Fine structure in the spectra of thermalized photoelectrons emitted from GaAs with a negative electron affinity

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Spectra of photoelectrons emitted from the Γ valley of GaAs with a negative electron affinity have been measured at 77 K with a resolution of 5 meV. These are the first such measurements. A fine structure which is seen in the spectra stems from particular features of the emission processes and of the thermalization of photoelectrons near the surface.

The surface of p^+-GaAs with an activating coating of Cs and O has an effective negative electron affinity, with the vacuum level lying below the bottom of the conduction band in the interior of the semiconductor.[1] If the doping is sufficiently heavy, the thickness of the space-charge region near the surface is much smaller than the electron thermalization length in the Γ valley, which is[2] $\geqslant$1000 Å , and the thermalized photoelectrons should pass above the space-charge region and escape into vacuum without any loss of energy. In this case the spectrum of photoelectrons in vacuum should reproduce the distribution of photoelectrons in the semiconductor. Studies have shown, however, that this is not the case and that, before they escape into vacuum, electrons lose a substantial fraction of their energy near the surface.[3] As a result, the photoelectron spectrum broadens and shifts away from its original position near the bottom of the conduction band in the interior of the semiconductor. The mechanism by which electrons lose energy as they pass above the space-charge region has not yet been clarified. All that is clear at this point is that the known bulk mechanisms for dissipation of electron energy in GaAs are too weak to explain the situation, and it becomes necessary to consider reflection from the activating coating, which would increase the time spent by the electrons in the space-charge region.[3]

The photoelectron energy loss in the course of photoemission has been studied experimentally by measuring and analyzing photoelectron spectra. In most of these studies, the spectra have been measured at room temperature on spectrometers with an inadequate resolution. It is probably for this reason that the photoelectron spectra have not revealed a fine structure due to the spectrum of the density of electron states near the surface. In the present study, we have measured the photoelectron spectra of GaAs with a negative electron affinity at 77 K, at a resolution of 5 meV, and at a high signal-to-noise ratio. These are the first such measurements. We have found an exponential tail on the photoelectron spectrum, which is due to an emission of thermalized electrons into

vacuum without an energy loss. Near the maximum of the photoelectron spectrum we find a fine structure, which is probably due to particular features of electronic processes which occur near the surface.

The measurements were carried out with vacuum photodiodes consisting of plane-parallel electrodes, a photocathode and a metal anode, mounted hermetically at the ends of a cylindrical housing of an aluminum oxide ceramic. We used a semitransparent photocathode on glass. The procedures for fabricating the photocathode, cleaning it, and activating it have all been described previously.[4] The active layer of the GaAs photocathode, with the (100) orientation, was doped with zinc to a concentration $p=6\times10^{18}$ cm^{-3}. The parts of the photodiodes were outgassed, activated, and hermetically attached to each other through indium seals in a three-chamber vacuum apparatus with a limiting pressure of 10^{-9} Pa. Photoelectron spectra were measured by differentiating delay curves with the help of lock-in detection. Distortions of the photoelectron spectra due to the space charge and reflection of photoelectrons from the anode were eliminated through an appropriate choice of measurement conditions and ranges. The resolution of the "analyzer," determined from the slope of the steepest parts of the photoelectron spectra, was twice the amplitude of the modulating voltage up to 5 meV. Absolute photoelectron energies were calibrated at 77 K by measuring the shift of the high-energy knee of the photoelectron spectrum as the photon energy was raised. The position of the boundary of this knee was determined by emission of ballistic photoelectrons excited by the light out of the heavy-hole band into the conduction band. The emission of ballistic photoelectrons in photocathodes illuminated from the rear side was observed in these experiments at active-layer thicknesses less than 1.5 μm. The calibration method was essentially the same as that used in Ref. 5. The only distinction was that the threshold shifts which we measured were described better by a theory using a heavy-hole mass of $0.8m_0$, rather than the $0.51m_0$ in Ref. 5. The apparent reason for this change is that for our test sample the short-wave boundary of the photoelectron spectrum is set by electrons excited out of the heavy-hole band along the (111) direction, with the largest effective mass.[2] We took the width of the band gap to be 1.50 eV at 77 K and 1.41 eV at 300 K; these figures incorporate the effects of the heavy doping. The light source was a halogen incandescent lamp with an MDR-23 monochromator. The diameter of the light beam (2 mm) was chosen much smaller than the diameter of the photocathode (20 mm), so that inhomogeneities and edge effects would not affect the results of the measurements. In the course of the low-temperature measurements, the photocathodes were immersed in liquid nitrogen. The data acquisition and processing were automated with the help of an IBM PC-386 with interface circuit boards.

Figure 1 shows photoelectron spectra measured at $T=77$ and 293 K. The energies of the exciting photons are also shown in this figure for each spectrum. The active layer on the semitransparent photocathode in this photodiode was reduced to 0.2 μm, so when electrons are excited above the bottom of the conduction band, the photoelectron spectra contain a high-energy knee due to an emission of nonthermalized photoelectrons. The short-wave boundary of this knee at $T=77$ K is determined by an emission of ballistic electrons. The position of this knee was found from the maximum of the second derivative of the photoelectron spectrum and was used for an absolute energy calibration of the photoelectrons. Analyzing the evolution of the shape of the knee with increasing photon

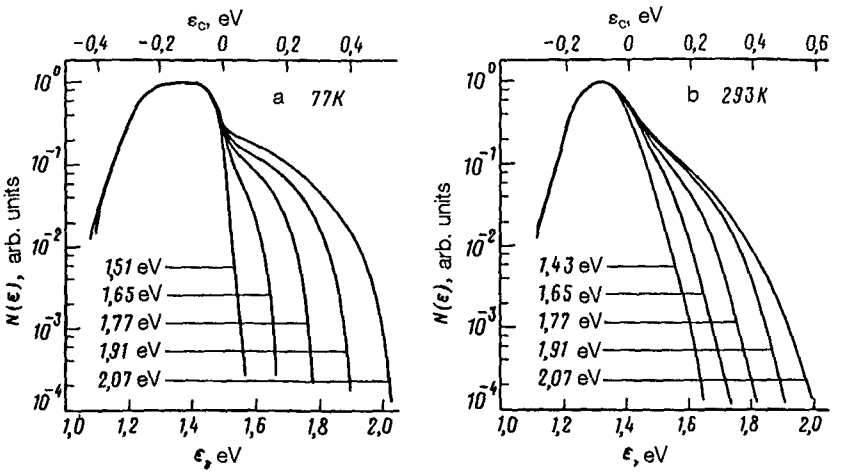

FIG. 1. Spectra of photoelectrons at various photon energies. The electron energy is reckoned from the top of the valence band, ε (lower scale), and from the bottom of the conduction band, ε_c (upper scale).

energy, we found no clearly defined features at $\varepsilon_k \approx 300$ meV. This was a surprising result, since for electrons at this and higher energies the scattering into the L valley is the primary thermalization mechanism. As a result, electrons accumulate in the L valley, and a structural feature in the form of a knee or peak arises in the photoelectron spectra.[5–7] It has also been assumed[6] that the probability for the escape of electrons from the L valley, which is higher than that from the Γ valley, is slightly above the threshold for electrons of the same energy. Our results show that this is not the case. The ratio of emission probabilities can apparently depend strongly on scattering by the surface, which is determined in turn by the methods used for cleaning and activation. Further studies are required to resolve this point.

It can be seen from Fig. 1 that, at given initial kinetic energies of the photoelectrons, the total intensity of the "hot" knee at 77 K is considerably higher (by about 20–25%) than that at 293 K. As the temperature is raised, there is accordingly an increase in the rate of electron thermalization. When photoelectrons are excited to the bottom of the conduction band, the hot knee disappears, and the high-energy wing in the photoelectron spectrum becomes exponential within 10^{-1}–10^{-4} of the crest of the peak. The slope of this wing is 9 meV at 77 K, and 29 meV at 293 K. In other words, it is essentially the same as the slope of the distribution of thermalized photoelectrons in the interior of the semiconductor. We thus see that the thermalized electrons from the tail of the distribution are emitted into vacuum without a change in energy distribution. The apparent reason is that the inelastic scattering of fast electrons in the space-charge region and in the activating coating is slight. With decreasing kinetic energy of the electrons, the shape of the wing of the photoelectron spectrum deviates from exponential. The reason for these deviations is that slow electrons near the bottom of the conduction band have a much higher probability to lose energy, being trapped in states in the space-charge region.

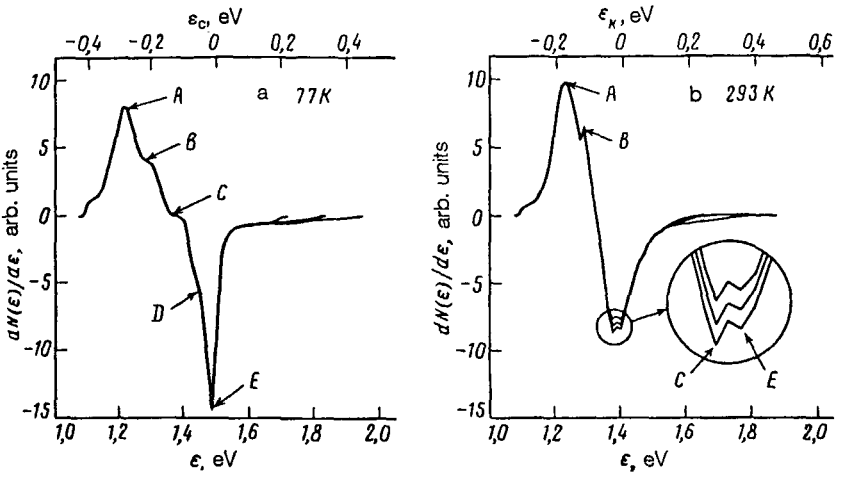

FIG. 2. Derivatives of the photoelectron spectra. The positions of the structural features in the spectra are reckoned from the bottom of the valence band. a: $\varepsilon(A)=1.22$ eV, $\varepsilon(B)=1.280$ eV, $\varepsilon(C)=1.370$ eV, $\varepsilon(D)=1.450$ eV, $\varepsilon(E)=1.490$ eV. b: $\varepsilon(A)=1.235$ eV, $\varepsilon(B)=1.280$ eV, $\varepsilon(C)=1.380$ eV, $\varepsilon(D)=1.40$ eV.

Quasisteady states in the space-charge region, which lie above the vacuum level, participate in photoemission. The shape of the photoelectron spectrum at the crest of the peak is the result of a competition between photoemission from these states (on the one hand) and thermalization followed by recombination (on the other). Surface states may also lead to the appearance of a fine structure in the photoelectron spectrum.

To bring out a fine structure, we calculated derivatives of each of the measured spectra. The results are shown in Fig. 2. We see that the derivatives of the photoelectron spectra corresponding to the two temperatures do indeed have a fine structure. The energy positions of these structural features, listed in the caption of Fig. 2, are the same in all the measured spectra, within the measurement errors. Peak A apparently corresponds to the position of the vacuum level. As the photoemitter is cooled to 77 K, this peak shifts 15 meV. At a level of about 50–60 meV above the vacuum level we find structural feature B in the spectrum of the derivative of the photoelectron spectrum. The shape of this feature depends on the temperature, but its position does not. At high energies, the features depend strongly on the temperature. In the spectrum of the derivative of the photoelectron spectrum, negative peak E shifts 90 meV as the temperature is lowered to 77 K. This shift corresponds precisely to the broadening of the GaAs band gap. It is not clear, however, whether the position of this structural feature coincides with the bottom of the GaAs conduction band or is indeed shifted 10 meV from it, as is indicated by Fig. 2. The problem is that this shift is close to the level of the systematic error in the calibration of the spectrometer. Structural feature D, shifted 30–40 meV from peak E, is observed only at 77 K. Feature C is observed at both temperatures, but its position varies over an interval of 60 meV, as measurements are carried out at different points on the photoemitter. The nature of the fine structure in the photoelectron spectrum other than features A and E is unclear. All we can do is suggest that structural feature B is associated with an

energy dependence of the transmission of a residual barrier, since it lies near the vacuum level, where the transmission controls the shape of the photoelectron spectrum. Feature D is probably a phonon replica of peak E, since it is separated from the latter by the energy of an optical phonon, and it becomes smeared as the temperature is raised. "Floating" feature C may be associated with the presence of a quasisteady surface level in the space-charge region; the position of this level would depend on slight changes in the potential profile near the surface and would thus vary from point to point.

The fine structure observed in the spectra of thermalized photoelectrons thus provides the first clear evidence that the near-surface thermalization and emission which occur in semiconductors with a negative electron affinity are complex.

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[1] R. L. Bell, *Negative Electron Affinity Devices* (Oxford U. Pr., London, 1973).
[2] B. P. Zakharchenya *et al.*, Usp. Fiz. Nauk **136**, 459 (1982) [Sov. Phys. Usp. **25**, 143 (1982)].
[3] A. L. Musatov *et al.*, Fiz. Tverd. Tela (Leningrad) **23**, 929 (1981) [Sov. Phys. Solid State **23**, 540 (198 1)].
[4] Yu. B. Bolkhovityanov *et al.*, Pis'ma Zh. Tekh. Fiz. **16**(4), 25 (1990) [Sov. Tech. Phys. Lett. **16**, 253 (1990)].
[5] H.-J. Drouhin *et al.*, Phys. Rev. B **31**, 3859 (1985).
[6] L. W. James and J. L. Moll, Phys. Rev. **183**, 740 (1969).
[7] Sh. M. Kogan *et al.*, Izv. Akad. Nauk SSSR. Ser. Fiz. **49**, 1745 (1985).

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