Field induced emission mechanism in ITO/glass/ITO system

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Abstract. Results of the field induced electron emission into the vacuum from glass-ITO film system have been presented. Thin Sn-doped In₂O₃ and Sb-doped SnO₂ layers have been deposited onto both surfaces of silica glass by using the constant-current ion sputtering method. The final structure of an emitter consists of a thin ITO film as electron emitting layer, the glass as dielectric and about 10³ nm ITO as the field electrode. When negative voltage is applied to the field electrode, it creates an internal field, which favors electron emission into vacuum. The studies have been carried out in the vacuum of 10⁻⁷ hPa. The mean electric field in the dielectric has been estimated to be 10⁶ V/m and E ≥ 10⁷ V/m in the ITO layer. The investigation showed that in the glass-ITO systems field induced electron emission and photoemission occur and that their yields depend on field intensity of the emitter, the ITO films thickness and the composition of the film. Electron emission occurs when polarizing voltage is applied and/or the film is UV illuminated. The paper presents a phenomenological model which takes into account some possible mechanisms of field induced emission into the vacuum. The model is based on the assumption that regions of enhanced and depleted charge carriers appear both in the semiconductor layer (ITO) and in the glass-ITO interface. The field and UV light induced electron emission phenomena occur in the studied emitters of ITO layers for the field intensity of the range from 1 to 10 MV/m.

1. Introduction
To study vacuum emission of electrons under the influence of an electric field, one uses the semiconductors known as transparent conducting oxides (TCO). These oxides have become widely used in a number of applications [1-3]. The most well-known TCO materials are: a tin-doped indium oxide and an indium-doped tin oxide (ITO). When they are properly doped, they have conductivity sufficient to play a role of an electrode in MIS systems. Moreover, since they show high transparency, it is possible to illuminate the sample and study a transient photoemission effect. Semiconductors under the influence of electric fields show some instabilities. They can occur due to the fluctuation of charge carrier concentration in different points of the volume and due to the instantaneous change of space charge growing exponentially in time and space. The effects are
basis for functioning of many electronic devices showing negative differential resistance [4, 5]. Due to this effect a semiconductor homogeneous at first, becomes electrically heterogeneous, because accumulation and depletion layers are created.

Some results of the study of electric field induced electron emission in the systems based on ITO semiconductors were presented in earlier papers e.g. [6, 7]. In the present paper an attempt to present a qualitative model of electron phenomena occurring on the surface of glass-ITO emitting layers with inner electric field has been undertaken. The system used in the study, which is in fact a polarized capacitor, has been found to be a source of not only ballistic electrons emitted into vacuum, but also (at an appropriate field intensity) a source of electrons from the states below the Fermi level.

2. Experiment part

The sample for the study of the field induced electron emission is a MIS-like structure: field electrode-glass-semiconductor (indium tin oxide). Oxide layers, which are doped: In$_2$O$_3$:Sn or SnO$_2$:Sb (ITO), are deposited onto a glass substrate. The final structure of the samples consists of 10-200 nm ITO as an electron emitting layer, 2·10$^5$ nm glass as a dielectric and about 10$^3$ nm ITO as a field electrode. The ITO layer is deposited on the opposite sides of the glass and shows a conductivity sufficient to play a role of the field electrode, which is polarized by the voltage $U_b$ from 0 do –2kV. In Fig. 1 the distribution of charge after applying $U_b$ voltage is shown.

Deposition of nanocrystalline indium-tin oxide films was performed by reactive dc sputtering technique [8,9]. The sputtered target was an alloy of indium-90% and tin-10% (In$_2$O$_3$:Sn) and tin-93% and antimony-7% (SnO$_2$:Sb). The doped ITO films appear to be wide gap n-type polycrystalline semiconductors with conductivity depending among others on doping concentration. The thinner the ITO film deposited on a glass substrate is, the higher is its resistance (nonhomogenity of the film, the island structure). The resistivity of the layers ranges from 8·10$^{-4}$ $\Omega$cm (200 nm thick) to 2·10$^{-3}$ $\Omega$cm (10 nm thick) [10]. The energy gap was found to be 3.5 to 4 eV wide. The gap was determined by examination of the absorption edge spectrum in UV. At a concentration of about 10$^{25}$ m$^{-3}$ the donor levels split and the semiconductor becomes degenerated. The ITO films on the glass substrate can be assumed to be degenerated when they are sufficiently thick so the influence of the substrate can be neglected. In spite of the fact that the crystalline structure as well as valence band electronic structure of In$_2$O$_3$ are considerably different from that of SnO$_2$, the electrical properties of the materials are known to be very similar to each other. The remaining electrical and optical properties of ITO layers are given in the papers [20-23].
This system might be presented by using the band model which is shown in Fig. 2a, where the structure was assumed to be ideal without surface states and without the applied bias voltage [11,12]. When the sample is polarized, the energy diagram changes, the semiconductor bands near the glass are bent upward and near the vacuum - downward (Fig. 2b).

Fig. 2. Energy band diagrams of MIS system for a) ideal structure without bias, b) structure glass-ITO with bias
$E_c$ - conduction band, $E_v$ - valence band, $E_f$ - Fermi level, $E_g$ - band gap, $E_i$ - middle of band gap, $W_F$ - work function, $\chi$ - electron affinity, $E_d$ - donor level, $U_b$ - bias voltage.

Fig. 3. Experimental arrangement
S – sample, AEE – energy electron analyzer, EM – electron multiplier, $U_a$ – accelerating voltage, $U_b$ – analyzing voltage, HV = 2.9 kV – channeltron’s voltage, $U_b$ – bias system, MPAA – multichannel pulse amplitude analyzer, IBM- computer.
The measurements were performed at the pressure of about $2 \times 10^{-5}$ Pa. The schematic diagram of the apparatus is shown in Fig. 3. The $U_b$ voltage from the range 0 V to -2 kV applied to the field electrode creates an internal field which favors electron emission into vacuum. Appropriate operational conditions for the electron multiplier are received by acceleration of electrons between the emitting film and the multiplier (EM). Electrons accelerated to the energy $eU_b$ create voltage pulses in the multiplier.

These pulses are recorded in the multichannel pulse amplitude analyzer (MPAA) accordingly to their height, and form so-called voltage pulse amplitude spectrum. The amplitude spectra (for various $U_b$) were measured for dark samples and samples illuminated by a quartz lamp.

3. Results

The amplitude spectra were examined for different values of bias voltage and for different thicknesses of ITO films. A plot of the number of pulses recorded during 500 seconds vs. the number of analyzer channel has been made. The height of the pulses in mV is related to the number of the channel. The spectra for selected voltage $U_b$ are shown in Fig.4.

![Fig. 4. Pulse amplitude spectra for different bias voltages.](image)

The pulse frequency $n$ which is a number of pulses recorded during 1 s, can be measured and the dependence of frequency $n$ on the voltage $U_b$ is presented in Fig.5-7. These dependencies successfully illustrate the influence of the voltage $U_b$ on electron emission intensity for ITO films of different thicknesses without UV illumination as well as under illumination.

The dependence $n = f (U_b)$ is also presented in the form of equation. For the unilluminated films 200 nm thick the pulse frequency $n$ is proportional to $U_b^{3/2}$ that resembles the well known Langmuir law for electron current in double electrode lamps, while for the films 100 nm thick $n \sim a \exp (U_b)$, which by analogy resembles intrinsic discharge in diluted gases.
For the thinnest films – 10 nm thick we observe the dependence: $n \sim U_b^5$, in which the high superscript ensures that in this case cascade multiplication of electrons occurs. Illumination of the ITO layers by UV light results in the significant increase in the induced photoemission yield, which is shown in Fig. 5-7.

One can also estimate the emitted electron energy using the method of retarding field. Energy spectrum of electrons can be seen in Fig. 8. From the plot we can see that the maximum of the spectrum corresponds to the small values of energy in the range of about 1 eV, but electrons of energy as high as about 10 eV are also detected.
Fig. 8. Energy distributions of electrons in the field induced electron emission for the sample with 100 nm thick ITO layer, a) $U_b = -500$ V, b) $U_b = -1700$ V.

4. Discussion

The studied system is a capacitor-like structure with a dielectric inside. When the difference of work functions between the system elements is neglected, then the applied voltage $U_b$ is distributed between glass ($U_g$) and semiconductor ($U_i$):

$$U_b = U_g + U_i \quad \text{where} \quad U_g = \frac{Q}{C_g}, \quad U_i = \frac{Q}{C_i}$$  \hspace{1cm} (1)

If we assume the flat band of the semiconductor, then capacitance $C_g$ and $C_i$ per surface unit [F/m$^2$] can be approximately presented:

$$C_g = \frac{\varepsilon_g \varepsilon_0}{d}, \quad C_i = \frac{\varepsilon_i \varepsilon_0}{L_D}, \quad \text{where} \quad L_D = \sqrt{\frac{kT \varepsilon_0 \varepsilon_i}{n_e e^2}}$$  \hspace{1cm} (2)

$L_D$ – Debye screening length, $n_e$ – charge carrier concentration, $e$ – electron charge.

Capacitance $C_i$ is related to the region with space charge in the ITO semiconductor. The value of $C_i$ depends on the depleted region width in the semiconductor layer, thus on the value of the voltage $U_b$. Total system capacitance is a series connection of $C_g$ and $C_i$ capacitances. Assuming: $d = 2 \cdot 10^{-4}$ m (glass thickness), $L_D \leq 2 \cdot 10^{-7}$ m (ITO thickness), $\varepsilon_g = 10$ and $\varepsilon_i < \varepsilon_g$, one can determine from equations (1) and (2), the dependency between the voltage distribution on the dielectric and on the semiconductor layer,

$$C_g = 2 \cdot 10^{-3} C_i \text{ and } U_i = 2 \cdot 10^{-3} U_g$$  \hspace{1cm} (3)

Taking this into account, one can estimate the electric field value in glass and in ITO layer (for instance for $U_b = 1$ kV: $U_g = 998$ V, $U_i = 2$ V):

$$E_g = \frac{U_g}{d} \approx 5 \cdot 10^6 \frac{V}{m}, \quad E_i = \frac{U_i}{L_D} \approx 10^7 \frac{V}{m}$$  \hspace{1cm} (4)

When a semiconductor (ITO layer) is under influence of the external homogeneous electric field, the free charge carriers are forced to change their spatial distribution (Fig. 2). Initially, at a
Moderate voltage $U_b$ applied, a relatively homogeneous polarization in the entire volume of semiconductor occurs without a formation of enhancement and depletion regions. The energy, gained by electrons as a result of these fields, is not larger than about $kT$. That is why the electrons cannot be emitted into vacuum. When the field increases, the energy of electrons accelerated in the field can obtain an energy larger than the thermal one, so $E > kT$. This additional energy can appear to be sufficient for hot electrons to be able to surmount the surface potential barrier [13, 14].

At high voltages of $U_b$ (more than 1 kV) conditions created in the semiconductor correspond to $E >> kT$. It means that in the ITO layer two separate regions are created: depletion at the glass surface and enhancement at the vacuum boundary. The field intensity at this region of ITO is of the order of $10^7$ V/m. With an increase of the field intensity the enhancement layer is narrowed, thus electron concentration is higher: this makes possible the Zener effect as well as the tunnel effect to occur [15]. On the basis of the same processes we can explain the influence of the ITO layer thickness on the dependences $n = f(U_b)$. With the increase of $U_b$ voltage the count frequency grows faster for 10nm thick ITO film than for 200 nm. For the thinner layers it is sufficient to apply lower $U_b$ voltage in order to create the same electric field intensity as in the case of the thicker layers application.

Possibility of electron emission into vacuum can be described by certain mechanisms mainly based on the bulk structural defects. This can be seen in diagram shown in Fig 9. In the ITO materials the main defects are oxygen vacancies and internodes ions of admixtures [16]. The top voids, pores or bulk vacancies can be sources of high local electric fields. These fields can produce avalanche multiplication of the electron stream. The normal emission takes place if electrons from the conduction band achieve energies higher than the mean thermal energy ($kT$). If this excess of energy is higher than the work function (lowered by field), then an electron can be emitted from the material. When a defect is present on a surface, then the field geometry is disturbed and electrons can be easily extracted by the local fields ($F > 10^7$ V/m). These effects dominate at mean values of fields. The similar role is played by the defects localized in the glass-ITO interface. Single defects in the electric field such as oxygen vacancies can form clusters leading to defect channels. The channel can be imagined as a space where electron can be accelerated without a loss of energy. It is possible when the enhancement zone is so thin, that the tunnel effect can occur.

![Fig. 9. Probable mechanisms of field induced electron emission phenomenon.](image)

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According to these assumptions four mechanisms of field induced vacuum emission can be distinguished: a normal emission of high energy electrons, emission from vacancies and surface defects, emission from vacancies and in the bulk defects, emission from full free channels - for instance as a result of avalanche development (Fig. 9).

5. Conclusion
Phenomenological model of field induced electron emission is based on an assumption that two zones are created: enhanced and depleted of charge carriers as a result of polarization in the ITO layer. Due to the field in the depleted zone, electron acceleration to the sufficient high energies is possible. In the enhanced zone, gathering of hot electrons and their emission into vacuum occur. The electron emission can take place both from the surface and from the bulk of ITO layer and also from the ITO-glass interface. The model assumes four main mechanisms concerning vacuum electron emission from the bulk: the normal emission, the surface defects, the bulk defects, the full free channel.

Surface emission is related to electrons from enhanced regions near the vacuum. Bulk emission refers to electrons from depleted regions at the glass surface boundary. Bulk emission demands higher electron energies than surface emission. The value of the field intensity in the glass is $10^7$ V/m, while in ITO layer $E > 10^7$ V/m.

Thin oxide layers deposited on the dielectric substrate show cluster structure with pores, vacancies and channels of a nanometer scale [13, 17-19]. Structures of this kind can create so-called full free channels, where the mean free path is sufficiently long for an electron to gain large energy due to the electric field. In defect channels the avalanche processes can be developed. I conclude that these effects do not create short circuits, which would result in irreversible changes in the samples.

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