temperature. The dash-dotted valence-band spectrum was taken after the surface was irradiated by the Al K $\alpha$  line for 20 min at room temperature. The dotted O 1s spectrum was taken from a Cs<sub>2</sub>O/Ge(111) surface with Al K $\alpha$  radiation. The inset shows the O 1s difference curve, obtained by subtracting the O 1s spectrum before annealing from that after annealing at 380 K, as well as the curve fitting with four components at 528.8, 530.0, 531.3 and 532.3 eV, respectively.

difference curve, obtained by subtracting the O 1s spectrum before annealing from that after annealing at 380 K, as well as the curve fitting with four components at 528.8, 531.3 and 532.3 eV, respectively. The signals between 533 and 535 eV in the difference curve are attributed to the growth of the Auger transitions of gallium.

During the oxidation of Ga, As and GaAs [15–19], it was found that the major O 2p structures of Ga<sub>2</sub>O<sub>3</sub>, As<sub>2</sub>O<sub>3</sub>, Ga–O–As, As=O and As–O species are located in the range of 5.0–5.6 eV. Faraci *et al* have proposed the formation of hybrid bonds in the O<sub>2</sub>/Cs/GaAs(110) system where oxygen bridges a Cs atom with a semiconductor element in a configuration Cs–O–O–X (X = As, Ga) or Cs–O–X [7]. Two atomic oxygen species were observed in the systems of O<sub>2</sub> + Cs/Si [20] and O<sub>2</sub> + K/Si [21, 22], which are bonded to alkali metal (Cs–O or K–O) and to Si (Si–O), respectively. Lamontagne *et al* have suggested that one is weakly bonded to Si and K atoms (K–O–Si) and the other is attributed to Si–O bonding [10]. In O<sub>2</sub> + Cs/Ge systems [9], the binding energies of the O 2p and O 1s features are  $4.0 \pm 0.3$  and  $529.0 \pm 0.3$  eV for Cs–O (or Cs–O–Ge) bonding and  $6.0 \pm 0.1$  and  $530.8 \pm 0.3$  eV for Ge–O bonding, respectively. The feature at 3.4 eV was observed but the peak around 7.3 eV was absent during annealing Cs + O<sub>2</sub>/GaSb(111) systems [23]. Therefore, we assign the features at 3.4 and 528.8 eV to the O 2p and O 1s levels of atomic oxygen bonded to Cs and Ga atoms (Cs–O–Ga). The peaks at 7.3 (in figure 1(a)) and 532.3 eV (in figure 1(b)) that emerge simultaneously after annealing may be associated with the O 2p and O 1s levels of Cs–O–As

bonding, since the separation between them is comparable with those of the Cs–O–Ga and Cs–O–Ge bonds [9]. The O 2p peaks around 5.6 and 9.4 eV (labelled A and B) and the O 1s line around 531.5 eV (labelled C) in this work are mainly attributed to the  $O^-$  species transformed from  $Cs_2O$  by x-ray irradiation as well as annealing [9, 14]. The O 1s peak around 530 eV should be related to As–O and Ga–O bonds (or Ga–O–As). The contribution of Ga–O–Ga bonding cannot be excluded, as its O 2p level may overlap with the peaks A [17].

The features of the  $O^-$ , Cs–O–Ga, Cs–O–As, As–O and Ga–O species in figure 1 grow with annealing temperature up to 620 K. The O 2p and O 1s signals arising from  $Cs_2O$  almost vanish in the spectra at 620 K. Subsequent annealing at 700 K causes a disappearance of the Cs–O–Ga bond. A new structure at 4.2 eV appears in the valence-band spectrum and the O 1s peak at 530 eV is dominant. The peak B disappears after annealing at 780 K. Finally, the main O 2p and O 1s peaks are located at 4.8 and 530.2 eV, respectively.

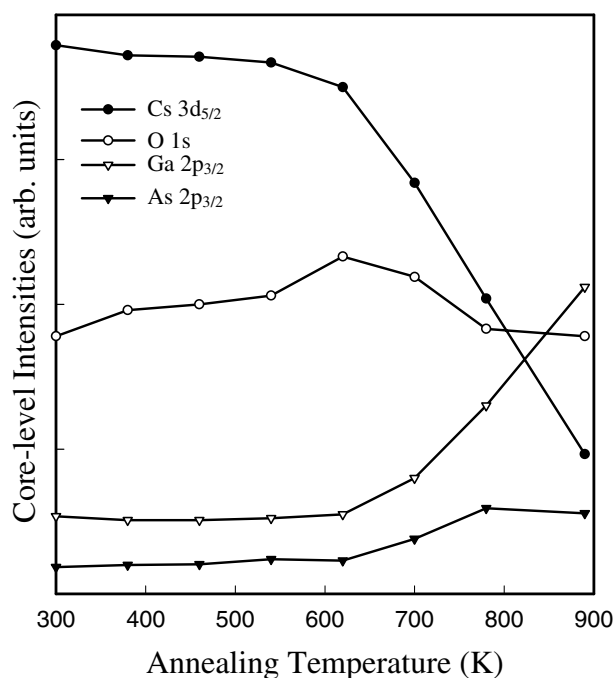


**Figure 2.** The As  $2p_{3/2}$  core-level (a) and Ga  $L_3M_{45}M_{45}$  Auger (b) spectra, taken for the clean,  $Cs_2O$ -covered and annealed GaAs(110) surfaces.

The As  $2p_{3/2}$  core-level and Ga  $L_3M_{45}M_{45}$  Auger spectra, taken from the clean,  $Cs_2O$ -covered and annealed GaAs(110) surfaces, are presented in figures 2(a) and (b), respectively. The As  $2p_{3/2}$  photoelectron is more surface sensitive than the As 3d signal while the Ga  $L_3M_{45}M_{45}$  Auger line is more sensitive to the chemical environment than the Ga  $2p_{3/2}$  and Ga 3d core levels. The difference spectra of the As  $L_3M_{45}M_{45}$  and Ga  $L_3M_{45}M_{45}$  transitions between the  $Cs_2O$ -covered and clean GaAs surfaces demonstrate the existence of shifted features at kinetic energies of 1221.8 ( $\Delta E_k = 3.6$  eV) and 1064.7 eV ( $\Delta E_k = 2.0$  eV), respectively (not shown here). After annealing the sample at 380 K, a 2.9 eV chemically shifted As  $2p_{3/2}$  peak becomes apparent in figure 2(a). The chemical shifts of the As 3d core level ( $\Delta E_b = 2.9$  eV) and As  $L_3M_{45}M_{45}$  Auger transition ( $\Delta E_k = 5.5$  eV) were also observed (not shown here), which is associated with the Cs–O–As and As–O bonds. There is detectable broadening in

the Ga 2p<sub>3/2</sub> spectrum and the shifted Ga L<sub>3</sub>M<sub>45</sub>M<sub>45</sub> structure ( $\Delta E_k = 2.0$  eV) moves to low kinetic energy ( $\Delta E_k = 2.5$  eV), which can be interpreted as the formation of the Cs–O–Ga and Ga–O bonds. The shifted As 2p<sub>3/2</sub> peak (figure 2(a)) increases in intensity with temperature up to 780 K and decreases dramatically at 890 K. A shifted As L<sub>3</sub>M<sub>45</sub>M<sub>45</sub> Auger component ( $\Delta E_k = 6.1 \pm 0.2$  eV) is present at temperatures over 700 K (not shown here), which is characteristic of the formation of As<sub>2</sub>O<sub>3</sub> [5]. Figure 2(b) shows that the main Ga L<sub>3</sub>M<sub>45</sub>M<sub>45</sub> peak arising from GaAs moves to low kinetic energy with temperature up to 460 K and then towards high kinetic energy for a further anneal. This behaviour is due to band bending since the same movements have been observed in the Ga 3d and As 3d core levels. One should note that the influence of the band bending on the As 2p<sub>3/2</sub> core level is less than the Ga LMM transition. This is most likely due to the different local environments since their escape depths are different. As the sample was annealed at 700 K, a distinct peak appears in the Ga LMM spectrum with a shift of 3.5 eV to lower kinetic energy while both Ga 2p<sub>3/2</sub> and Ga 3d lines are broaden (not shown here). This component increases in intensity and shifts to low kinetic energy ( $\Delta E_k = 4.1 \pm 0.2$  eV) for further annealing, indicating the formation of Ga<sub>2</sub>O<sub>3</sub> on the basis of previous studies [5, 18].

Before annealing, the curve fitting of the O 1s spectrum reveals the presence of at least four different kinds of atomic oxygen species while only Cs<sub>2</sub>O was observed in the valence-band spectrum. Noting that the Cs<sub>2</sub>O intensity decreases dramatically in the O 1s core-level spectrum but slightly in the valence band after annealing at 380 K, we believe the Cs<sub>2</sub>O decomposition occurs at the interface as UPS is more sensitive to the surface. Figure 1 reveals that x-ray irradiation transforms Cs<sub>2</sub>O into the O<sup>−</sup> species on the top surface and facilitates the interfacial reaction forming the Cs–O–Ga bond.



**Figure 3.** The variations of the integrated intensities of Cs 3d<sub>5/2</sub>, O 1s, Ga 2p<sub>3/2</sub> and As 2p<sub>3/2</sub> core levels for the Cs<sub>2</sub>O/GaAs(110) surface with annealing temperature.

The integrated intensities of Cs 3d<sub>5/2</sub>, O 1s, Ga 2p<sub>3/2</sub> and As 2p<sub>3/2</sub> core levels as a function of annealing temperature, given in figure 3, exhibit two distinct stages. In the first stage (300–620 K), the Cs<sub>2</sub>O decomposition is accompanied by increases in the intensities of the O<sup>-</sup>, Cs–O–Ga, Cs–O–As, As–O and Ga–O species. The slight decreases in the Cs 3d<sub>5/2</sub> intensity and the growths of the O 1s signal in this stage suggest that some Cs atoms are desorbed from the surface. In the second stage (700–890 K), the fast Cs desorption is observed, which is associated with the decomposition of the Cs–O–Ga and Cs–O–As bonds and the formation of Ga<sub>2</sub>O<sub>3</sub> and As<sub>2</sub>O<sub>3</sub>. The Cs–O–Ga bond disappears (figure 1) and the shifted Ga L<sub>3</sub>M<sub>45</sub>M<sub>45</sub> ( $\Delta E_k = 3.5$  eV) (figure 2(a)) and As L<sub>3</sub>M<sub>45</sub>M<sub>45</sub> ( $\Delta E_k = 6.1$  eV) Auger features are observed after annealing at 700 K. Figure 3 shows that the Ga 2p<sub>3/2</sub> signal grows rapidly while the intensity of the As 2p<sub>3/2</sub> core level increases slightly at 780 K and decreases at 890 K. The As<sub>2</sub>O<sub>3</sub> species is not stable at temperature over 523 K [17], so that the As<sub>2</sub>O<sub>3</sub> evaporation and the As<sub>2</sub>O<sub>3</sub> reaction with substrate GaAs to form Ga<sub>2</sub>O<sub>3</sub> occur in this stage, leading to the decreases in the O 1s intensity and the intensity difference in the Ga 2p<sub>3/2</sub> and As 2p<sub>3/2</sub> core levels. From figure 1(a), we can see that the Cs–O–As bond is more stable than the Cs–O–Ga bond.

Similar to the Cs<sub>2</sub>O/Ge(111) surface [9], the GaAs(110) surface covered by the Cs<sub>2</sub>O overlayer has a work-function value of  $0.85 \pm 0.1$  eV. The surface dominated by the O<sup>-</sup>, Cs–O–Ga and Cs–O–As species remains NEA with a work-function value of about 1.1 eV. The work function of the surface increases to 2.3 eV after 890 K annealing as a small amount of caesium remains on the surface.

#### 4. Conclusion

The Cs<sub>2</sub>O/GaAs(110) surface has been studied by electron spectroscopy as a function of annealing temperature. The Cs<sub>2</sub>O-covered GaAs surface exhibits metallic behaviour and has a work-function value of  $0.85 \pm 0.1$  eV. The results show that the Cs<sub>2</sub>O species is sensitive to x-ray irradiation, forming the O<sup>-</sup> species on the top surface and leading to the interfacial reaction. The decomposition of the Cs<sub>2</sub>O species in the temperature range of 300–620 K is accompanied by growth of the O<sup>-</sup>, Cs–O–Ga, Cs–O–As, As–O and Ga–O species. The surface dominated by the O<sup>-</sup>, Cs–O–Ga and Cs–O–As species has a work-function value of about 1.1 eV. For further annealing, the fast Cs desorption is associated with the decomposition of the Cs–O–Ga and Cs–O–As bonds and the formation of Ga<sub>2</sub>O<sub>3</sub> and As<sub>2</sub>O<sub>3</sub>. Meanwhile the As<sub>2</sub>O<sub>3</sub> evaporation and the As<sub>2</sub>O<sub>3</sub> reaction with substrate GaAs to form Ga<sub>2</sub>O<sub>3</sub> occur.

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