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GIANT TEMPERATURE DEPENDENCE OF THE WORK FUNCTION OF GaP

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Both the clean and cesiated $(\bar{1}\bar{1}\bar{1})$ surfaces of n- and p-type GaP show very large shifts of work function upon cooling when the surface is illuminated with 1.7-eV light: Φ increases for p-type and decreases for n-type material. This is attributed to reduction of surface charge by photoexcitation of electrons into or out of surface states. The surface-state density is $\sim 4\times 10^{12}$ cm^{-2} and is unaffected by submonolayer quantities of Cs.

Fischer recently reported the observation of a very large (0.55 eV) decrease in the work function of Cs-covered n-type GaAs upon cooling with liquid nitrogen.[1] We have studied the change in work function of GaP as a function of temperature. Our results indicate that the work-function changes occur also on clean GaP surfaces and that the changes are greatly reduced when the sample is kept in the dark. This suggests that the effects reported by Fischer are due to peturbation of surface charge by incident light rather than to changes in surface-state density or distribution as suggested by Fischer.[1]

Work functions were determined in a glass low-energy electron-diffraction (LEED) apparatus by the retarding-potential technique, measuring the sample potential required to retard an incident electron beam (10 V, 5×10^{-9} A). For absolute calibration, a polycrystalline tungsten ribbon was intermittently substituted for the GaP sample during each experiment. The contact potential between the GaP and W ribbon was reproducible to ± 0.1 eV while changes in Φ_{GaP} were reproducible to ± 0.02 eV; Φ_W after flashing to 2500°K was assumed to be 4.5 eV.

After sputtering with Ar for several hours followed by annealing to 825°K, LEED patterns showing the expected symmetry of the $(\bar{1}\bar{1}\bar{1})$ surface were obtained which did not alter with further sputtering and annealing. Deposition of Cs^+ from a heated zeolite source[2] caused a gradual reduction of diffraction intensity with substrate at either 300 or 77°K; there was no evidence for greater ordering at low temperature. Cs coverage was calculated from the ion current to the sample. While this calculation tends to yield too large a value, the estimated error in coverage was less than a factor of 2.

It was observed that the work function of the clean $(\bar{1}\bar{1}\bar{1})$ surface as measured in the dark of an n-type, S-doped (5×10^{17} cm^{-3}) GaP crystal did indeed decrease with temperature (see Table I) but only by 0.2 eV, as compared with Fischer's value of 0.6 eV. Notice that Fischer measured changes in the work function of GaAs from the energy distribution of photoemitted electrons[3] and thus under constant illumination. When we illuminated the sample (6×10^{-4} W/cm^2 between 1.6 and 1.97 eV measured by a calibrated Eppley thermopile) the change between 300 and 77°K was 0.65 eV (see Table I). The final value of Φ depended strongly on crystal illumination at 77°K. Increasing illumination intensity caused a larger decrease in Φ. When the illumination was removed, Φ slowly increased back to the dark value with a time constant of ~30 sec. We also studied a p-type sample. When a Zn-doped (2×10^{18} cm^{-3}) GaP crystal was studied, the work func-

Table I. Work function (in eV) of GaP $(\bar{1}\bar{1}\bar{1})$ measured in the dark and illuminated by a microscope lamp (6×10^{-4} W/cm^2).

	n type	p type
300°K		
Dark	2.95	3.05
Light	2.80	3.30
77°K		
Dark	2.75	3.22
Light	2.15	3.79

tion of the clean $(\bar{1}\bar{1}\bar{1})$ surface increased on cooling to 77°K by about 0.17 eV (see Table I). Notice, however, there was a larger increase if measurements were made under illumination and the apparent change of work function was 0.49 eV. As with the n-type crystal, the time constant for returning to the "equilibrium" Φ (no illumination) was ~50 sec at 77°K compared with ~1 sec at 300°K.

The work function of a Cs-covered surface decreased with increasing Cs coverage as expected, but also exhibited the same light-induced changes as the clean surface until the Cs coverage exceeded 6×10^{14} cm^{-2}. At higher coverages the magnitude of the changes decreased until at 1×10^{15} Cs/cm^2, Φ was no longer sensitive to light.

We interpret these results as due to variation in surface-state occupancy rather than variation in surface-state density or distribution as proposed by Fischer.[1] The changes in Φ were primarily produced by light rather than by temperature decrease. The changes reflected departure from equilibrium which decayed when the excitation was removed with a temperature-dependent relaxation time. It was evident from the LEED patterns that no structural change occurred on cooling either on the clean or the Cs-covered surface of GaP, and since changes in Φ were observed on both clean and covered surfaces, Cs was not responsible.

The light energy necessary to produce the changes in Φ was 1.5-1.7 eV, less than the GaP bandgap of 2.24 eV; therefore, injection of carriers by the light to produce a surface photovoltage did not occur.[4,5] We propose that photoexcitation of electrons into donor states for the p type and out of acceptor states for the n type was responsible for the observed changes in surface potential. Because of the long relaxation time of the surface states located far from the band edges, a moderate light flux was able to maintain a significant change in surface charge.

From the magnitude of $\Delta\Phi$ the density of surface states can be estimated. Assuming that with the most intense illumination the surface charge was zero (flat bands), then $\Delta\Phi$ is the band bending produced by N_S charged-surface states. On the clean surface

$$N_S \sim N_B X \sim \left(\frac{N_B \epsilon \Delta\Phi}{2\pi e}\right)^{1/2} = 4\times10^{12}\ \mathrm{cm}^{-2},$$

using the Schottky approximation. N_B is the density of ionized bulk states and X is the width of the space-charge layer. Since the low-energy electron beam used to probe the surface potential did itself cause some charging of the surface, the true surface-state density is probably slightly greater than the estimate.

In summary, the surface states on clean GaP (and presumably also on GaAs) are "slow" enough so that optical interactions can produce significant departures from equilibrium as indicated by changes in surface potential. Submonolayer quantities of adsorbed Cs decrease the work function without apparently affecting the band bending and surface-state density. The density and energy distribution of the surface states can be conveniently measured spectroscopically, and these results will be presented in detail elsewhere.

It is worth pointing out that, just as care must be taken with light in the work-function measurement, electron-beam charging effect has to be minimized. In our experiment, equilibrium values of Φ were determined by first holding the crystal at a potential to retard the electron beam entirely for several minutes; the bias was then reduced rapidly to determine the threshold for current collection.

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