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The energy distribution of field-emitted electrons from GaAs crystals

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Abstract

Energy spectroscopy of electrons emitted from GaAs crystals of n- and p-type conductivity has been studied for different values of the applied electric field as well as for different surface conditions at the emitting surface of the crystals. Analysis of the electron energy spectra for the n-GaAs emitter shows that the electrons forming the field-emission current for the near degenerate n-type semiconductor originate from the valence band. A physical mechanism that could possibly lead to predominant emission from the valence band of the n-type semiconductor has been proposed. The electron energy distribution has also been measured for the p-GaAs field emitters. The results show that it depends essentially on the external field applied to the surface. Electron field emission from a p-type semiconductor has been discussed with consideration of tunnel current from the surface self-consistent quantum well.

1. Introduction

Many phenomena occurring in the near-surface region of a semiconductor, when a strong electric field is applied to the surface, are explained by taking into consideration both the size effect (two-dimensional quantization of electron gas) and the energy distribution of electrons [1]. Although the basic properties of electronic states are well documented theoretically [2, 3], there is still a need for future accurate experimental data. Field-electron-emission methods are useful in such studies since they provide a means of continuous visual surface control during the experiment, and besides, they enable emission from different crystal directions to be investigated under identical conditions. Field-emission studies of semiconductors in many cases were limited to current–voltage (I – V) measurements. Those I – V data were interpreted in the framework of Stratton's calculations derived for semiconductors and based on the classical Fowler–Nordheim theory of electron field emission [4, 5].

Experimental studies of the semiconductor field-emission properties around the world have significantly increased during last decades due to the development of vacuum microelectronics [6]. At present semiconductors, and in particular wide-band-gap materials, have been recognized as suitable field-emission materials, which are of great importance in the creation of both ion and electron sources,

and in the improvement of technology of solid state devices. Tunnel currents in solid state devices are similar to field electron emission through a potential barrier on a semiconductor–vacuum interface as it was shown in [7, 8]. It causes additional interest to these problems.

This paper focuses on field-electron-energy spectroscopy (FEES) because this analytical technique can provide a deeper insight into the field-emission mechanism and allows determination the electronic band-structure origin of field-emitted electrons.

2. Experimental procedure and software package

Field emitters of 1 mm × 1 mm × 15 mm dimension oriented in the (100) crystallographic direction were made of GaAs single-crystals with different types of conductivity, namely: n-type crystals with carrier concentration $n = 8.6 \times 10^{17} \text{ cm}^{-3}$, Sn-doped, and p-type crystals with carrier concentration $p = 10^{20} \text{ cm}^{-3}$, Zn-doped. The tips were formed by chemical etching in the standard CP-4a solution for 3–5 min. Both the final tip radius and the tip shape were determined by the light microscope with a digital camera operated in the recording mode. This allows fabrication of GaAs tips with a high degree of geometrical reproducibility. The top of each tip was cleaned by field desorption technique gradually to produce

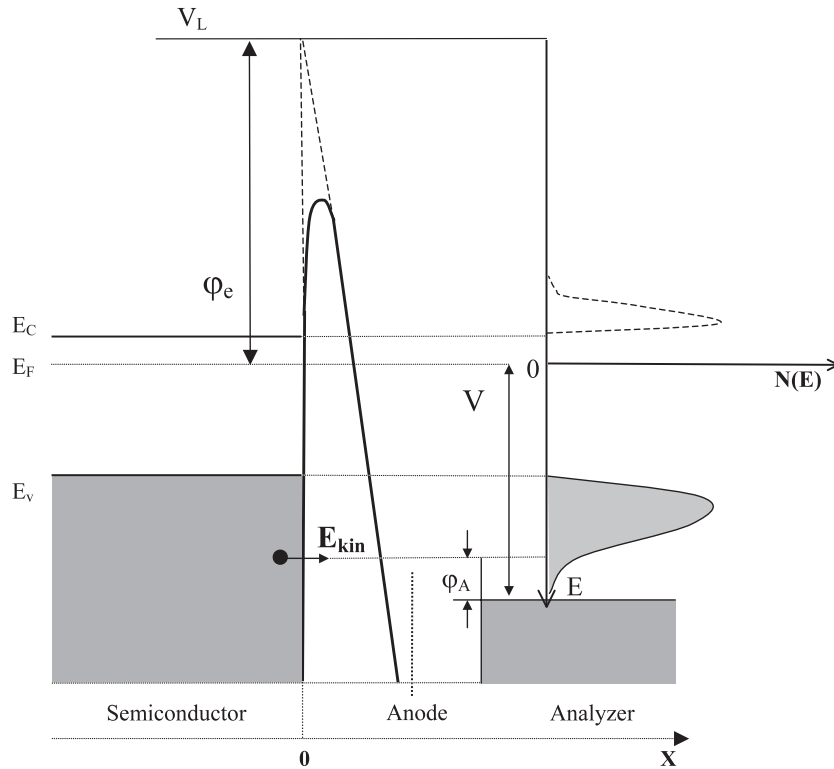


Figure 1. Simplified energy diagram of a semiconductor field emitter. A negative voltage V is applied to the emitter with respect to the analyzer; E_{kin} —kinetic energy of the field electrons; ϕ_A —analyzer work function; ϕ_e —emitter work function; E_F —the Fermi level which serves as a reference energy in the spectra; V_L —the vacuum level. The dash curve shows an expected FEED for emission from the c-band.

an atomically clean emitting surface with typical symmetrical emission pattern.

The I – V characteristics were measured for the several stages during the process of surface cleaning as well as for the atomically clean surface. The probe-hole technique was used to study the emission current from different parts of the emitting surface. We also used the field-electron-energy distribution (FEED) analysis which consisted of energy spectra measuring of emitted electrons by the electron spectrometer with a spherical deflector with a deflection angle of 135° , described in [3]. Our energy analyzer permits an accurate measurement of the energy distribution with resolution of 0.02 eV (when electron energy is about 3 keV) in a range of analyzed energies about 6 eV below the Fermi level, E_F . It was also possible to observe the emitting surface in the field-emission electronic microscope with the resolution of 20 Å when studying the I – V characteristics and the FEED spectra. All measurements were performed at ultra-high vacuum pressure of 10^{-7} Pa.

The general principle of the FEED spectra measurements is shown in figure 1, which illustrates the relationship between the measured kinetic energy, E_{kin} , of the electron emitted from an energy level E , the potential V , applied between the cathode and the analyzer, and the analyzer work function ϕ_A . The field-emitted electrons which pass through the anode probe hole are then collected by the analyzer. The Fermi level of the semiconductor may serve as a reference energy level, as its energy related to the Fermi level of the analyzer only depends on the applied voltage. Hence, it is convenient to plot all FEED

spectra in terms of $(E - E_F)$, i.e. $E - E_F = E_{kin} - eV + \phi_A$. The energy of the tunneling electron decreases from left to right, i.e. downward from the vacuum level.

It appears that the FEED analysis of semiconductors is a very difficult experimental task in comparison with the study of metals. One of the main difficulties here is that the anode voltage, applied to the spectrometer electrostatic lenses, should be corrected on the internal potential drop, caused by the field-emission current drawn from a semiconductor. For example, the voltage drop along the field emitter of a high resistivity semiconductor as measured by means of the retarding potential technique reaches several hundreds of volts. When using FEES, the potential drop is measured by a shift of the FEED spectrum from its initial position to the right in the low-energy region. After that, the corresponding compensating voltage is applied to the field emitter to return the spectrum in the required region of measurements. It is more convenient to do this operation automatically. The other difficulties appeared for semiconductor field emitters are discussed in the part 4. Therefore, the control of the experiment and data processing were performed in this study with the help of IBM computer, in-house built spectrometer voltage control blocks and specially developed software package.

The experimental results obtained in the course of previous field-emission studies [9–11] allowed us to formulate the tasks for software development and specifications, which are needed for studies of various semiconductor materials. Thus a special software package, named FEESA, was developed for the multipurpose electronic measuring system,

based on the field electron energy analyzer. FEESA tests both the spectrometer control system and the measuring electric circuit to check for a possible circuit break and its location.

FEESA allow feasibility to graduate, under different experimental conditions, each voltage applied to spectrometer electrostatic lenses while making 10 000 discrete steps along the graduated curve. These graduated curves are saved in 30 parameters database. It is also possible to control the measurements in real physical parameters (e.g. electrostatic lens voltage), which is more convenient than following DAC step scale. Besides, FEESA enables to determine the optimum operating mode for a field emitter. One can visually observe the FEED curves during the data accumulation process and correct any operating mode manually. As it is common for a field-emission study, the measured values of the emission current are varied in the range of several orders of the initial magnitude. Therefore, the graphic spectra data are normalized to the maximum peak intensity for various field intensities automatically. This is done to avoid any mistakes in the measurement program. To study the field dependence of the FEED curves it was possible to measure spectra at a signal level from 0.01 to 10^6 e s⁻¹, which can be compared only when they are normalized to the common peak intensity.

The FEESA can choose the following operating conditions: the energy resolution, the voltage step to scan the electron energy distribution and the acquisition time period depending on the signal level. Moreover, FEESA makes it possible to return to the initial state at any time and to repeat any measurement in the identical operating mode.

The FEESA allows analysis of unlimited volume of the accumulated data, for instance, data can be sorted, classified, grouped, summed up, averaged and processed in a different way. Further these data can be exported to commercially available software packages for mathematical and graphical treatment. Our software package was created for the ‘electron spectrometer—computer’ interface that provides the range of analyzed energies of the field-emission electrons up to 10 eV below the vacuum level provided that the FEED curves are measured with the scan step from 20 meV for anode voltage in the range of 100–4000 V. To decrease statistical spread of the experimental data and to increase a volume of accumulation of the count electrons, in other words, to improve the ‘signal-to-noise’ ratio, typically, each measured FEED spectrum was recorded by both methods: either by several scans of the emitted electrons in the range from zero up to 10 eV as the sum consisted of a required number of individual spectra or by the continuous accumulation of the counted electrons in the spectrum point for chosen energy of electrons. The acquisition time period can be varied from 0.01 s up to 100 min depending on the signal level.

The FEESA is a Delphi-5 program for Windows 98 (and later editions) and it is easily converted to UNIX systems. Acquisition and data processing modules can be installed on two separate LAN/Internet-connected computers. FEESA allows real time data processing. The created registration system can be attributed to the corresponding top level control systems in the world and it was used for the FEED measurements in this study.

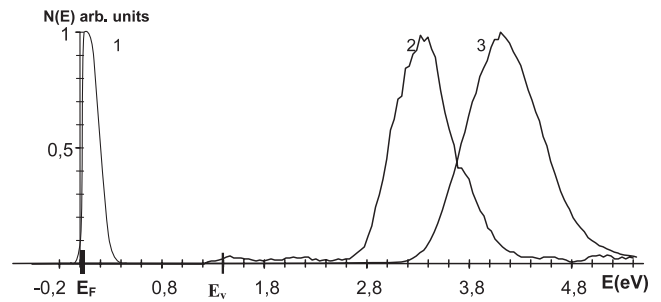


Figure 2. FEED for the n-GaAs surface with oxide layer. (1) $I = 10^{-11}$ A; (2) $I = 10^{-8}$ A; (3) FEED from W surface is shown for comparison.

3. Results

The FEED curves and the I – V characteristics of the field-emission current were measured in the wide range of electric field, i.e. from the operating rate of single-electron counting $N(E)$ up to the critical current value I_c , limited by the emitter destruction caused by the current drawn from the emitter. The electron spectra were measured by numerous scanning of emitted electrons, provided that spectra can be measured in six orders of the current magnitude. It was adopted as a criterion for the minimum measurable signal when summing lots of independently normalized spectra produce the same spectrum as a single long measurement. To find the influence of a possible heating of a crystal by the emission current, drawn from the crystal, both the cyclic and back-forward methods of voltage changing were used during FEED studying. No difference in the FEED curves was observed in such measurements.

Firstly, the electron spectra were measured for the n-GaAs monocrystal covered by a thin film of intrinsic oxide. The energy-distribution plots for field-emitted electrons are presented in figure 2 for different values of the applied field. The electron energies E along the X axis are measured from the Fermi level E_F . In our case the n-GaAs crystal is a nearly degenerate semiconductor and E_F coincides with the bottom of the conduction band. The shift of the FEED curve to the right side in figure 2 corresponds to the downward shift from the vacuum level. The density of the emission current along the Y axis is in arbitrary units and the spectra are normalized to a common peak. It should be noted, that it is impossible to estimate the value of the electric field intensity for a semiconductor emitter correctly, without taking into account the screening of the external field by the charge, localized in surface states. This problem will be treated later. In this paper the corresponding values of anode voltage and electron account rate are used to describe the field intensity.

The initial position of the FEED curve for the semiconductor tip, covered by thin dielectric layer, depends on the value of the internal potential drop in the dielectric layer. All the observed curves are characterized by a single peak. The spectrum position as well as its high-energy edge are shifted downwards, towards the lower-energy region up to 3 eV below E_F for this particular sample, with increasing the emission current drawn from the tip (figure 2, curves 1 and 2).

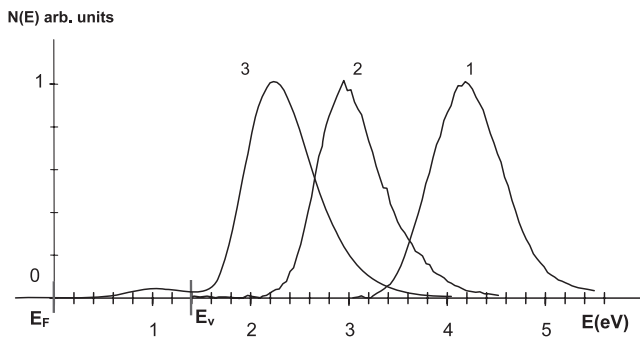


Figure 3. FEED for the n-GaAs surface (1)—oxide layer; (2)—stage of desorption; (3)—atomically clean surface.

The half-width of the distribution curve increases on 0.15 eV at that rate.

Further, the FEED curves were measured at the different stages of oxide desorption from the emitting surface of the n-GaAs crystal. At all stages of field desorption the curves have the similar shapes with a single peak, whose initial position as well as the high-energy edge of spectra are shifted upwards, to the vacuum level, when cleaning the emitting surface (figure 3). It is seen that the high-energy edge of the electron distribution for an atomically clean surface corresponds to the energy level $E_L = 1.4$ eV below the Fermi level, which serves as a reference energy in the FEED spectra (it can be seen in figure 1). Our results show that for the near degenerate n-GaAs crystals, investigated in this work, the energy level $E_L = 1.4$ eV corresponds to the top of the valence band E_v , taking into account the energy-gap value E_g of the GaAs crystal $E_g = 1.4$ eV.

The shapes of the FEED curves and their positions were reasonably reproducible for the $\langle 100 \rangle$ and other crystallographic directions, while the tip was turned up to 60° from the tip axis, and measurements were taken at various times, up to several hours after cleaning the tip. The log plots of I/V^2 as a function of $1/V$ for the GaAs tips with an atomically clean surface are linear (figure 4). The characteristics are reproduced many times under the same conditions until the current drawn from the semiconductor does not exceed the critical value I_c . No thermo and photosensitivity of the emission current was observed for the n-GaAs crystals.

The FEED curves were also measured for the p-GaAs crystals to compare with that obtained for the n-type crystals. The typical FEED curves for the atomically clean surface of the p-GaAs emitter are shown in figure 5. It can be seen that both the shape of the curve and its energy position depend significantly on the external field intensity. At low fields two peaks can be noticed in the FEED curve, while at higher fields the FEED curves are characterized by a single peak located in the high-energy region.

We would like to note, that all original FEED spectra, corresponding to the low electric fields, contain usually a number of sharp peaks depending on the noise level. As a rule, the spectra measured at low signals were smoothed in this work with the help of standard polynomial processing program. All spectra in this paper are arbitrarily normalized to a common

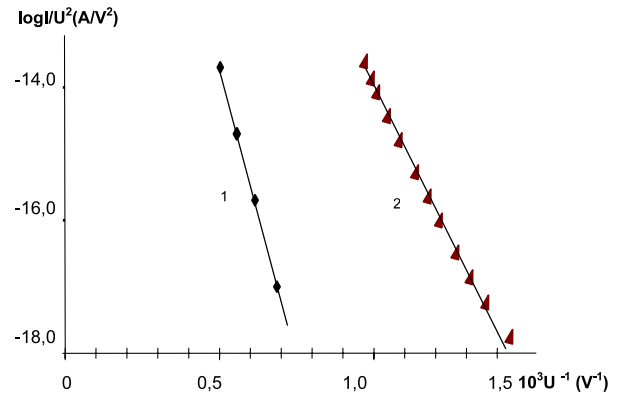


Figure 4. I - V plots for the n-GaAs field emitter: (1)—with oxide layer; (2)—atomically clean (after desorption).

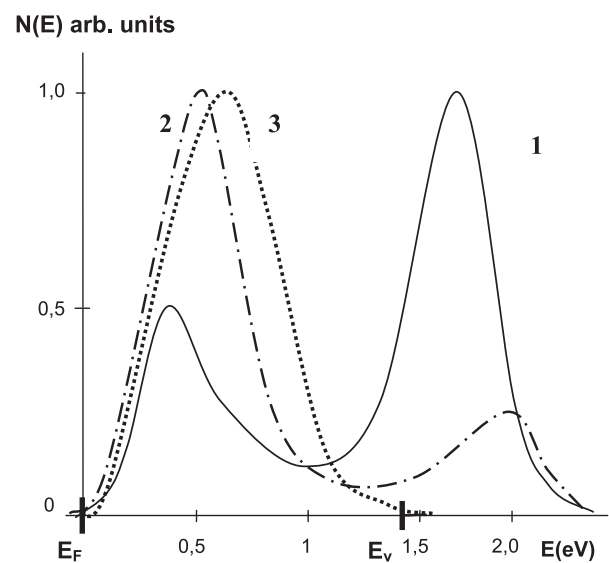


Figure 5. FEED for the p-GaAs atomically clean surface (1)—electron count $0, 1 \text{ e s}^{-1}$ (2)—electron count 3 e s^{-1} (3)—electron count 100 e s^{-1} .

peak because the emission current, measured under various field and surface conditions, differ more than several orders of the current magnitude as it was described above in the part 2.

4. Discussion

Field electron emission from semiconductor tips can be accompanied, in principle, by a large variety of phenomena associated with the electric field penetration into the bulk of a semiconductor. They are as the following: bending of bands, that leads to the difference in the carriers' concentrations in the near-surface region and that in the bulk; heating of current carriers that results in the different recombination conditions; field ionization of impurity centers; impact multiplication of the carriers; Zener breakdown and a feasible mechanical stress under strong electric field, that could lead to the anisotropy of the emission properties. Therefore, we studied the semiconductor crystals with low resistivity to minimize a

possible influence of these phenomena, when analyzing the results of the FEED measurements.

The experimental FEED curves (figures 2 and 3) clearly show that the field-emission current from n-type GaAs is formed by electrons originated from the valence band only, that is $j_v \gg j_c$ for the n-GaAs crystals, investigated in this study. This is rather unexpected and non-evident result for electron emission from the n-type near degenerate semiconductor. The half-width of the experimental energy distributions are in the range predicted by Stretton's theory for the field emission from the valence band [5]. The modern registration system and the field electron spectrometer used in this experimental study are quite capable of making the precise measurements which are necessary to detect any peculiarities in the FEED spectra at the level of single-electron counting, but no electrons from the conduction band have been detected.

We would like to note, that the lack of the electrons from the c-band in the experimental FEED spectra was observed before, for the case of the (100) emitting plane of the n-Ge crystal [10]. This was connected, as outlined in [3], with the relationship between the electron momentum components for the electrons in the near-surface region. Indeed, for the specular transmission through the potential barrier, depending only on the x -coordinate, the transmission probability depends on the electron state only through the value of the ' x -directed' energy in the barrier region (figure 1). Thus, $D(\varepsilon - \varepsilon_\perp)$ is the probability, that an electron of energy ε incident on the surface barrier is transmitted, where: $\varepsilon_\perp = (p_y^2 + p_z^2)/2m$ and p_y, p_z are the tangential components of the conserved quasi-electron momentum components. If ε_\perp is sufficiently large, the probability of electron emission from the conduction band is too small, as it occurs in the known case of the (100) plane of germanium and therefore, this would lead, according to Modinos [3], to relationship $j_v \gg j_c$ for the Ge(100) plane even for the case of the degenerate electron gas in the conduction band.

The above described model is suitable for the field electron emission from the Ge(110) plane. However, the experimental study of the FEED spectra for the other crystal plane of Ge crystals, namely, the (111) plane of the n-Ge crystal, did not also reveal the electrons originated from the c-band [11, 12]. Moreover, in these studies the emitter was mounted on a tilting device so, that the various crystal planes of the single-crystal surface and tip areas up to 60° off the tip axis could be probed. Nevertheless, no electrons from the c-band have been observed. This means that relationship $j_v \gg j_c$ is rather general feature of field emission from the n-type crystals than its peculiarity, connected with the specific crystallographic direction. Our results presented in this paper show that the emission current from various planes of the n-GaAs crystals is also formed by the electrons originated from the valence band as it was observed in the previous publications for the Ge crystals.

We would like to notice that for the clean GaAs field emitter at the high field intensity the high-energy tail can be observed (figure 3, curve 3) in the same energy range that it was observed in [13]. No explanation of the 'tail' there was done. The energy position of the distribution's leading-edge appears to be related to the emission contribution from

the surface states, disposed in the GaAs forbidden gap. An additional reason supporting our interpretation is that the 'tail' depends on the cleaning of the emitting surface.

Now we consider a possible mechanism leading to relationship $j_v \gg j_c$, that has been experimentally revealed in this study for all probed directions of emission from GaAs single-crystals. Why electron emission from the conduction band is not observed in the FEED spectra should be explained by lower electron concentration in the conduction band than in the valence band (that is $n_c = 10^{18} \text{ cm}^{-3}$ and $n_v = 10^{22} \text{ cm}^{-3}$, respectively) and therefore $j_v \gg j_c$. The other reason should be connected with the larger effective mass of electrons m in the GaAs valence band than that in the conduction band (near in ten times). These two reasons could explain the signal difference no more than in 5 orders of magnitude. However, our registration system and the field-emission electron spectrometer used in this study with help of FEESA program would allow signal detection from the c-band even if it less by 6 orders of that from the v-band (it is described in detail in the part 2) but the c-band electrons was not revealed.

We can propose an additional mechanism leading, in general, to the decrease in the electron emission from the conduction band of the n-type semiconductor. It is the processes the electron-hole (e-h) recombination in the near-surface region that increase essentially when the strong electric field is applied to the semiconductor surface. The strong electric field can activate some centers in the forbidden band near the surface. It can also produce the additional centers for e-h recombination as well as to increase their cross sections. These processes can lead to a decrease in contribution of the c-band electrons to the total emission current.

The results obtained in this study also demonstrate the main features of the field electron emission from a p-type semiconductor. A strong electric field on the semiconductor surface produces the self-consistent quantum well for electrons in the conduction band as it is shown in figure 6. The stronger the electric field applied to the surface, the deeper the well. At low electric field there are two peaks in the FEED curve corresponding to electrons from the quantum well (fast group) and from the valence band (slow group). When the electric field increases, the peak caused by electrons emitted from the quantum well increases also. At higher field the FEED curve consists of one peak corresponding to electrons from the quantum well. According to [14], the typical depth of the self-consistent quantum well reaches the value of 0.5–0.7 eV with the width of the well about 10–15 Å, if the electric field is stronger than $2 \times 10^7 \text{ V cm}^{-1}$, that is just for our case of field electron emission. Such small thickness allows electrons to fly ballistic through the well region. The density of electrons, which are attracted to the surface by strong electric field, in the self-consistent quantum well here is more than 10^{13} cm^{-2} . The results of electron emission from semiconductor tips [8] show that the tunnel current of electrons from the self-consistent quantum well has appeared to be smaller, than the tunnel current of electrons from the valence band. The charge density in the self-consistent quantum well determines the magnitude of the tunnel current of electrons from the valence band.

When the electric field is relatively weak the p-type semiconductor tips are dielectric tips, because there are no

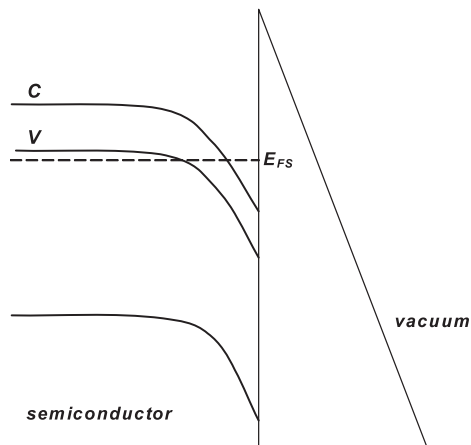


Figure 6. Energy diagram of the p-type semiconductor tip. The bottom of the conduction band and the top and the bottom of the valence band are shown on the left. The external potential barrier is shown on the right.

electrons in the conduction band to tunnel into vacuum. The strong electric field mixtures the conduction and valence band states as it is shown in figure 6. Therefore, the current in vacuum and in thin layer of the p-type semiconductor is carried out by electrons, however, in the bulk of semiconductor crystal this current has hole nature. The change in the peak position as field increases shows the change in the energies of electrons contribute the emission current. With the increasing the electric field, the penetrability of the external potential barrier increases favoring the emission from the lower-energy levels.

The essence of the problem is the fact that electrons, which are in the valence band, do not carry current because the valence band is full. Meantime, all electrons in the valence band may carry the tunnel current through the vacuum–semiconductor interface. The strong electric field is needed to attract electrons to the surface. Their concentration density, calculated as a volume one, accounts for 10^{18} – 10^{20} cm^{-3} , while the magnitude of the electron density in the valence band is 10^{22} – 10^{23} cm^{-3} . The electrons in the conduction band are not giving a high tunnel current by themselves. But this current drives the much higher tunnel current from the valence band to vacuum.

In general, we can conclude, that when the strong electric field is applied to the semiconductor surface equilibrium is established between electrons and holes in the bulk of a p-type semiconductor and electrons and holes, which are in the surface self-consistent quantum well. The energy levels of the valence and conduction bands may have the same energy values if the electric field on the vacuum–semiconductor

interface is strong enough and as a result the change of the electron current to the hole current may be treated as Zener breakdown.

5. Conclusions

The energy distribution for electrons emitted from the GaAs single-crystals of n- and p-type conductivity have been studied for different values of the applied electric field as well as for different surface conditions at the emitting surface. Analysis of the electron energy spectra for the n-GaAs emitter shows that electrons forming the field-emission current originate from the valence band. This means that current carriers in the through cathode–anode system change their energy at the semiconductor–vacuum interface. A physical mechanism that could possibly lead to a relationship $j_v \gg j_c$ for a n-type semiconductor has been proposed. The FEED curves measured for the p-type GaAs show the composite dependence on the applied field which has been discussed.

Acknowledgments

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