Switching of Band Bending at the Nonreactive CsO_x/GaAs(110) Interface

C. Laubschat, M. Prietsch, M. Domke, E. Weschke, G. Remmers, T. Mandel, J. E. Ortega,[a] and G. Kaindl

Institut für Atom und Festkörperphysik, Freie Universität Berlin, Arnimallee 14, D-1000 Berlin 33, Germany

(Received 9 January 1989)

The behavior of band bending in nonreactive interfaces between thin CsO_x films and GaAs(110) is studied by photoemission. Successive cesium and oxygen exposures change the CsO_x stoichiometry in a way that leads to a back-and-forth switching of overlayer metallicity and band bending. For both *n*- and *p*-type GaAs(110), oxygen-rich nonmetallic overlayers create almost flat-band conditions, while cesium-rich metallic overlayers result in Fermi-level positions close to midgap. These observations demonstrate the dominant influence of metal-induced gap states in nonreactive metal-semiconductor interfaces.

PACS numbers: 73.30.+y, 73.20.Hb, 79.60.Gs

The investigation of metal-semiconductor interfaces has raised increasing interest in the recent past mainly due to technological aspects.[1,2] Despite widespread applications of Schottky diodes, the basic mechanisms of Schottky-barrier formation are still not fully understood and are being discussed in a controversial way. It is by now well accepted that interfacial states in the semiconductor band gap play a crucial role in determining band bending and hence the Schottky-barrier height. Essentially two types of such interfacial states are discussed: (i) defect states that are connected with vacancies or antisite defects in the interfacial layer of the semiconductor,[3,4] and (ii) virtual gap states of the semiconductor coupling to itinerant electronic states of the overlayer that penetrate a few Å into the semiconductor.[5-9] In the case of metallic overlayers, these states are denoted as metal-induced gap states (MIGS). Both types of interfacial states can play a role at metal-semiconductor interfaces, raising the question of their relative importance in determining the Fermi-level position. In the case of GaAs(110), both the defect states and the MIGS have been claimed to result in a Fermi-level position close to midgap.[4,8,9]

In this context, core-level photoemission (PE) from interfaces formed by depositing thin metal films on single-crystalline semiconductor substrates has proven to be a powerful tool for gaining detailed information on band bending from the binding energies (BE) of semiconductor core levels. In addition, the PE line shapes contain information on interfacial reactivity and overlayer metallicity, allowing an analysis of their influence on band bending during interface formation. Recently, an abrupt change in Fermi-level position upon metallization of the overlayer was observed for the reactive Tm/GaAs(110) interface; it was attributed to a change in the dominant band-bending mechanism from defect-state to MIGS pinning.[10] A dominance of MIGS relative to defect states was also concluded from a PE study of the Na/GaAs(110) interface,[11] where the same Fermi-level positions were obtained for reactive and nonreactive interfaces in the case of thick metallic overlayers.

In the present Letter, we report on the first observation of an adjustable band bending as a function of overlayer metallicity for nonreactive interfaces of Cs oxides with GaAs(110). While approximately 2 monolayers (ML) of Cs on both *n*- and *p*-type GaAs(110) lead to interfacial Fermi-level positions close to midgap, additional deposition of oxygen causes a drastic decrease in band bending, with Fermi-level positions close to those of the uncovered substrates. This behavior is explained by oxidation of the Cs overlayer, i.e., loss of its metallic properties, while the GaAs substrates are chemically unaffected. Consecutive deposition of Cs leads again to a metallization of the overlayer and hence to Fermi-level positions close to midgap, as in the original cesium-metal-exposed case, while subsequent oxygen exposure results in a further strong decrease in band bending. These observations strongly support the applicability of the MIGS model in the case of nonreactive interfaces.

The PE measurements were performed with synchrotron radiation from the HE-PGM-2 beam line at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) employing a hemispherical electron-energy analyzer operated in normal-emission geometry. The overall-system resolution (FWHM) was $\simeq 0.2$ eV (at $h\nu = 84$ eV), and BE changes could be determined to an accuracy of ±0.1 eV. Mirrorlike (110) surfaces were obtained by cleavage of Si-doped *n*-type GaAs or Zn-doped *p*-type GaAs (with dopant concentrations of $\simeq 3\times10^{17}$ atoms/cm^3), that were kept at temperatures of 140 ± 20 K. Cs films were deposited from commercial chromate dispensers with deposition rates of $\simeq 0.5$ ML/min. Relative coverages were calibrated via deposition time (estimated accuracy of ±10%), while absolute coverages were obtained from the coverage dependence of the plasmon energy (estimated accuracy of ±30%).[12] During oxygen exposure the ion gauge was kept operating, and a small amount of molecular oxygen may be activated.[13]

Figure 1 shows representative wide-scan PE spectra for a cleaved *n*-type GaAs(110) surface, and (b)–(d) after successive cesium and oxygen exposures at $\simeq 140$ K, as well as (e) after annealing at 800 K. The spectrum from freshly cleaved *n*-type GaAs(110) [Fig. 1(a)] is dominated by intense emission from the As-3*d* and Ga-3*d* core levels, while the valence-band emission is very weak. Deposition of 2 ML of Cs [Fig. 1(b)] results in additional emission lines from the Cs-5*s* and Cs-5*p* core levels as well as in strong satellites for all PE lines at $\simeq 2$ eV higher BE (indicated by arrows) that are assigned to extrinsic plasmon-energy losses in the Cs layer. Additional adsorption of 12 L [1 Langmuir (L) $= 10^{-6}$ Torr Sec] oxygen [Fig. 1(c)] leads to a quenching of these satellites as well as to the appearance of a multipeaked, O-2*p*-derived valence-band emission that is assigned mainly to Cs_2O_2 (Refs. 14 and 15). Upon subsequent deposition of 2 ML of Cs [Fig. 1(d)], this oxide layer is chemically reduced mainly to Cs_2O, leading again to the appearance of plasmon-loss satellites.

The absence of chemically shifted components in the As-3*d* and Ga-3*d* core-level PE lines [Figs. 1(a)–1(d)] clearly shows that the oxidation of the Cs adsorbate layer is not affecting the chemical composition of the substrate at the interface. On the other hand, annealing of a CsO_x/GaAs(110) interface at $\simeq 800$ K [Fig. 1(e)] leads to additional components shifted to higher BE by $\simeq 3.5$ eV (As 3*d*) and $\simeq 1$ eV (Ga 3*d*), respectively, due to substrate oxidation.[13] These observations show that the CsO_x/GaAs(110) interface formed at $\simeq 140$ K is nonreactive and abrupt.

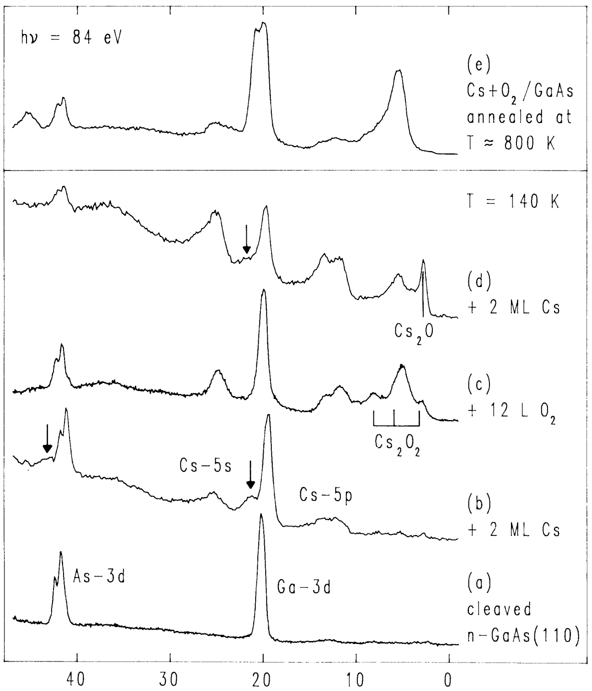

FIG. 1. Wide-scan PE spectra of (a) a cleaved *n*-type GaAs(110) surface at $T \simeq 140$ K, and (b)–(d) after successive depositions of cesium and oxygen. Plasmon-loss satellites are marked by arrows. For comparison, the spectrum of a CsO_x/GaAs(110) interface after annealing at $\simeq 800$ K is shown in (e). The spectra are normalized to equal height.

In Fig. 2, the Ga-3*d* PE core-level lines are shown in more detail for both *n*- and *p*-type substrates, exposed successively to cesium, oxygen, cesium, and oxygen. The striking information contained in Fig. 2 is the fact that even repeated exposures with cesium and oxygen, respectively, shift the Ga-3*d* lines in opposite directions for

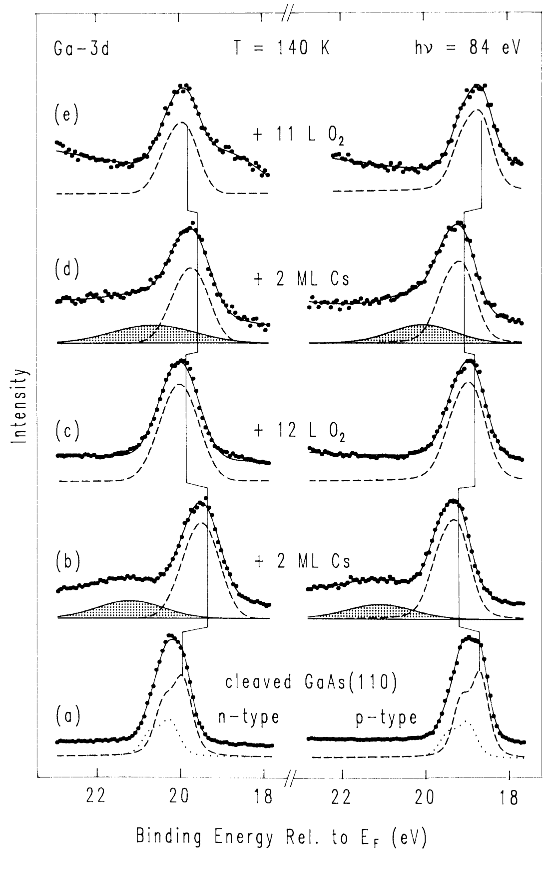

FIG. 2. Ga-3*d* PE spectra of cleaved *n*- and *p*-type GaAs(110) surfaces and after successive cesium and oxygen exposures ($T \simeq 140$ K). Dashed subspectra represent the substrate bulk, dotted subspectra represent the substrate surface, and the shaded subspectra correspond to plasmon-loss satellites that are assigned to overlayer metallicity. The shoulder at $\simeq 19$ eV BE in (e) is attributed to O-2*s* emission. The vertical solid line traces the positions of the Ga-$3d_{5/2}$ components. Note the obvious correlation of band-bending–induced BE shifts and overlayer metallicity monitored by plasmon-loss satellites. The spectra are normalized to equal height.

both *n*- and *p*-type substrates. Spectra (a) and (b) at the bottom of Fig. 2 reveal that the initial deposition of 2 ML of Cs causes BE shifts of $\simeq 0.6$ eV in opposite directions for *n*- and *p*-type GaAs, which are attributed to band bending towards a common Fermi-level position close to midgap typical for alkali-metal/GaAs(110) interfaces.[11,12] The appearance of a plasmon-energy-loss satellite (shaded subspectrum) at $\simeq 2$ eV higher BE [Fig. 2(b)] reflects a delocalization of valence electrons in the Cs layer, indicating overlayer metallization. It was previously found that a plasmon-loss energy of $\simeq 2$ eV is reached when the Cs overlayer metallizes at coverages between 1.5 and 2 ML.[12] In this way we use the plasmon-loss satellites as a monitor for metallization. Upon additional adsorption of 12 L oxygen, the plasmon-loss structures disappear [Fig. 2(c)], signaling a demetallization of the overlayer due to oxidation. This causes the backshifts of the Fermi-level positions to almost the original values observed for freshly cleaved *n*- and *p*-type GaAs(110). By additional deposition of 2 ML of Cs, the metallicity of the overlayer as well as the Fermi-level positions close to midgap are reestablished [Fig. 2(d)], while another exposure to 11 L oxygen [Fig. 2(e)] results again in a nonmetallic overlayer accompanied by a strong decrease in band bending.

The spectra in Fig. 2 were least-squares fitted with a superposition of Gaussian lines for instrumental and inhomogeneous broadening convoluted with a Lorentzian containing lifetime effects (FWHM $=0.2$ eV). They consist of spin-orbit–split doublets with intensity ratios close to 3:2 and a splitting of 0.46 ± 0.02 eV,[11,12] plus a background that was approximated in all cases by straight lines. This curve-fitting procedure is most clearly visible in the spectra of the freshly cleaved GaAs substrates presented in Fig. 2(a), which are deconvoluted into bulk (dashed) and surface (dotted) components. Note also the Ga-3*d* BE difference of $\simeq 1.3$ eV for *n*- and *p*-type GaAs that reflects the different Fermi-level positions in the GaAs band gap close to the conduction-band minimum (CBM) in case of *n*-type and the valence-band maximum (VBM) in case of *p*-type GaAs(110), respectively.

The variation in band bending upon successive cesium and oxygen exposure on GaAs(110) kept at $\simeq 140$ K is shown in more detail in Fig. 3. This data plot clearly shows that a common Fermi-level position is obtained for *n*- and *p*-type GaAs(110) for a Cs coverage of 2 ML,[12] while overlayer oxidation leads to a decrease in band bending for both doping types, approaching flat-band conditions. The second Cs exposure results again in an increase in band bending, but a common Fermi-level position is no longer obtained. The second oxygen exposure flattens the bands again.

In this way it becomes clear that the switching of overlayer metallicity is directly related to the changes in band bending. Such a behavior unambiguously rules out defect states near midgap as a possible cause for band bending at these interfaces, since defects can obviously not be removed by oxidation. On the other hand, the initial Fermi-level positions for *n*- and *p*-type GaAs(110) are not completely reproduced by oxidation of the metallic overlayer, reflecting the fact that the CsO_x/GaAs(110) interface represents some kind of a semiconductor heterojunction.[16] Therefore, the Fermi-level positions for *n*- and *p*-type GaAs(110) are expected to be governed by the energetic positions of the CBM and VBM, respectively, of the cesium-oxide overlayer, which in turn may be expected to change with overlayer stoichiometry. Such a dependence on stoichiometry could be the reason for our observation of slightly different Fermi-level positions after the first and second oxygen exposures (see Fig. 3).

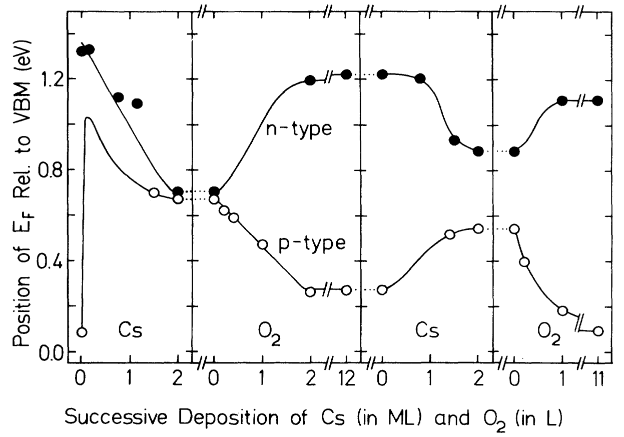

FIG. 3. Variation in Fermi-level position with respect to the VBM (accuracy of ± 0.1 eV) for *n*- and *p*-type GaAs(110), kept at $\simeq 140$ K, as a function of successive depositions of cesium and oxygen. The data are obtained from least-squares fits of As-3*d* and Ga-3*d* PE spectra (see Fig. 2) and contain a correction for finite sampling depth of the PE measurements (Refs. 11 and 12). The initial band-bending curve for Cs/*p*-GaAs(110) is taken from Ref. 12.

Differences in overlayer stoichiometry may also be responsible for the fact that the original metal-induced band bending is not fully reproduced upon the second deposition of 2 ML of Cs on the oxidized interface. The chemical reduction of Cs_2O_2 during the second Cs deposition [see Fig. 1(d)] may produce a mixture of Cs_2O and metallic Cs that is characterized by a lower density of conduction electrons than is effective in an elemental Cs overlayer. Such a mechanism is actually supported by the lower plasmon energy of $\simeq 1.5$ eV observed in this case [see Fig. 2(d)]. Furthermore, inhomogeneities in the overlayer may result in some kind of a Cs/Cs_2O/GaAs(110) multilayer structure, where the influence of the cesium-metal layer on the semiconductor is screened by the oxide layer. Both effects tend to decrease the density of MIGS, which may then not be sufficiently high for a complete band bending to a common Fermi-level position for both *n*- and *p*-doped substrates, as observed (see Fig. 3). Such a common Fermi-level position is theoretically expected for band bending through MIGS[5–9,17] and has been observed recently upon metallization.[11,12]

In summary, the present work clearly shows that the Fermi-level position at nonreactive interfaces between Cs oxides and GaAs(110) is directly related to the metallicity of the overlayer. This observation provides strong evidence for the validity of the MIGS model, and conclusively rules out the concept of defect states close to the center of the band gap of GaAs as the origin of the observed band-bending effects in the case of nonreactive interfaces.

The authors acknowledge valuable discussions with Professor Miranda. This work was supported by the Bundesminister für Forshung und Technologie, Project No. 05 313AX B2/TP3.

(a)On leave from Departamento de Fisica de la Materia Condensada, Universidad Autonoma de Madrid, Cantoblanco, E-28049 Madrid, Spain.

[1] E. H. Rhoderick, *Metal-Semiconductor Contacts* (Clarendon, Kensington, Australia, 1980).

[2] L. J. Brillson, Surf. Sci. Rep. **2**, 123 (1982).

[3] W. E. Spicer, P. W. Chye, P. R. Skeath, C. Y. Su, and I. Lindau, J. Vac. Sci. Technol. **16**, 1322 (1979).

[4] I. Lindau and T. Kendelewicz, CRC Crit. Rev. Solid State Mater. Sci. **13**, 27 (1986).

[5] V. Heine, Phys. Rev. **138**, A1689 (1965).

[6] E. Louis, F. Yndurain, and F. Flores, Phys. Rev. B **13**, 4408 (1976).

[7] M. L. Cohen, Adv. Electron. Electron Phys. **51**, 1 (1980).

[8] J. Tersoff, Phys. Rev. Lett. **52**, 465 (1984).

[9] F. Flores and C. Tejedor, J. Phys. C **20**, 145 (1987).

[10] M. Prietsch, M.Domke, C. Laubschat, and G. Kaindl, Phys. Rev. Lett. **60**, 436 (1988).

[11] M. Prietsch, C. Laubschat, M. Domke, and G. Kaindl, Europhys. Lett. **6**, 451 (1988).

[12] M. Prietsch, M. Domke, C. Laubschat, T. Mandel, C. Xue, and G. Kaindl, Z. Phys. B (to be published).

[13] G. Landgren, R. Ludeke, Y. Jugnet, J. F. Morar, and F. J. Himpsel, J. Vac. Sci. Technol. B **2**, 351 (1984).

[14] C. Y. Su, I. Lindau, and W. E. Spicer, Chem. Phys. Lett. **87**, 523 (1982).

[15] B. J. Moss and W. A. Goddard III, J. Chem. Phys. **63**, 3523 (1975).

[16] R. W. Grant and J. R. Waltrop, J. Vac. Sci. Technol. B **5**, 1015 (1987).

[17] A. Zur, T. C. McGill, and D. L. Smith, Phys. Rev. B **28**, 2060 (1983).