Domination of adatom-induced over defect-induced surface states on p-type GaAs(Cs,O) at room temperature

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The unpinned behavior of the Fermi level, photovoltage, and recombination velocity is demonstrated experimentally at room temperature for a p-type GaAs(Cs,O) interface by means of photoreflectance and photoluminescence techniques. This behavior manifests itself as the multiple reversible switching of surface band bending, the amplitude of photoreflectance, and photoluminescence intensity under alternate deposition of cesium and oxygen on a clean surface of epitaxial p-type GaAs layers. The results prove that cesium-induced donorlike surface states dominate over defect-induced states.

The nature of electronic states at semiconductor surfaces and interfaces is still not completely clarified despite extensive experimental and theoretical studies (see, for example, Refs. 1–14). In a number of theoretical models,[1–3] surface states induced by crystal defects or disorder were considered as the reason for the Fermi level pinning that was observed experimentally in many cases. In particular, the Fermi level pinning on a GaAs surface was attributed by Spicer *et al.*[1] to intrinsic surface defects arising at chemisorption of alien atoms. Although originally the unified defect model (UDM) proposed in Ref. 1 was based on the experiments done on cleaved (110) faces of GaAs single crystals, later this model together with its modifications was considered as a universal explanation of the surface states and applied to other faces of GaAs and other III-V semiconductors.[2]

Further development of the techniques of crystal growth and surface preparation questioned the universal character of UDM.[8–14] Instead of rigid pinning, variations of the Fermi level, which correlate with adsorbate electronegativity, were observed at the surface of layers grown by molecular beam epitaxy (MBE) after the removal of a protective arsenic overlayer.[8] Defect-free metal/semiconductor interfaces were also obtained by deposition of a metal over a xenon interlayer.[9] The increase of photoluminescence and the unpinned behavior of the Fermi level were observed after sulfur treatment of the GaAs surface.[10,11] A convincing example of the unpinned behavior is the reversible variations ("switching") of the Fermi level on a GaAs surface observed under alternate deposition of cesium and oxygen.[12] These reversible variations show that cesium-induced donorlike surface states[12–14] dominate over the defect-induced surface states. Up to now the switching was observed on cleaved (110)GaAs surfaces and only at low temperatures ($T \approx 100$ K), when chemical reactions on the surface are suppressed.[12,14] Therefore it was possible to reconcile[12,14] the unpinned behavior at low temperature with the UDM which predicts the formation of intrinsic defects and Fermi level pinning at higher (room) temperature. In this paper we report the observation of the reversible switching of band bending and other electronic properties of the surface of epitaxial p-type GaAs under alternate deposition of Cs and O_2 at room temperature. The results prove that the unpinned rather than pinned behavior of the Fermi level is an inherent property of a carefully prepared surface of epitaxial GaAs. Preliminary results were published in Ref. 15.

In the present work homogeneously doped p- and n-type GaAs layers of (100), (110), and (111) faces grown by liquid phase epitaxy (LPE) were used together with MBE-grown UP^+ and UN^+ structures specially designed for the precise determination of surface band bending by photoreflectance spectroscopy.[16–18] A UP^+ (UN^+) structure consisted of a Be(Si)-doped ($N = 2 \times 10^{18}$ cm^{-3}) 1000-nm-thick $p(n)$-type GaAs layer grown on a (100)GaAs substrate and a thin ($d_c = 100$ nm) undoped cap layer.

The surface preparation technique[19] included removal of oxides in the isopropyl-alcohol solution of HCl. This treatment was done in a glove box filled with pure nitrogen in order to avoid surface oxidation and uncontrolled contamination. A nitrogen-filled transfer vessel and a loading chamber were used to transfer samples from the glove box into ultrahigh vacuum (UHV) without contact with room atmosphere. Auger measurements

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showed that after such treatment the surface was enriched with 1–2 monolayers (ML) of arsenic and covered by a submonolayer amount of chlorine and carbon-contained species, which were removed by the heat cleaning of a sample in UHV at relatively low temperature $T \approx 400\,^{\circ}$C. The heat cleaning was performed by direct current flow.

A halogen lamp with a grating monochromator and a He-Ne laser with the wavelength of 632.8 nm were used for the measurements of modulated photoreflectance[16–18] (PR) and photoluminescence (PL) intensity $I_{\rm PL}$.[20] The surface electric field was determined from the positions of the extrema of Franz-Keldysh oscillations in PR spectra as described in Refs. 16–18. The band bending φ_s was calculated from the measured values of the field. Together with the band bending, we studied the evolution of the amplitude of the photoreflectance signal. The amplitude of PR is proportional to the modulation of surface potential under modulated illumination, that is, to the modulated surface photovoltage (SPV).[21] SPV originates from the screening of the surface electric field by free photoexcited charged carriers and from the capture of photoelectrons by surface states. The photoluminescence studied here originates from the radiative recombination of photoelectrons and holes in the bulk of the GaAs layer, but the intensity of PL is controlled by the surface recombination rate.[20] Thus PR and PL techniques enabled us to monitor the surface band bending (which depends on the equilibrium filling of surface states), as well as the surface capture and recombination rates of nonequilibrium photoelectrons.

It should be noted that the surface photovoltage averaged over the modulation period causes systematic reduction of the measured values of band bending.[18,22,23] To minimize an error in φ_s related to the photovoltage, we measured the PR spectra at low laser light intensity of about 0.05 mW/cm^{-2}. Additional measurements at various light intensities and at elevated temperatures up to 200 °C allowed us to estimate this error to be below 0.1 eV.

Photoreflectance spectra measured on a clean surface of a UP$^+$ structure and after successive deposition of Cs and O_2 are shown in Fig. 1. One can see that after each Cs deposition the period and the amplitude of Franz-Keldysh oscillations increased. After oxygen exposure the oscillations shrank and the amplitude decreased by about a factor of 50. The detailed evolution of band bending φ_s and the amplitude of the PR signal $(\Delta R/R)_0$ on UP$^+$ (open symbols) and UN$^+$ (closed symbols) structures is shown in Fig. 2 for the first three cycles of Cs-O deposition. Band bending φ_s = 0.30 eV was observed at the clean surface of the UP$^+$ structure. This value is lower than φ_s = 0.5–0.7 eV reported for the MBE-grown p-type GaAs(100) surface decapped from the protective arsenic overlayer.[24] At the first Cs deposition on a clean surface, the band bending increased rapidly from φ_s = 0.30 eV to a maximum of 0.70 eV at Cs coverage θ = 0.2 ML and then slowly decreased down to φ_s = 0.55 eV at θ = 1 ML. Subsequent oxygen exposure caused a decrease of φ_s to 0.27 eV. Further alternate deposition of Cs and O_2 led to reversible switching of the band bending between large cesium and small oxygen values. Similar switching of φ_s was observed in Ref. 12 at low temperatures. The amplitude of photoreflectance, which is proportional to the surface photovoltage, behaved qualitatively similarly to the band bending. It is seen from Fig. 2 that the variations of φ_s and $(\Delta R/R)_0$ are much smaller for n-type GaAs than for p-type GaAs.

Multiple reversible switching of electronic properties was also observed on the surface of homogeneously doped p-type GaAs layers grown by LPE (see Fig. 3). Maximal and minimal values of φ_s, $(\Delta R/R)_0$, and $I_{\rm PL}$ are shown in Fig. 3 up to the ninth cycle of alternate Cs and O_2 deposition. It is seen that the amplitude of switching did not decrease up to the sixth cycle. Starting from the third cycle almost flat bands with $\varphi_s \approx 0.07\pm0.02$ eV were observed after oxygen exposure. The switching was observed on (100), (110), and (111) crystal faces of p-type GaAs layers grown by LPE. Again, for homogeneously doped n-type GaAs layers, φ_s and $(\Delta R/R)_0$ were nearly constant.

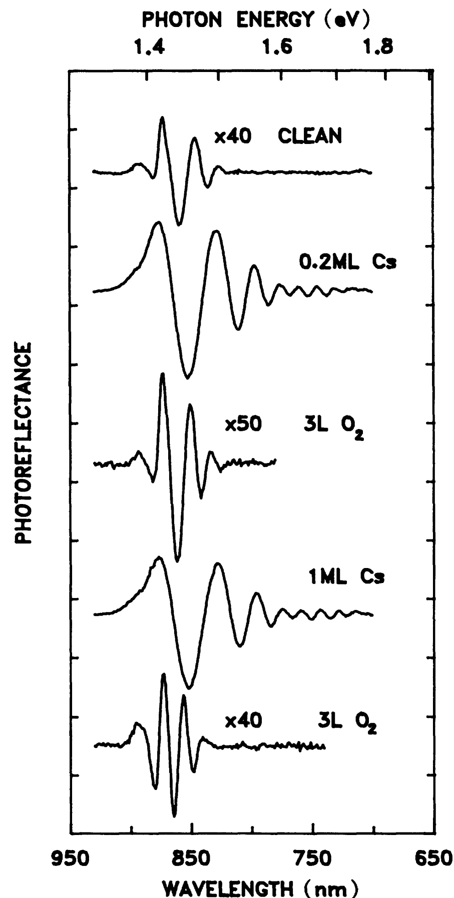

FIG. 1. Photoreflectance spectra of a UP$^+$ structure. The upper curve corresponds to a clean surface, the other curves were measured after successive deposition of Cs and O_2, as indicated in the figure. The deposition was done at T=300 K. The doses were measured in monolayers (ML) for cesium and in langmuirs (L) for oxygen (1 L = 10^{-6} Torr s). Reversible switching of the period and amplitude of Franz-Keldysh oscillations are clearly seen.

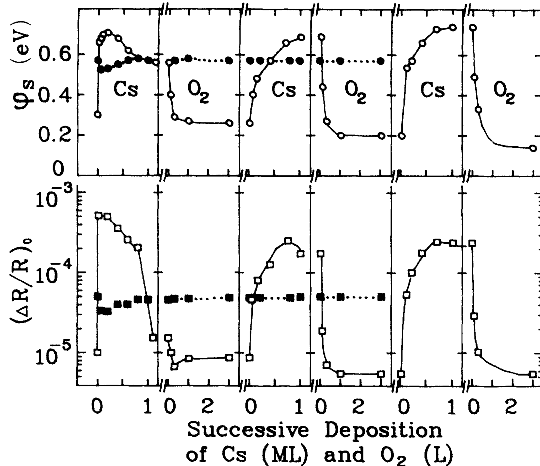

FIG. 2. The evolution of band bending φ_s and photoreflectance amplitude $(\Delta R/R)_0$ for the first three cycles of successive deposition of Cs and O_2 on clean surfaces of UP^+ (open symbols connected with solid lines) and UN^+ (closed symbols connected with dotted lines) structures.

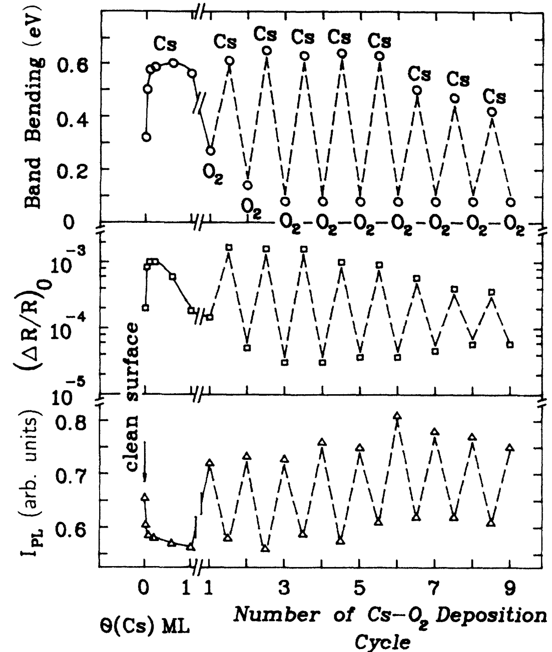

FIG. 3. The evolution of band bending φ_s, photoreflectance amplitude $(\Delta R/R)_0$, and photoluminescence intensity I_{PL} at multiple alternate deposition of Cs and O_2 on a clean surface of homogeneously doped p-type GaAs with doping concentration equal to 1.5×10^{17} cm^{-3}. The deposition of the first layer of Cs is shown in detail. The dose of Cs in all cycles corresponded to one monolayer; the dose of O_2 was equal to 20 L in the first cycle, 4 L in the second cycle, and 1 L in all other cycles.

The results presented in Figs. 1–3 prove that on a p-type GaAs(Cs,O) interface formed at room temperature, the band bending and other electronic properties are determined not by defects,[1,2] but by adatom-induced surface states.[12–14] Apparently, at small coverages $\theta <$ 0.2 ML, cesium atoms act like surface donors, which donate electrons to the bulk of p-type GaAs, charge the surface positively, and thus cause the increase of equilibrium band bending.[13,14] The overshoot of φ_s that takes place with increasing coverage $\theta > 0.2$ ML is due to gradual evolution of the surface states induced by individual cesium adatoms into the metal-induced gap states.[5–7,12] The increase of PR amplitude, which is proportional to SPV, can be explained by the increase of photoelectron capture on positively charged donorlike surface states at the initial stage of Cs deposition. The decrease of the SPV at higher cesium coverages (close to one monolayer) is probably due to the lateral leakage of photoelectrons to recombination centers along the conducting Cs layer. Under oxygen exposure the neutralization of the Cs-induced donorlike surface states and the respective decrease of band bending takes place under oxygen exposure due to the oxidation of cesium. Moreover, the observation of flat bands after few Cs-O deposition cycles indicates that the reduction of the concentration or some kind of compensation of the surface states responsible for the initial band bending takes place rather than generation of new defect-induced states.

The behavior of band bending in n-type GaAs is also consistent with the role of cesium-induced states as surface donors. Band bending on a clean surface of n-type GaAs is determined by the negative charge of initial acceptorlike surface states. At $\theta < 0.1$ ML, a small decrease of φ_s is explained by partial discharge of the surface by cesium-induced donors, which lie in energy above the acceptor states. The restoration of the initial band bending at $\theta \approx 1$ is due to the movement of Cs-induced surface states toward the position below the surface acceptor levels.

The relation between possible structure of the Cs-O overlayer and the observed multiple reversible switching is still not clear. It was shown by means of x-ray photoelectron spectroscopy that during the alternate deposition of Cs and O_2, the amount of Cs on the surface increased linearly with the overall cesium exposure.[25] This rules out the model of the switching as periodical reproduction of the same GaAs(Cs,O) structure by alternate adsorption and desorption of the adsorbates. Further studies are needed to choose among the models that explain switching by electron charge transfer through a Cs-O overlayer, or by cluster structure of the overlayer.[26]

In conclusion, multiple reversible switching of surface electronic properties was observed at room temperature under alternate deposition of cesium and oxygen on different crystal faces of epitaxial p-type GaAs layers. This unpinned behavior proves the domination of the adatom-induced surface states over the defect-induced states on the p-type GaAs(Cs,O) interface.

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[1]W. E. Spicer, P. W. Chye, P. R. Skeath, C. Y. Su, and I. Lindau, J. Vac. Sci. Technol. **16**, 1422 (1979).
[2]W. E. Spicer, T. Kendelewicz, N. Newman, R. Cao, C. McCants, K. Miyano, I. Lindau, Z. Liliental-Weber, and E. R. Weber, Appl. Surf. Sci. **33/34**, 1009 (1988).
[3]H. Hasegawa and H. Ohno, J. Vac. Sci. Technol. B **4**, 1130 (1986).
[4]L. J. Brillson, Comments Condens. Matter Phys. **14**, 311 (1989).
[5]W. Mönch, Rep. Prog. Phys. **53**, 221 (1990).
[6]J. Tersoff, Phys. Rev. Lett. **52**, 465 (1984).
[7]J. Ortega and F. Flores, Phys. Rev. Lett. **63**, 2500 (1989).
[8]R. E. Viturro, J. L. Shaw, C. Mailhiot, L. J. Brillson, N. Tache, J. McKinley, G. Margaritondo, J. M. Woodall, P. D. Kirchner, G. D. Pettit, and S. L. Wright, Appl. Phys. Lett. **52**, 2052 (1988).
[9]G. D. Waddill, I. M. Vitomirov, C. M. Aldao, S. G. Anderson, C. Capasso, J. H. Weaver, and Z. Liliental-Weber, Phys. Rev. B **41**, 5293 (1990).
[10]E. Yablonovitch, C. J. Sandroff, R. Bhat, and T. Gmitter, Appl. Phys. Lett. **51**, 439 (1987).
[11]M. S. Carpenter, M. R. Melloch, M. S. Lundstrom, and S. P. Tobin, Appl. Phys. Lett. **52**, 2157 (1988).
[12]C. Laubschat, M. Prietsch, M. Domke, E. Weschke, G. Remmers, T. Mandel, J. E. Ortega, and G. Kaindl, Phys. Rev. Lett. **62**, 1306 (1989).
[13]W. Mönch, Europhys. Lett. **7**, 275 (1988).
[14]R. Cao, K. Miyano, T. Kendelewicz, I. Lindau, and W. E. Spicer, Appl. Phys. Lett. **54**, 1250 (1989); Phys. Scr. **41**, 887 (1990).
[15]V. L. Alperovich, A. S. Jaroshevich, A. G. Paulish, and A. S. Terekhov, Pis'ma Zh. Eksp. Teor. Fiz. **55**, 289 (1992) [JETP Lett. **55**, 288 (1992)].
[16]D. E. Aspnes, in *Handbook of Semiconductors*, edited by T. S. Moss (North-Holland, Amsterdam, 1980), Vol. 2, p. 109.
[17]C. Van Hoof, K. Deneffe, J. De Boeck, D. J. Arent, and G. Borghs, Appl. Phys. Lett. **54**, 608 (1989).
[18]X. Yin, H.-M. Chen, F. H. Pollak, Y. Chan, P. A. Montano, P. D. Kirchner, G. D. Pettit, and J. M. Woodall, Appl. Phys. Lett. **58**, 260 (1991).
[19]Yu. G. Galitsin, V. I. Poshevnev, V. G. Mansurov, and A. S. Terekhov, Prib. Tekh. Eksp. **4**, 191 (1989).
[20]H. Hasegawa, H. Ishii, T. Sawada, T. Saitoh, S. Konishi, Y. Liu, and H. Ohno, J. Vac. Sci. Technol. B **6**, 1184 (1988).
[21]T. Kanata, M. Matsunaga, H. Takakura, Y. Hamakawa, and T. Nishino, J. Appl. Phys. **68**, 5309 (1990).
[22]M. H. Hecht, Phys. Rev. B **41**, 7918 (1990).
[23]M. Alonso, R. Cimino, and K. Horn, Phys. Rev. Lett. **64**, 1947 (1990).
[24]D. Mao, M. Santos, M. Shayegan, A. Kanh, G. Le Lay, Y. Hwu, G. Margaritondo, L. T. Flores, and J. P. Harbison, Phys. Rev. B **45**, 1273 (1992).
[25]V. L. Alperovich, V. N. Kuzaev, S. V. Shevelov, and A. S. Terekhov (unpublished).
[26]M. G. Burt and V. J. Heine, J. Phys. C **11**, 961 (1978).