The Fermi level is not pinned at the p-GaAs(100) surface during adsorption of cesium and oxygen

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It is possible to control the extent of band curvature and the rate of surface recombination during the deposition of cesium and oxygen on a p-GaAs(100) surface at $T = 300$ K. This observation is evidence that the Fermi level is not pinned by defect states.

The experiments reported here show that the alternate deposition of cesium and oxygen on an atomically clean p-GaAs (100) surface, under conditions such that adsorption is accompanied by chemical reactions, leads to a repeated and reversible switching of the surface potential from flat bands to half the width of the band gap. This result means that the curvature of the bands in the GaAs(Cs,O) system is determined by the charge at states induced by electropositive and electronegative adatoms,[3,5] not by the charge at surface defects.[1,2]

The experiments used a layer of p-GaAs:Ge with a hole density $p = 1.5 \times 10^{17}$ cm^{-3}, grown by liquid-phase epitaxy on a substrate of semi-insulating GaAs(100). The procedure for preparing an atomically clean surface includes treatment with a solution of HCl in isopropyl alcohol. This treatment removes oxides and enriches the surface in arsenic. The layer is then transferred to an ultrahigh-vacuum apparatus (without making contact with the laboratory atmosphere) for a subsequent thermal cleaning.[6] The cesium and oxygen are deposited from channel sources through the thermal decomposition of cesium chromate and barium peroxide. The photoreflection spectrum $\Delta R/R$ (Refs. 7 and 8) and the integral photoluminescence intensity $I_{\rm phl}$ are measured. These properties depend on the band curvature φ_s and the surface recombination rate v_s.

Figure 1 shows photoreflection spectra of a p-GaAs surface after thermal cleaning in ultrahigh vacuum and a subsequent deposition of cesium and oxygen. We see that

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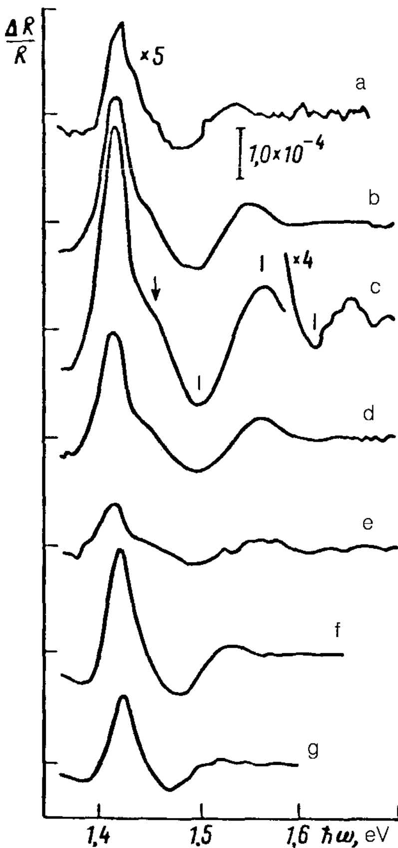

FIG. 1. Photoreflection spectra of a *p*-GaAs (100) surface after thermal cleaning (curve *a*), after sequential deposition of cesium (*b–e*), and after sequential deposition of oxygen (*f,g*). The thickness of the cesium coating, θ [in monolayers (ML)], is as follows: b—0.02; c—0.10; d—0.5; e—0.7. The oxygen exposure [in langmuirs (L)] is as follows: f—0.2; g—1.0. Spectra *f* and *g* were measured at a pump-laser intensity an order of magnitude higher than for spectra *a–e*. The positions of the oscillation extrema are marked by the vertical line segments on one of the spectra.

substantial and nonmonotonic changes occur in both the height and shape of the spectra. The deposition of cesium increases the period of the Franz–Keldysh oscillations, while oxygen reduces this period. These results are evidence of corresponding changes in the near-surface electric field F_s (Refs. 7 and 8). In addition, in the case of cesium deposition, a structural feature—a knee—appears at $\hbar\omega = 1.45$ eV on the short-wave wing of the main photoreflection peak (this feature is marked by the arrow in Fig. 1). Once a sufficiently large oxygen exposure is reached (>1 L), this feature disappears. The field F_s is determined from the positions of the extrema of the oscillations, by a method which has been used previously.[7] The band curvature φ_s is calculated from F_s and p in the Schottky model. Here we allow for the circumstance that the maximum field in the space-charge region is determined from the positions of the extrema, in accordance with Ref. 8.

Figure 2 shows the evolution of the band curvature φ_s and of the photoluminescence intensity I_{phl} during the systematic deposition of cesium and oxygen. After thermal cleaning we find $\varphi_s = 0.35$. The deposition of cesium leads to an increase and then a saturation (at $\theta \geqslant 0.2$ ML) of the band curvature, at a level $\varphi_s \approx 0.65$ V. A further deposition of O_2 reduces φ_s to 0.25 V. The photoluminescence intensity, in

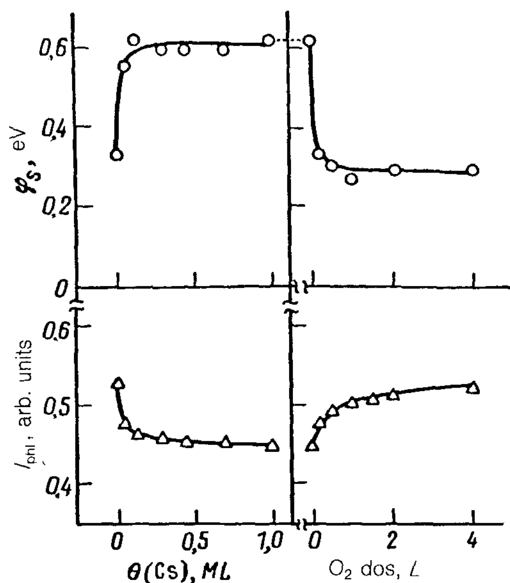

FIG. 2. Evolution of the band curvature and of the photoluminescence intensity during the deposition of Cs and O_2 on a clean surface. The lines connecting the experimental points have been drawn to aid the eye.

contrast, decreases during the deposition of cesium and increases during the deposition of oxygen. During further alternate deposition of cesium and oxygen, we observe repeated and reversible switchings of φ_s and I_{phl} (Fig. 3). This evolution of the band curvature has been seen previously on cleaved *p*-GaAs (110) surfaces, but only at low temperatures, at which chemical reactions resulting in the production of defects are suppressed.[4,5] The amplitude of these switchings does not decrease up to the sixth cycle. Beginning with the third cycle after the deposition of oxygen we observe essentially flat bands. The residual band curvature is less than $\varphi_s \simeq 0.07 \pm 0.02$ V.

The reversibility of the switching of φ_s shows that surface defects have no important influence on the formation of the band curvature even at room temperature, at which many of the cesium atoms are chemisorbed on GaAs. The chemisorption of cesium resulting in the production of microscopic dipoles was monitored on the basis of the lowering of the threshold for the (external) photoelectric effect. Surface states are apparently produced by defects[1,2] only in the stage of the chemical and thermal preparation of the surface. These states determine the initial band curvature. The decrease in φ_s to the point of flat bands and the increase in the maximum values of I_{phl} (Fig. 3) with increasing cycle number are evidence of a passivation of defect states. We believe that the increase in the band curvature during the absorption of Cs is caused by a capture of holes by surface states induced by adatoms and by the formation of Cs^+ ions. We worked from the initial part of the $\varphi_s(\theta)$ curve to estimate the fraction of Cs atoms which give up electrons to the interior of the GaAs. We found $\approx 3\%$, in contrast with the figure of 100% for the (110) surface at a low temperature.[4] The reason for the stabilization of the Fermi level near the middle of the band gap at $\theta \geqslant 0.2$ may be "universal":[9] The increase in the positive charge of the surface which results from the capture of holes by surface states induced by cesium adatoms is

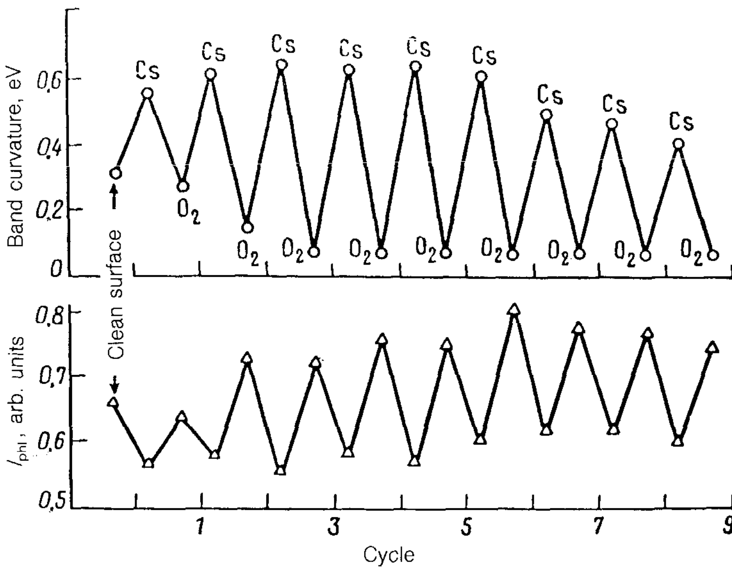

FIG. 3. Switching of the band curvature and of the photoluminescence intensity during the alternate deposition of cesium and oxygen. The Cs exposure in each cycle corresponds to the deposition of one monolayer; the O_2 exposure is 2 L.

limited by a capture of electrons, due to an increase in the surface concentration of electrons. The decrease in the band curvature during the deposition of O_2 results from a decrease in the density of surface states during the chemical interaction with oxygen. The additional knee which appears at $\hbar\omega = 1.45$ eV is apparently due to a penetration of the rapidly damped electric field of the microscopic dipoles into the semiconductor. The behavior of I_{phl} corresponds qualitatively to the dependence of the rate of surface recombination, v_s, on the extent of the band curvature,[10] but more than that dependence is operating. Changes in v_s are also caused by changes in the concentrations and capture cross sections of the recombination centers, since we do not observe a single-valued relationship between I_{phl} and φ_s in the experiments.

In summary, the adsorption of cesium and oxygen on an atomically clean *p*-GaAs (100) surface at room temperature does not lead to a pinning of the Fermi level by surface defects. The extent of the band curvature varies over a broad range, from $E_g/2$ during the deposition of Cs to the point of flat bands during the deposition of O_2. The apparent reason for the fundamental differences between the results found here and the results found on cleaved (100) faces[1] appears to lie in the special properties of the (100) surface.[11]

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