

# Quality Control Methods Based on Electromagnetic Field-Matter Interactions

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## 1. Introduction

Field-matter interactions are very attractive for practical applications in contactless and rapid analysis. Here, two types of effects, induced by irradiation of solids with electromagnetic waves, are considered: acoustoelectric effect and surface photo-charge effect (SPCE) together with the possibilities for their application in a large area of quality control activities.

The transverse acoustoelectric voltage (TAV) effect is discussed in details as a typical example of an acoustoelectric effect. Application of TAV for control of semiconductor substrates and devices is considered.

The presented paper offers also a detailed review of our recent studies on SPCE and its possible applications for surface structures visualization, semiconductor characterization, sensors for fluids, composition analysis, food control, etc. The emphasis is put on the nearly universal nature of the SPCE. Experimental approaches and setups for detecting the studied effects are also described as well as the main experimental results, highlighting the advantages and disadvantages of the quality control methods based on TAV and SPCE.

## 2. Acoustoelectric phenomena

The acoustoelectric effect is due to interaction of the quasi-static electric field, induced by the propagation of an acoustic wave in a piezoelectric material, with the charge carriers of the irradiated area. Acoustic wave (volume or surface type), propagating in a solid, produces a mechanical deformation, which, in case of piezoelectric solid, creates an electric field. The surface acoustic waves (SAW's) are more interesting and closer to the subject of this paper.

The next considerations concern SAW propagating along the surface of a piezoelectric material, on top of which, at a distance shorter than the SAW wavelength, a semiconductor plate is placed (Fig. 1). In this case, the interaction between the SAW and the charge carriers is induced by the electric wave, accompanying the acoustic wave, which extends away from the piezoelectric.

Such a structure has several advantages: piezoelectric substrates with a high value of the electro-mechanical coupling coefficient can be used; various semiconductor materials can be pressed against the piezoelectric providing a small mechanical perturbation for the SAW propagation, etc. By using special supports placed parallel to the SAW propagating

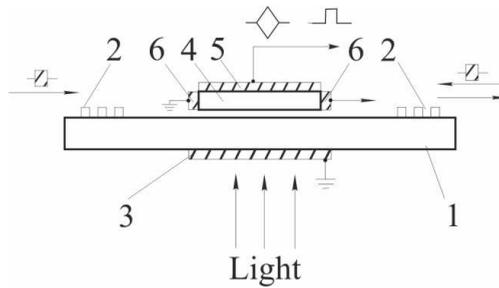


Fig. 1. Testing structure for acoustoelectric interaction: 1 - piezoelectric; 2 - SAW transducer; 3 - bottom electrode; 4 - semiconductor; 5 - top electrode; 6 - electrodes for detection of the longitudinal acoustoelectric effect

direction, the air gap between the semiconductor and the piezoelectric can be controlled and made as small as 50 - 500 nm. For achieving high power and large region for the acoustoelectric interaction, the width of the acoustic path is usually about 2 mm. A metal electrode, usually grounded, is deposited on the bottom surface of the SAW delay line (a piezoelectric with deposited input and output SAW transducers). In combination with the electrodes, deposited on the top surface and/or the front and back sides of the semiconductor, the bottom electrode is used for measurements of the parameters of various acoustoelectric effects. In order to monitor a constant air gap and to use this setup for spectral analysis or device design, the bottom electrode should be optically transparent. A semi-transparent thin gold layer is commonly used for this purpose, but it has some disadvantages. The separated medium structure requires a high-quality polishing of both surfaces as well as a high plane parallelism between them.

Since in a layered structure (Fig. 1) the electric field penetrates away from the piezoelectric structure, an effective interaction between the SAW and the free carriers in a semiconductor, pressed against the piezoelectric surface, is possible. If the semiconductor surface is not homogeneous because of non-uniform distribution of the impurities in the active area, the efficiency of the acoustoelectric interaction will change. This way, information about the processes, taking place on the surface or in the volume, can be obtained.

The studies of such layered piezoelectric-semiconductor structures could be very important for analysis of various physical properties (e.g. non-destructive characterization of the electronic properties of semiconductors) as well for the design of various devices such as converters from optical images into electrical signals, convolvers, acoustoelectric memory - an effect described firstly in [Korshak et al.,1976], etc.

When electric field penetrates into the semiconductor, it leads to a redistribution of the charge carriers and a periodic spatial variation of their density, which, in turn, causes acoustoelectric interaction, i.e. an interaction between the acoustic wave and the electron system of the semiconductor. The field induced by SAW has its longitudinal and transverse components. It should be noted that the acoustoelectric effects cannot be fully understood in the frame of the linear acoustoelectric interaction. The acoustoelectric phenomena, generated by SAW propagation, are due to both linear and non-linear components of the acoustoelectric interaction. The non-linear acoustoelectric interaction can cause acoustoelectric effects of combined frequencies as a result of non-linear interaction between two SAWs. One of the effects provoked by this interaction is the convolution of the two signals. Closely related to the convolved signal is the transverse acoustoelectric voltage.

TAV represents the potential difference across the electrodes 3 and 5 in Fig. 1 induced by the transverse component of the electric field, generated by the SAW. The signal from the convolution of the two signals applied to the SAW transducer 2 is measured on the same electrodes. The voltage induced by the longitudinal component of SAW's electric field could be measured across the electrodes 6. This component is responsible for charge carrier transfer. The experimental results correlate well with the theoretical model, based on the assumption that both polarity and magnitude of the voltage are determined by the carriers trapped in the surface states.

When acoustic power increases, the traps get filled and the surface under the contact charges negatively, so the polarity of the "trapping" TAV is opposite to the one of the "principle" effect. Such simultaneous occurrence of the two types of TAV has been observed for the structure  $\text{LiNbO}_3\text{-Si}$  and in  $\text{CdS}$ . At a certain acoustic power, the sum of the two effects will become zero and further increase of the acoustic power will lead to a sign reversal of the voltage.

The TAV effect provides a large area for investigations. The obtained results on the kinetics and polarity of TAV are contradicting [Kunigelis, 1978; Fritz, 1981]. These problems are discussed and clarified in [Konstantinov, L. et al., 1985; Ermolova, O. et al., 1985; Ivanov, O., 1989] The effects of TAV relaxation versus the rise and fall times of the optical excitation pulse at constant SAW parameters were investigated in [Ivanov & Germanova, 1988].

#### **TAV – application for qualitative semiconductors characterization**

The TAV-based method is considered to be very promising for characterization of the electrical properties of semiconductors. It is contactless, very sensitive and the measuring equipment is relatively simple. In addition, there are no special requirements to the exciting electrode (5 in Fig. 1), deposited on top of the semiconductor. Controlling the penetration depth of the electric field into the crystal is possible by appropriately adjusting the distance between the semiconductor and the piezoelectric according to the Debay length and the SAW wavelength. The method allows rapid comparative qualitative analysis of semiconductor surfaces (the relative distribution of the surface states concentration could be monitored); characterization of semiconductors with high defect density by TAV spectroscopy (the influence of the trapped charges on the transverse acoustoelectric voltage), etc. Because of TAV's high sensitivity, the method can be used for the analysis of samples with high resistivity, which cannot readily be characterized with other methods.

When a radio frequency (RF) pulse is applied to the input transducer of the delay line, a relaxation response is generated in a direction normal to the SAW propagation plane in piezoelectric-semiconductor structure. The amplitude and the relaxation time of this response, as well as their dependence on the duration and the amplitude of SAW pulse depend on the interaction between the wave and the free carriers in the space charge layer, so they can provide information on some surface and volume electronic properties and parameters of the semiconductor. Usually, apart from the interaction with the SAW pulse, optical excitation and/or DC pulses are applied to the semiconductor simultaneously. This allows more dependences to be established experimentally – for example, the dependence of TAV on the wavelength and the intensity of the incident radiation, on the pulse magnitude and polarity, etc. These measurements could provide information about the energy distribution of the recombination centers and traps in the band gap of the semiconductor, their coefficients of trapping and relaxation for the majority and minority carriers, the cross-

section for optical excitation, etc. Some difficulties in the assessment of these characteristics exist due to the complicated nature of the processes involved [Ivanov, 1989].

Concerning experimental difficulties, it has to be noted that the amplifier used for the TAV measurements should have high input impedance, providing conditions, similar to those of an open circuit. Most probably, a lot of the published results were obtained when an amplifier with inappropriate input parameters had been used, so spurious circuit effects were added to the effective relaxation processes in the structure or even dominated in the output signal. It causes some doubt in the reliability of some of the experimental data, reported in the literature. Another problem is that the kinetics of the transverse acoustoelectric effect was not profoundly studied, although it may contribute significantly to the explanation of the charge trapping effect and the determination of the trap parameters.

There are some improvements in the measured structure which could be introduced. It was established [Borissov et al., 1985] that the use of a transparent conductive layer of  $\text{SnO}_2$  as a bottom electrode in the structure presented in Fig. 1 has a number of advantages and is of crucial importance for the studies of acoustoelectric interactions and for the registration of the spectral dependences.

In spite of the difficulties discussed above, the possibilities for many practical applications of the TAV-based method for semiconductor characterization are indisputable, which was confirmed by the experiments described below.

A TAV-effect-based new method for a rapid analysis of semiconductor surfaces was developed [Strashilov et al., 1987; Ivanov, 1989] which includes scanning of the studied surface with a narrow beam of monochromatic light and detection of the generated TAV signal. The analysis was qualitative and comparative, i.e. only the relative distribution of the surface states' concentration could be monitored. Fig. 2 shows a TAV amplitude profile, obtained by scanning the surface of a n-type Si plate (specific resistance of  $10^3 \Omega\cdot\text{cm}$ ), in the middle of which a circular region with p-type conductivity was created. The location of the p-zone is clearly observed in both horizontal and vertical directions.

The influence of the trapped charges on the TAV at the Si-  $\text{SiO}_2$  interface has been investigated in order to extend the application of TAV spectroscopy for characterization of semiconductors with high defect density. The effect of compression on the electronic state was investigated and a pressure threshold was observed, above which the TAV magnitude decreases and a relevant number of stress-induced traps are created on the Si -  $\text{SiO}_2$  interface. This threshold determines the values of the applied voltage for non-destructive measurements - they should be below the threshold.

Since the TAV-based method is very sensitive, it can be used for the analysis of samples with high resistivity, which cannot readily be characterized with other methods. An example for this application is the characterization of the interface of high-resistivity ZnSe-GaAs heterostructure by single and double TAV spectroscopy. The method is used for studying of the interface band and the impurity transitions of the heterostructure at room temperature. From the TAV spectrum, a conduction band offset of 0.059 eV has been determined.

The TAV effect could be applied for modification and analysis of semiconductor surfaces with specific properties via acoustic wave stimulated absorption - an application of great interest. The contactless control provides conditions for continuous monitoring and/or in-time termination of the process.

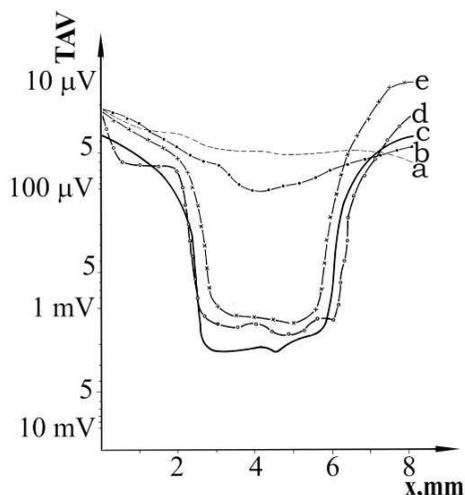


Fig. 2. Variations of TAV amplitude on laser beam scanning of the surface of a p-type area in a n-type Si plate. Curves (a - e) correspond to a laser beam shift of 1 mm in vertical direction

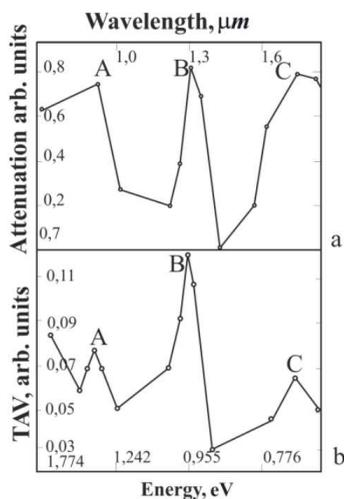


Fig. 3. Spectral dependence of the SAW attenuation (a) and the TAV amplitude (b)

A number of works are devoted to the spectral dependence of the TAV effect. Such measurements could provide information about the surface conductivity spectrum as well. The peaks in the surface photo-conductivity spectrum could be attributed to optically-induced electron transitions which were also registered by other methods. These peaks can also be used to derive the value of the band gap energy as a function of the temperature. In cases requiring more detailed information, simultaneously obtained spectral dependences characteristic for several acoustoelectric effects could be used. Such experiments are performed for CdS samples where the dependences of the SAW attenuation coefficient, the

convolution signal and the transverse acoustoelectric voltage on the wavelength of the incident light are studied. An interesting feature is the peak at 480 nm wavelength (2.6 eV), which was assigned to the intrinsic absorption edge of the material and gives the band gap energy. The experiment showed that the transverse effect is more sensitive than the SAW attenuation and the convolution signal.

The relaxation of the transverse acoustoelectric effect was studied in a number of papers as a prospective technique for characterization of semiconductor properties. A combination of relaxation dependences and spectral investigations has been also used since it provides some additional possibilities for analysis. It is established that the incident light wavelength strongly influences the transverse effect and causes SAW attenuation ( $\alpha$ ). The positions of the characteristic minima in the spectral dependences of the relaxation time and the peak positions in the  $\alpha$ -dependences coincide.

A plot of the TAV amplitude for an epitaxial layer of GaAs as a function of the wavelength of the incident light as well as the spectrum of the SAW attenuation due to acoustoelectric interaction are presented in Fig. 3. The two spectra exhibit many identical features, which is an evidence for the common physical nature of their origin. Some differences which could be seen are due to the different impact of the semiconductor parameters on the two effects. The peaks in these spectra are also attributed to optical excitation: band-to-band electron transitions (peak A) and surface levels-to-conduction band electron transitions (peaks B, C). The TAV technique is applied for determining the band gap energy as well as the energies of the impurity level transitions in a GaAs layer (1.4  $\mu\text{m}$  thick), deposited on a vicinal Si (100) substrate by molecular beam epitaxy. It is shown that they are slightly lower compared to the bulk GaAs. This might be attributed to the influence of the residual strain on the band structure of GaAs, deposited on Si. It was also pointed out that at low temperatures the dependence of the TAV on bias voltage considerably changes.

The investigation of the transverse acoustoelectric effect is a fascinating field in solid state physics [Ivanov, O., 1989]. A complete solution of the aforementioned problems and the establishment of the exact relationships between the amplitude and the kinetics of the transverse effect and the semiconductor parameters will extend the field of its applications.

### 3. Surface Photo-Charge Effect

A new type of electromagnetic field-matter interaction effect was observed during our studies on the TAV effect. It was established that when the sample 4 from Fig. 1 was illuminated with modulated light, an alternating voltage was generated across the electrodes 3 and 5 in absence of acoustic wave when the sample is a metal one. Russian and American scientists took part in this study as well. The wavelength of the radiation was selected appropriately to exclude the contribution of the external photoelectric effect. It was observed later that the effect takes place under exposure of each solid to light and RF radiation. The next part will be completely devoted to our own studies in this field.

The SPCE represents generation of an alternating voltage when a solid interacts with a modulated electromagnetic field. The voltage frequency is equal to that of the incident radiation. The potential electric difference between the irradiated sample and the common ground of the system is measured experimentally. The SPCE is a very fast effect: for example, an irradiation with 20 ns laser pulse results in a signal response which reproduces precisely the waveform of the incident pulse [Pustovoi et al., 1989a]. The rapidity of SPCE is

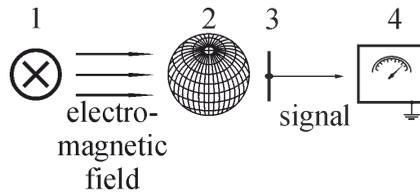


Fig. 4. A general scheme of the SPCE observation: 1- electromagnetic field source, 2 - irradiated solid, 3 - signal-measuring electrode, 4 - measuring device

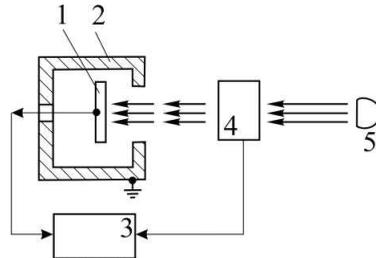


Fig. 5. Experimental setup: 1-specimen, 2-screen, 3-measuring device, 4-modulator, 5-light source

of great importance for many practical applications. The SPCE-based interaction takes place between arbitrary source of electromagnetic radiation and any solid. Unlike the case of acoustoelectric interactions where the presence of a piezoelectric layer or crystal is required, the excitation of SPCE does not need additional structures or elements on the sample. A basic scheme for observation of the SPCE is presented in Fig. 4.

Possible mechanisms causing SPCE are proposed and analyzed, but they could not be considered complete or determinative.

As the experiments have shown, the arising of a signal from a solid after electromagnetic irradiation is a universal feature of solids. SPCE has been registered in the frequency range 1Hz-1Gz, infrared, visible and the beginning of ultraviolet. Our hypothesis is that the effect exists in the whole frequency range of the electromagnetic radiation. SPCE can be induced only by modulated incident radiation. The lack of response upon non-modulated field is evidence that the detected signal is induced by the SCPE.

An important feature of the SPCE is the dependence of the signal created by it on the specific characteristics of the irradiated object. This creates numerous opportunities for fast and contactless analysis of solids, liquids and gases.

### 3.1 SPCE in conductors and semiconductors

It is well known that under appropriate energy of the photons, optical radiation, incident on the surface of a conductor, may lead to emission of electrons. The theory of the photoelectric effect in metals was developed by Tamm [Tamm, 1975]. According to the theory, the simultaneous conservation of the energy and the momentum of free electrons is impossible, thus the photoelectric effect is due solely to the presence of a sharp non-uniformity on the conductor surface leading to an exponential decay of the wave functions of the electrons. Since in the near-surface region of a conductor the distribution of charges is non-uniform, a so-called double layer is formed on the conductor-vacuum interface. This layer is mainly

responsible for the photoelectric effect in metals. The electrostatic field of this layer repels the free charges away from the surface.

In the case of SPCE, the incident radiation creates a force acting on the medium. The magnitude of that force in the simplest case is proportional to the gradient of the permittivity. This force causes a redistribution of the electrons near the surface of the conductor and a corresponding change in the electrostatic potential of the double layer, i.e. the incident radiation induces a macroscopic dipole momentum on the surface of an isolated conductor. If the conductor is electrically connected to another solid conductor with a zero potential for a certain period of time, determined by the time constant of the system, an electric current will flow between the conductors until a new stationary distribution of the surface charges and potentials is established [Pustovoit et al., 1989b]. This charge flow or the macroscopic polarization of the conductor, induced by illumination, can be experimentally measured. The change of the double layer's potential depends on both the surface features and the intensity of the incident radiation, being proportional to the intensity or to the square root of the intensity when the latter is low or high respectively.

The SPCE in conductors was studied in details [Pustovoit et al., 1989; Pustovoit & Ivanov, 1989]. A large number of various conductors and semiconductors: metals Zn, Cd, Al, Pb, Mg, Au, Cu and copper alloys, etc., semiconductors: Si, GaAs, GaP, ferrites and ceramic superconducting materials were experimentally investigated. A good qualitative agreement between the experimental data and the theoretical predictions was observed. It was established that the amplitude of the voltage varied from sample to sample, i.e. it depends on the composition and some other parameters of the material under study. The dependence of the voltage amplitude on the modulation frequency of the incident radiation was studied, as well as the generated voltage as a function of the intensity of the incident radiation. Dependence of the SPCE on the incident angle or the polarization of the radiation was investigated but not observed. It was established that in some cases, the history of the sample (e.g. previous illumination) affects the SPCE.

A scheme of the experimental setup for SPCE studies in conductors is shown in Fig. 5. The illuminated sample 1 is placed on a grounded shield 2 and is illuminated by the light from source 5, amplitude-modulated by mechanical modulator 4. The voltage due to the surface photo-charge effect is registered by device 3, synchronized with the modulator 4. Both a voltmeter (selective or phase-sensitive) and an oscilloscope were used as detectors. A measuring device with high input impedance (100 M $\Omega$ ) was used. At high intensity of the incident radiation and a strong SPCE (for example in Si plates), the input impedance of the detector could be lower at some measurements.

It should be pointed out that the measurements are contactless, i.e. there is no need of special electrodes or even a physical contact between the conductor under study and the exciting electrode. The measured signal was registered due to the mutual electrostatic induction with an electrode, placed in a close proximity.

The logarithmic dependence of the SPCE voltage on the laser beam intensity at  $\lambda=633$  nm for Cu samples is shown in Fig. 6, when the output laser power was varied in the range 50  $\mu$ W - 17 mW. The signal was proportional to the intensity  $I^\alpha$ . Such a relationship was also obtained for a Cu sample of the same dimensions, but with the output laser power varying in the range (3- 400) mW at  $\lambda=514.5$  nm. [Pustovoit et al., 1989]. At low laser intensities,  $\alpha$  is about 0.8. As the intensity increases, the value of  $\alpha$  approximates 0.5. Similar results were derived for various metals (Al, Pb, Au, Cd, Mg) and semiconductors (Si and GaAs).

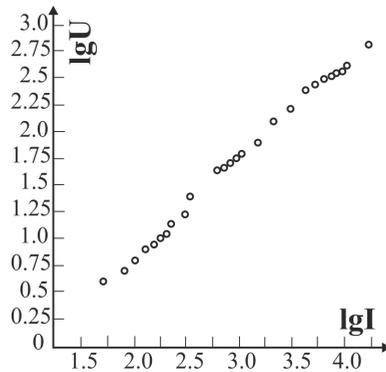


Fig. 6. Dependence of the SPCE signal on the optical irradiation intensity for a copper plate

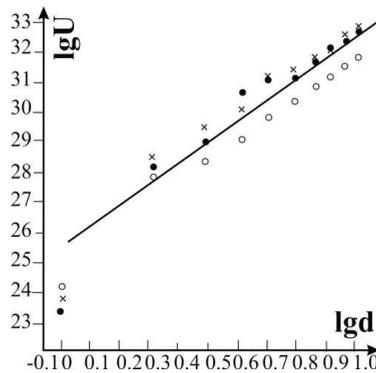


Fig. 7. Dependence of the SPCE signal on the diameter of the irradiated area for three different measurements under the same conditions

In some cases the SPCE signal significantly depends on the area of the illuminated spot. An example is shown in Fig. 7 for a Cu sample exposed to light with wavelength  $\lambda=633$  nm.

When the illuminated solid is a semiconductor, the incident light can induce generation of carriers, provided that the photon energy is higher than a certain value (higher than the bandgap energy in case of electron hole generation due to band-to-band excitation, for example). High intensities could cause a high electron hole density.

As in the case of conductors, the SPCE in semiconductors is also due to the interaction of incident radiation with the free carriers in the medium, but the voltage induced by incident photons of arbitrary energy is due to the redistribution of charges already accumulated in the near-surface region. According to some theories, the photo-conductivity and the photo-voltage effect are the main contributors to the SPCE in semiconductors [Ivanov et al., 1995a]. The voltage change of the surface due to charge redistribution is measured capacitively, so there is no net charge current across the sample. Thus, the photo-induced charge is restricted within the space charge region of the semiconductor sample, resulting in total charge redistribution, compensated by potential variation within the semiconductor space charge region. In equilibrium, the optical generation of free charge carriers is balanced by recombination at the surface and by diffusion in the bulk.

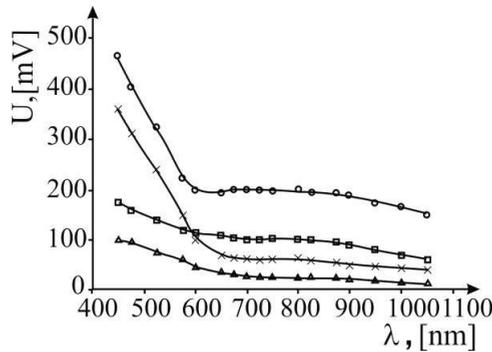


Fig. 8. SPCE spectral dependences for copper - O, lead - x, gold -  $\Delta$ , brass

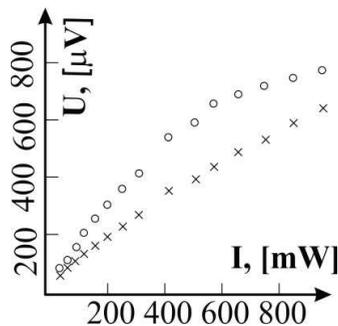


Fig. 9. SPCE signal amplitude as a function of incident light intensity for pegmatite (x) and Teflon (o)

Experimental investigations of the SPCE in a large number of various conductors were reported also in [Vankova et al., 1997]. A generation of voltage at illumination with non-monochromatic light was detected in all measured samples. The amplitude of the voltage varied from sample to sample, i.e. it depends on the composition of the material under study.

Another series of studies on spectral dependences of the SPCE at conducting surfaces was performed as well which proved that the SPCE and the external photoelectric effect in metals are two different phenomena. The SPCE spectral dependencies for Cu, Pb, Au and brass in the range 400-1100 nm were studied [Ivanov et al., 2000]. They are shown in Fig. 8. A strong decrease of the voltage at  $\lambda \sim 600$  nm is observed which is probably due to the cut-off of the external photoelectric effect. At larger wavelengths ( $\lambda > 600$  nm), the voltage is approximately constant; since in this spectral region the external photoelectric effect does not contribute to the signal, the response is determined by the surface photo-charge effect and thus both effects are separated. It is clear that the SPCE contributes to the signal at  $\lambda < 600$  nm as well, but it is screened by the much stronger external photoelectric effect. The existence of signals in the beginning of the infrared region is another indicator that the effect observed is not the external photo-effect.

The spectral dependence of the surface photo-charge effect for a photoelement in the range 450-3200 nm was also measured. A sharp decrease of the signal was observed between 450

and 700-800 nm. At  $\lambda > 800$  nm, the signal remained nearly constant up to 3200 nm. This dependence was similar to the one shown in Fig. 8.

The results discussed above show that a clear distinction between the SPCE and the well-known external photoelectric effect in metals exists and the two effects can be separated.

### 3.2 SPCE in dielectrics

The SPCE was induced in all studied dielectric samples [Ivanov et al., 1994; Ivanov et al., 1995a] when they were exposed to amplitude-modulated non-monochromatic or, in some cases, to He-Ne laser light in the visible region. Since the irradiated structure had very high output impedance, as in the case of conductors, a measuring device with high input impedance was required. For avoiding voltage generation due to the illumination of the measuring electrode itself, it was wrapped in black photographic paper.

It was established that the generated SPCE voltage depends on the type of the illuminated material. Figure 9 shows the voltage amplitude as a function of the intensity of the incident light beam for two dielectric samples: Teflon and pegmatite. The influence of the sample thickness on the voltage amplitude was also investigated for different dielectric materials. The samples thickness varied in the range 3–30 mm. It was observed that the SPCE signal sharply decreases with increase of the thickness up to 10 mm. Further increase of the thickness makes the signal diminish more gradually.

Since most of the measured materials were good thermal insulators, it is very unlikely that the generated voltage is due to thermal electromagnetic field, induced by heating of the measuring electrode. Besides, in some cases, the measured signal from the sample was considerably stronger than that obtained at direct illumination of the electrode.

Possible reason for the appearance of potential difference, generated in dielectric samples, could be the presence of dipole molecules on the dielectric surface, caused by absorption or other phenomena. The force created by the incident light is proportional to the gradient of the electrical permittivity of the medium, as in conductors, and leads to redistribution of the absorbing molecules along the surface of the dielectric. As a result, the latter becomes electrically charged [Ivanov et al., 1994].

It is quite possible that the mechanism of the SPCE differs for various types of materials, but nevertheless it should be emphasized that the effect can be induced in any solid upon illumination.

### 3.3 Megahertz excitation of the SPCE

When the frequency range of the SPCE exciting signal varied from 1 Hz to 1 GHz a response signal was observed after taking all necessary precautions to avoid spurious circuit effects. A large number of practically all types of solid samples with suitable dimensions were subjected to irradiation and SPCE was induced in each one of them. The results for some of them are presented in Table 1.

No amplitude modulation was applied. The amplitude of the generated voltage was different for each sample. Stronger SPCE signal was observed for conductive samples. The phase of the signal also varies from sample to sample.

It was also observed that a slight change in the sample position leads to a considerable change of the generated voltage. For more precise quantitative measurements a special holder, firmly fixing the sample, should be designed.

A systematical study of the SPCE was performed with incident radiation frequencies in the spectral range up to 1000 MHz. The tested materials were textolite, Si, poly-oxy-ethylene, glass, cardboard and quartz. For all the samples, the SPCE voltage was generated in the whole measured range. The fact that the SPCE can be induced by irradiation with electromagnetic field with frequency up to 1 GHz, and in the visible and nearby spectral range, led to the hypothesis that SPCE exists in the whole frequency range of the electromagnetic waves since it is very unlikely that there is an "interruption" in any spectral range.

Material	Size, mm	Signal, mv	Irradiating voltage $U_{pp}$ , V
Silicon	0,48X20X70	5	0,15
Copper	0,9X15X70	6,8	0,15
Molybdenum	0,6X20X68	5,7	0,15
Piezoceramics	2,1X16X65	3,6	0,15
Potato (freshly cut sample)	2,7X20X70	8,4	4
Cardboard	1,4X20X70	4,5	40
Walnut (wood)	0,7X20X70	1,4	40
Oak (wood)	0,5X20X70	1,6	40
Teflon	2,3X20X70	1,6	40
Epoxy	1,5X20X70	3,8	40
Glass	2,4X20X70	8,6	40
Textolite	1,6X20X70	2,8	40
Quartz	1X20X70	1,4	40
Teflon	2,3X20X70	0,8	40
Poly-oxy-ethylene	2,4X20X70	3	40
Plexiglass	19X20X70	1,4	40

Table 1. SPCE signal values for some materials at incident radiation frequency of 141 kHz

Another group of experiments was performed on the relationship between the amplitude of the signal and the thickness and width of samples of the same composition. They showed that the amplitude of the signal grows with increase of the sample's thickness and width, i.e. the amplitude grows with the increase of the irradiated volume. An equation describing the relationship between the volume of the irradiated object and the generated voltage would be of great interest.

The temperature dependence of the voltage amplitude was studied for a poly-oxy-ethylene sample in the range from room temperature to 90°C. This material has a first order phase transition at 72°C. Initially, there was a slow signal increase with the temperature rise, followed by a sharp increase as the temperature reached ~70°C. This way the possibility to establish a first-order phase transition in this material by following the temperature dependence of the SPCE voltage amplitude was demonstrated as well as the fact that the SPCE signal amplitude depends not only on the composition and the volume of the irradiated material, but also on the processes taking place within the bulk of the investigated object.

A distinctive feature of the SPCE, induced by radiation in the MHz frequency range, is that no amplitude modulation of the incident electromagnetic field was required contrary to the

visible range case. Up to now, SPCE has not been registered at illumination with non-modulated light. The experiments in the MHz range showed that in fact, an alternating voltage with frequency equal to the one of the incident radiation was generated. However, there are no electronic devices for signals with frequency in the range of  $10^{15}$  -  $10^{13}$  Hz. The amplitude modulation of the incident light enables the measurement of the low-frequency envelope of the signal.

The explanation of the SPCE will probably require new ideas. Density functional theory (DFT) including external electromagnetic fields effects is one of the possible approaches considered at present for the description of SPCE physical mechanisms.

Summarizing all experimental results on the SPCE described above, it could be concluded that the effect takes place in all solids under irradiation with electromagnetic field in the whole spectral region. The frequency of the generated potential difference coincides with the frequency of the incident electromagnetic wave. The amplitude of the SPCE voltage depends on the specific parameters of the irradiated solid. The process is very fast and allows contactless measurements from a distance.

#### **4. Practical applications of SPCE**

As discussed above, the SPCE is an inherent feature of all solids, subjected to irradiation with electromagnetic fields with frequency in various spectral ranges. The specific features of the SPCE are a prerequisite for many attractive applications including quality control.

##### **4.1 Visualization of surface structures**

Since the SPCE is sensitive to the specific features of the illuminated surface, various structures (mechanical structures, irregularities, defects, impurities, ion-implanted regions, etc.), formed on the surface of each solid, can be visually observed on a monitor. For a better resolution, the intensity and the wavelength of the incident radiation should be selected carefully in each particular case, for obtaining a maximal change in the measured SPCE voltage at a minimal variation of the parameter under study. A depth profile of the distribution of a certain structure can also be obtained by varying the wavelength of the incident laser beam.

An automated system for measurement of the surface density of current carriers and the electrical permittivity of conducting materials was developed [Ivanov et al., 1995b]. It could be used for analysis of the electron topography of conducting surfaces (semiconductors, metals, ferrites or conducting ceramics). The sample (together with an appropriate support) is mounted on a small positioning stage providing X-Y motion in its own plane by two computer-controlled electric motors. It allows the illumination spots to be positioned and the whole surface of the studied sample to be scanned. The phase and the amplitude of the generated voltage depend on the surface properties at the illuminated spot. The sample is scanned by a normally incident pulse-modulated He-Ne laser beam with 40  $\mu\text{m}$  diameter of the focal spot. The scanning area is 30x30 mm with a step of 10  $\mu\text{m}$ . The size of the scanning area and the scanning step could be easily improved by using more precise optical stage and finer step motors. The voltage difference arising in result of irradiation of the sample is measured by a selective voltmeter synchronized to the chopper frequency. The measured signal is applied to an analog-digital converter and to the computer, which drives the step motors for X- and Y-translations. The signal may be taken from an electrode placed near the

scanned sample, but not directly connected to it. All measured data and graphics go to the computer memory. A computer program processes the data. The results are presented as a three-dimensional plot. The amplitude of the SPCE voltage is plotted along the Z-axis, normally to the surface.

The main problem of such setup is that the system producing the signal has a high-impedance output, so the measuring device must have high input impedance. With illuminating power of 1W, the signal from metals, ceramics and ferrites is about some microvolts, for semiconductors the signal is stronger and could reach some millivolts at much lower irradiation intensities.

The described system possesses high flexibility since it can be applied for investigations of all kinds of conducting surfaces. It was found out that besides the amplitude, the signal phase also changes, as a function of the surface condition. This is going to be used to derive additional information by measuring simultaneously the phase and the amplitude of the signal. Also, it is intended to extend the automation of the system by adding computer control of the illuminating beam wavelength. Since the penetration of the light in depth varies with the wavelength, this will be equivalent to a depth scan. The results will enable the application of the described device for identification of any solid surface. Such a device can be used as a microscope as well, because the minimal area of the observed region is determined only by the diameter of the laser beam and the scanning step. The analysis is quite fast, no complex equipment is required and no metal contact has to be deposited on the sample. The combination of all these advantages makes such a device very interesting.

The results from the investigation of GaP sample with sulphur impurities with a specific resistivity of  $10^{-1}$   $\Omega\cdot\text{cm}$  are shown in Fig. 10. The tested plate was a round wafer with a diameter  $d=43$  mm, cut perpendicularly to the growth axis of the crystal. A part of the crystal surface with dimensions  $21\times 29$  mm, including the central area, was scanned with a step of 1 mm by laser beam (wavelength 633 nm, focal spot 50  $\mu\text{m}$ , modulation frequency 170 Hz, intensity 1.8 mW). It was known that an accumulation of impurities exists in the central region of the plate, which is recognized from the sharp increase in the SPCE voltage on the 3D plot in Fig. 10.

The dependence of the SPCE voltage on the surface properties was also studied in a Si plate, implanted with boron ions [Pustovoit et al., 1989a]. The dependence, shown in Fig. 11 reveals that the signal depends dramatically on the surface properties – it describes precisely the form of the implanted region.

A Si plate with specific resistivity of 50  $\Omega\cdot\text{cm}$  and dimensions  $12\times 12\times 0.35$  mm was also studied. He-Ne laser beam with  $\lambda=633$  nm was used for illumination. The diameter of the illuminated spot on the surface of the plate was 40  $\mu\text{m}$ . There was a 2.5 mm wide mechanical scratch within the central region of the plate. A 4 mm wide area, including the scratch, was scanned. The results, presented in Fig. 12 (a), reveal once again that the amplitude of the SPCE voltage significantly depends on the surface features. It should be pointed out that the phase of the signal was different for the smooth and the scratched surface.

An interesting fact was observed during the measurements: the contrast of the 3D pattern response depends substantially (inversely proportional) on the intensity of the laser beam (Fig. 12 (b) and (c)). This was confirmed by a series of experiments with various values of the laser beam intensity.

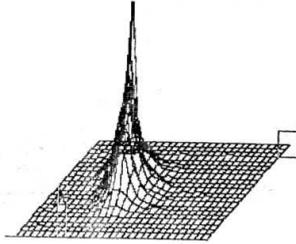


Fig. 10. Scan of a GaP plate

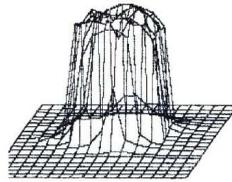


Fig. 11. A silicon plate zone pattern for a:  $\lambda=633$  nm, light spot diameter 100  $\mu$ m

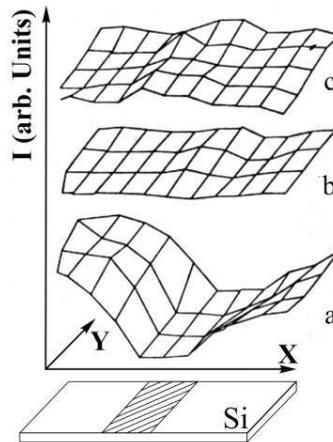


Fig. 12. Response distribution for a silicon plate. The scanned area along the x-axis is ca. 4 mm and the width of the scratched (hatched) area is ca. 2.5 mm; laser beam intensity: a- 30 $\mu$ W, b-300 $\mu$ W, c-700 $\mu$ W

The experiments described above showed that an optical contactless method based on the SPCE can extensively be used for approximate analysis of the surface topology. Besides, such a method is universal since it can be applied to characterize any kind of surfaces.

#### 4.2 Contactless characterization of semiconductors

Different methods have been used for investigation of defect states at semiconductor surfaces and interfaces [Berglund, 1966; Lang, 1974; White, et al., 1976; Hurtes et al., 1978, Balland et al., 1986, Tapiero et al., 1988].

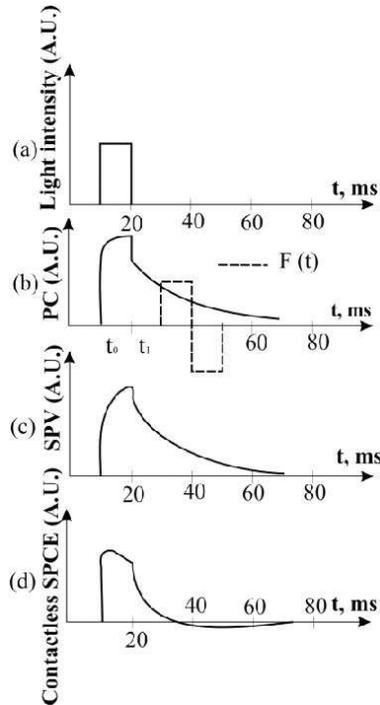


Fig. 13. Time dependence of the exciting light intensity (a); rise and decay transients of PC (b), SPV (c); and contactless SPCE (d) in the GaAs single crystal at 300 K

The SPCE temperature and spectral dependences provide information about the surface electron states and could be used for characterization of semiconductors. This technique is, to a large extent, similar to the contactless TAV technique for semiconductor characterization. In the SPCE-based method, the energy and the relative density of the trap levels can be estimated from the derivative of the SPCE voltage dependence on the energy of the incident photons.

The SPCE and the photo-current (PC) induced by excitation with short light pulses with high intensity and wavelength in the spectral range of the semiconductor's intrinsic absorption were studied for GaAs [Davydov et al., 1994]. No direct electric contact to the sample is necessary for the registration of the deep level (DL) spectrum, provided that a double pulse integrator (lock-in, double-boxcar) and a computer convolution of the SPCE transients are applied. This spectrum can be received in a wide temperature range. If the crystal surface is scanned with a light beam at a temperature corresponding to a maximum in the DL spectrum, this procedure may be applied for contactless determination of the DL density distribution profile along the scanning direction.

Figure 13 illustrates the PC transient (b), the SPV (surface photo-voltage) transient for a crystal with ohmic contact (c) and the SPCE transient for a crystal without any electrodes (d) at a temperature of 300 K. Three regions in the PC transients are observed: 1) a rapid rise to a stationary state (the generation of non-equilibrium carriers is balanced by recombination and trapping); 2) a rapid decay (recombination of free carriers); 3) a slow relaxation (recombination of trapped carriers, thermally released into the semiconductor's bands).

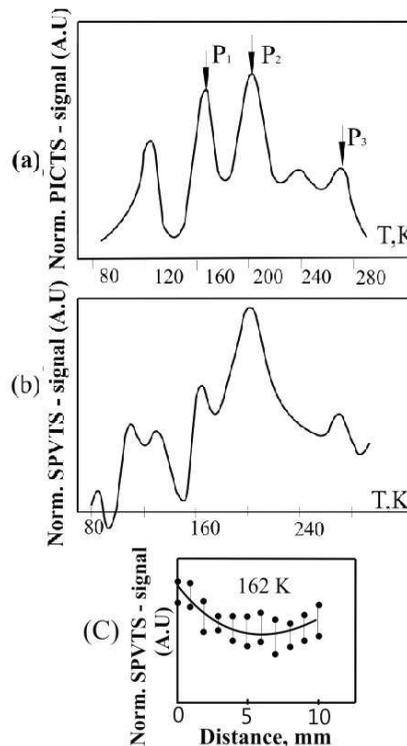


Fig. 14. DL spectra in GaAs single crystal, derived from the PC (a) and SPCE transients (b), linear distribution of P1-deep level density (c)

In order to obtain the DL spectrum of a GaAs crystal, the PC, SPV and SPCE transients were registered in the temperature interval 77–300 K and the data were stored in a computer. The slow relaxation range of each transient was found. The thermal emission from the traps to the semiconductor bands, determined by the charge carriers, was obtained and a correlation procedure was applied for the numerical analysis.

Some of the mathematical considerations used for data processing of the Photo-Induced Current Spectroscopy (PICTS) were applied to the temperature dependence of the SPCE decay transient, which allowed contactless obtaining of information on defects and impurities present in the semiconductor [Davidov et al., 1994]. The results are similar to the ones derived from the DL spectrum and the spatial distribution of the DL density along the semiconductor surface can also be obtained.

Figure 14 displays the PICTS spectrum (a) and the DL spectrum derived from the SPCE relaxation transients (b) for GaAs sample. The latter spectrum is considered as a surface photo-voltage transient spectrum (SPVTS). The comparison of these spectra shows that the same DL (P1, P2, P3) dominate markedly the PC decay transients and the SPCE relaxation transients in the same temperature intervals. The considerable differences in the depicted spectra (both in the relative intensities of the DL bands and in the disappearance of one and appearance of another DL) could be related to strong trapping into surface electronic states that reflected in the SPVTS spectrum.

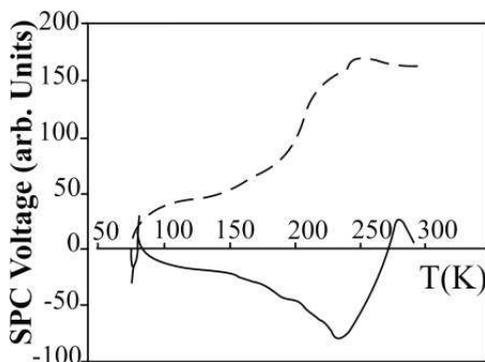


Fig. 15. SPCE voltage temperature dependencies at 633 nm (dashed line) and 488 nm (solid line)

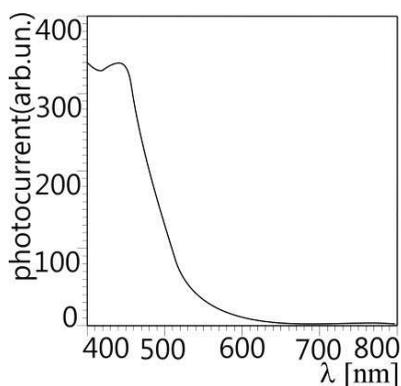


Fig. 16. Spectral dependence of the DC photo-current normalized to a constant light intensity

However, the PICTS spectrum significantly depends also on the depth of the light-excited semiconductor layer. The latter is determined by the light absorption depth and the diffusion length of the charge carriers. Obviously, such dependence may be attributed to a non-uniform DL distribution along the crystal depth.

To demonstrate the contactless SPVTS method, the surface of a GaAs crystal was scanned in order to investigate the P1 - DL density distribution profile along the scanning direction. The P1 centre parameters were not determined from the SPVTS data, since no relevant mathematical procedure exists at present. The variations of the SPVTS signal (Fig. 14 c) registered during a crystal surface scan at 162 K (P1 band maximum in the DL spectra) indicate a V-shaped distribution of the P1 - DL density. This is in agreement with the results obtained by PICTS in a sandwich-structured Ge(Au)-GaAs-Ge(Au). GaAs samples passivated with a thin ZnSe film of variable thickness were also investigated by SPCE [Abbate et al., 1995].

The temperature dependence of the magnitude and polarity of the surface photo-charge effect in CdS was experimentally studied for optical excitation in both the subbandgap and the intrinsic absorption spectral range [Ivanov & Konstantinov, 1999]. CdS single crystals

with high dark resistivity (about 10 G $\Omega$ ) and prismatic “real” surface were studied. The dimensions of the samples were 2 cm x 1 cm x 0.5 mm. The samples were illuminated by an Ar-ion or He-Ne laser beam (laser power of  $\sim 5$  mW/cm<sup>2</sup>), mechanically chopped at 183 Hz. The results are shown in Fig. 15.

The spectral dependences of the measured DC photo-current for the same samples are presented in Fig. 16. The experiments were conducted at  $\lambda=488$  nm and  $\lambda=633$  nm, because the photon energy at 488 nm is higher, while at  $\lambda=633$  nm it is smaller than the CdS bandgap ( $\sim 2.41$  eV). Excitation of electrons from the valence to the conduction band via direct band-to-band transitions is induced and, in result, the concentration of free electrons increases. This leads to a significant increase in the photo-conductivity in this spectral range. As a consequence, a negative SPCE voltage is generated at low temperatures. The magnitude of the voltage increases with the temperature (T) rise.

An example for characterization of semiconductor devices was reported in [Das et al., 1992]. In particular, MOS devices on Si were experimentally studied. The depletion, accumulation and inversion regions of the device were clearly distinguished. These curves can be used for characterization in a similar manner as the CV plots.

### 4.3 Sensors for fluids

It was observed that any variations in the fluid characteristics induce a corresponding change in the electron properties of the irradiated solid-liquid interface, and in result - a change in the registered SPCE signal. Therefore, provided that all other conditions remain constant, changes in fluid properties can be detected. A sketch of a setup for such measurements is presented in Fig. 17 [Ivanov & Konstantinov, 2000].

The illuminated substrate 1 should be very sensitive to SPCE (e.g. a semiconductor) for a higher voltage to be generated. The exposing radiation could be non-monochromatic or monochromatic, the latter being preferred. Since the sensitivity of the SPCE depends on both the type of the surface states at the interface 2 and the changes taking place in the studied fluid 3, appropriate wavelength, providing optimal response, should be used. The SPCE voltage is measured on the electrode 4, coupled to suitable equipment. In the case of gas or vapour sensors, a solid with maximal adsorption capacity to the respective fluid should be used as a substrate.

It should be noted that to achieve a reliable result, it is necessary to select carefully many parameters: the type of the structure that generates the signal, the wavelength and intensity of the incident radiation, the parameter of the electrical signal which has to be measured, the material of the irradiated surface, the method for signal registration, the measurement conditions, the additional influences, etc. There are many parameters that need to be optimized. The goal is a minimal change in the controlled variable to cause maximum changes in the measured electrical signal. When it is once made for a specific task, all experimental conditions should be kept constant.

Since the surface states are very sensitive to charge redistribution upon illumination, high sensitivity can be achieved in a certain spectral range. SPCE can be induced in any solid and therefore, a suitable solid together with an appropriate spectral range of the incident radiation can be assigned to any fluid in order to avoid undesirable effects as hysteresis, slow relaxation, etc.

Ar-ion laser with a power of 250 mW at the liquid-surface interface was used as radiation source. The illumination spot was the same in all the experiments in order to avoid setup

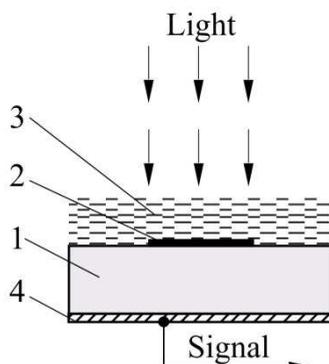


Fig. 17. Setup for the observation of SPCE at liquid-solid interface: 1-solid, 2-solid-liquid interface, generating the signal, 3-fluid under study, 4-electrode

effects. 15 ml of liquid were used in each measurement. The experimental data showed that the SPCE signal is highly sensitive to any changes in the composition and the properties of the studied fluid.

A characteristic feature of the SPCE in liquids is that the potential difference, created by SPCE, has a unique value for each liquid. For example, the amplitudes of the measured signal for several, arbitrarily selected liquids, are: tap water - 190  $\mu\text{V}$ ; filtered water - 209  $\mu\text{V}$ ; distilled water - 175  $\mu\text{V}$ ; alcohol - 115  $\mu\text{V}$ ; ammonia solution - 65  $\mu\text{V}$ ; acetone - 50  $\mu\text{V}$ ; coffee (used as an opaque liquid) - 15  $\mu\text{V}$ .

The experimental results, concerning the SPCE in liquids, showed that this effect is very attractive for prospective practical applications. Under certain conditions, the SPCE signal is a function of the composition or other properties of the liquid and could be implemented as an analytical method, similar to the potentiometric methods in analytical chemistry.

As an example, a gasoline quality control device could be developed since the SPCE signal differs for leaded or unleaded gasoline with various octane grades: A-86 - 29  $\mu\text{V}$ ; A-93 - 54  $\mu\text{V}$ ; A-93/unleaded/ - 63  $\mu\text{V}$ ; A-96 - 46  $\mu\text{V}$ ; A-95 /unleaded/ - 64  $\mu\text{V}$ ; A-91 /unleaded/ - 59  $\mu\text{V}$ . These samples (30 ml each) were supplied by the Laboratory of Fuel. The amplitudes of the SPCE signal for a series of fuels, purchased from regular gas stations were: diesel - 48  $\mu\text{V}$ ; A-86 - 31  $\mu\text{V}$ ; A-93 - 52  $\mu\text{V}$ ; A-95 /unleaded/ - 68  $\mu\text{V}$ .

These experiments demonstrate the possibility for qualitative detection of different liquids or variations in some liquid characteristics. Further development and calibration of the proposed method would make possible a quantitative analysis as well.

Variations of the SPCE signal were also registered upon mixing two liquids. For example, if only one drop of ammonia solution was added to 200 ml of drinking water, a 15% decrease in the amplitude of the signal was detected, whereas the signal increased by 10% when one drop of acetone was added in the same amount of water.

Another group of experiments was performed showing that by varying the type of electrode and the illumination conditions, the SPCE signal may become dependent on the volume of the liquid. This provided an opportunity for another device - a new type level-meter for liquids to be designed.

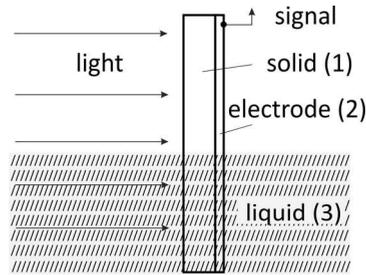


Fig. 18. Level-meter scheme: solid stick with deposited measuring structure on it (1); electrode (2); liquid (3)

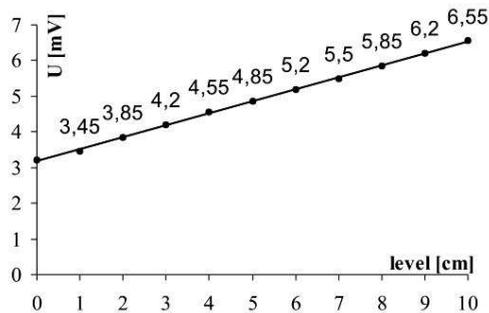


Fig. 19. SPCE response versus the petrol level

It was found that, in case of a suitably chosen structure, proportionality between the potential difference, caused by the SPCE, and the level of a certain liquid of interest can be achieved.

The essence of the idea for this type of level-meter is to put irradiated solid surface in contact with the controlled liquid. Since the electron properties at a solid surface influence essentially the interface with an overlying fluid layer, one can expect that optically-excited changes in such a system will induce measurable signals. This way, with all other conditions constant, it is possible to detect changes in the fluid. It is reasonable to expect that any kind of changes in the fluid will cause corresponding changes at the exposed interface, thus changing the SPCE signal.

The basic scheme of the device is shown in Fig. 18: (1) is a solid, in the shape of a stick. Its length is larger or at least equal to the height of the tank in which the liquid (3) is stored. A measuring structure is deposited on the stick. The stick was irradiated with modulated electromagnetic field of ultrahigh frequency. The detected SPCE signal was measured with an electrode (2) which is also placed along the length of the stick. For some device structures, the signal could be very sensitive to small changes (of the order of 0.1 mm) in the level of the liquid. Since the SPCE is characteristic for all kinds of solids, there is a large enough variety of materials which can be used to design working structures suitable for the mentioned purposes. The problem is to select the best materials for each particular case: type of liquid under control, working conditions, required accuracy, depth of the tank, etc.

As far as the measurement of liquid fuel levels is the most widespread case, a small laboratory model was constructed. It can be used to measure levels up to 10 cm of unleaded

petrol 95H. The structure employed shows about 100% change of the electric signal when the liquid level varies from 0 to 10 cm. The measurement accuracy is 0.4 mm and can be increased simply by technical improvement. As it can be seen from Fig. 19, there is a linear dependence between the SPCE signal and the gasoline level. During the measurement, a selecting technique and amplification of 20 dB were used. Since the SPCE is a quite fast effect, the analysis is in real time, i.e. the measurement and the reading are performed at the moment of the level variation.

Since electric signals are measured, the question about the possible hazards of electric flash and fire arises. It must be noted that the generated potential differences are very small - of the order of nanovolts and microvolts. Such differences exist, generally, in any solid, no power supplies are required and the measuring technique does not pose additional risks. The device can be designed with electrical wiring separated from the liquid fuel.

Usually, when liquid fuels are concerned, a requirement arises to measure the level of the water at the bottom of the tank. It should be noted that even the laboratory model described can indicate the presence of water there. Both the levels of the fuel and the water can be measured simultaneously. The investigations performed so far did not reveal any difficulties of principle for the implementation of such device. However, many problems should be solved before the device leaves its laboratory-prototype stage. For example, a possible problem, which could lead to the appearance of additional errors, is the condensation of vapours on the measuring structure. Some preliminary tests in this respect were carried out. Hot water vapour was supplied to a closed chamber, in which the level-meter had been placed, until saturation was achieved. At these extreme conditions, the experimental error was about 1 mm. One way to avoid such problems is to improve the measuring structure in order to minimize the influence of the condensation. Otherwise, precautions should be taken to control the condensation.

The proposed level-meter has a simple design, requires small investments for production and, in addition, is sensitive to very small variations in the liquid level. An important advantage, in comparison to the level-meters for liquid fuels commercially available at present, is that no moving parts are involved. Hence, the results are not influenced by variations in the relative weight of the liquid and there is no chance for micro-particles to hamper the free movement of the float, used in other level-meters. The device has many advantages and can be competitive to the technical solutions currently available. The flowing velocity of a liquid can also be monitored by SPCE, since, at certain conditions, the generated voltage depends on this factor as well.

The experiments showed also that the precipitation of a substance in a solution on the surface could also be monitored. It is obvious that the precipitated substance affects the surface properties and, as a result, changes in the SPCE signal should be observed. For example, variations of the SPCE signal after precipitation of  $\text{CaCO}_3$  from water on a metal surface were detected [Ivanov & Konstantinov, 2002].

The SPCE can prospectively be used for a complementary analysis together with the already existing methods for liquid control. The main advantage of such an analytical method is its universal nature - since SPCE voltage can be generated for all types of liquids, the method can be applied for characterization of any liquid. Various practical applications may be developed. The combination of optical probing of the sample and electrical detection of the generated signal is also of great importance. Provided that a suitable measuring structure is

selected, minimal amounts of liquid (even a small drop), would be sufficient for the analysis. The proposed method is universal - it can be used to study various fluids under different conditions. The measurements are rapid, real-time and contactless. No complex equipment and serious financial investments are required.

#### 4.4 Chemical composition test

The dependence of the SPCE signal on the chemical composition of the illuminated solid could find application in qualitative monitoring of the composition of various samples [Ivanov et al., 2008]. SPCE for example was used to analyze the composition of 50-cent coins (50 stotinki BGN), since they were subjected to widespread counterfeiting according to the information provided by the Bulgarian National Bank (BNB). It should be noted that there is a limited number of methods for real-time and contactless control of coins.

The development of a device for this was based on the standard type scheme for SPCE observation (Fig. 4). The sample 2 was irradiated with a modulated electromagnetic field 1. The voltage, induced by the SPCE, was measured on the electrode 3, which is in proximity to the sample 2. The signal was registered with a suitable device - a lock-in nanovoltmeter in this case. The frequency of the irradiating electromagnetic field was 144 kHz.

Initially, a large number of genuine pieces, which were in circulation, were measured in order to determine the range of the generated signals. Next, various counterfeits were tested. The comparison of the obtained results revealed that identification of the genuine from the counterfeit coins was completely possible. It was even possible to identify the types of counterfeits. A number of tests were conducted, some of them in the presence of experts from the BNB. 100% identification of the fake from the genuine coins was demonstrated. The amplitudes of electrical signals caused from SPCE and measured on counterfeits were significantly different from these for original coins. A comparison of the results showed that identification of real and counterfeit coins by the proposed method is clearly detectable, primarily due to the chemical composition. This is shown in Fig. 20, which is a one-axis graph. On the axis, the amplitudes of electrical signals are set caused by SPCE measured over 100 investigated coins. Three of them are counterfeits and they are easily found on the graph because they are out of the area of signals of the genuine coins. It is even possible to identify several different types of counterfeits, this way revealing their origin. Since the measured signals are instantaneous, the method basically finds application where an instantaneous identification is necessary. Generally, this is a real-time analysis. However, the effect is very sensitive and the whole device together with all the necessary electronic sections has to be placed in a dense metal shield. We believe that without any difficulties, the detector could be designed relatively economically and small in size, so as to be installed in any coin-operated machine.

The SPCE cannot be used to determine the exact amount of various components in an unknown sample. It can only be applied to detect whether or not the sample meets a certain standard. It is possible to trace the change of a certain impurity in a series of samples provided that the rest of the components are kept constant. This requires preliminary calibration. Theoretically, it is possible that a combination of different alloys generates a signal coinciding with the one of a genuine coin. However, such a coincidence is very unlikely and is of no practical significance. Yet, if the counterfeiters have at their disposal high-tech equipment enabling them to create and reproduce such a sample, they would rather create an ideal replica (in composition and weight) of the original coins.

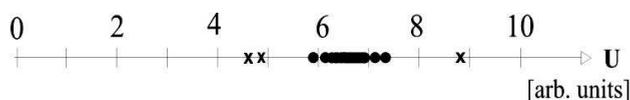


Fig. 20. The SPCE signal amplitudes, measured over 100 investigated coins:  $\times$  - counterfeit coins;  $\bullet$  - genuine coins

Presently, the commercially available detectors for real-time identification of fake coins most often operate on the principle of weight or dimensions measurements. Detectors based on composition control should be more accurate and reliable. An appropriate approach could be the building-in the proposed device into the detectors, used at present, controlling this way two parameters simultaneously. It has to be noted, however, that for successful implementation of the proposed method, the genuine coins should meet a certain standard. Otherwise, the SPCE-based identification could be considerably affected. Here, a new application emerges - analysis of the composition of coin billets prior to their stamping. The ones not complying with the standards should be returned for melting. Improvement of the standardization will undoubtedly enhance the quality and security of the coins in circulation.

The proposed device may find application in many areas - banks, shops, coin-operated machines, etc.

Besides the protection of the national currency, the SPCE-based composition tests may find many other applications. For example, various types of absorbing filters for gases and liquids can be monitored in order to determine when they have to be replaced. The absorption of the filtered substances causes changes in the chemical composition of the filter. The latter could be detected by using a SPCE-based device.

The SPCE could be used for monitoring of environmental pollution as well. This non-destructive, continuous and real-time test could also find application in areas such as ecology, industry, car production, military equipment, etc.

As far as security is concerned - analysis of drinking water (tap water or the one supplied to the army in field operations) is a very attractive possibility. Any change in the chemical composition, due to contamination with harmful substances, can be detected by the corresponding variation in the SPCE signal.

#### 4.5 Milk and food quality control

Since milk is of great importance as a food source, supplement or ingredient, a large number of analytical methods have been developed for its investigation, including biochemical, microbiological, serological methods, etc. Principal disadvantages of commonly utilized methods are related to their slowness, problems with consumables, and the need of laboratory conditions. These methods usually require reagents, some of which are expensive, extremely unstable, and very toxic or carcinogenic. Instantaneous tests, not requiring any consumables, are still in great demand. An appliance based on the SPCE could be developed to be portable, easily operated without expensive consumables, providing fast results, and not requiring a laboratory environment [Ivanov & Radanski, 2009].

A scheme of the experimental setup is similar to that in Fig. 17. A continuous wave diode laser generating 25 mW at  $\lambda=655$  nm was used as a source (L) of incident radiation. The incident light beam was chopped into periodic pulses with a modulation frequency of 800

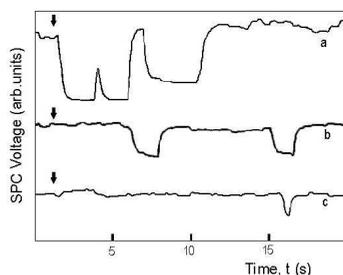


Fig. 21. Signal variation for 20 s after dripping of concentrated acetic acid in the incident spot of the laser beam: a) after the first drop; b) after the second drop; c) after the third drop. The milk was well stirred after each drop for homogenization

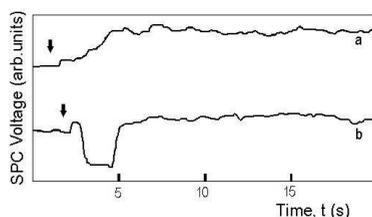


Fig. 22. Influence of the antibiotic kanamycin dripped in the incident spot of the laser beam on the signal amplitude for 20 s: a) at addition of 10 drops of a 30% solution of  $H_2O_2$  in milk (being stored 2.5 hours before the test) to 200 ml of milk; b) pure milk signal

Hz by using a modulator (M). This value was chosen to be far from the network frequency of 50 Hz where the most parasitic signals could appear and, at the same time, to be in the working range of the optico-mechanical modulator. A pulsed laser or a pulsed LED could also be used instead of such a modulator. The milk sample was placed in the measuring arrangement. The latter is a small vessel in which two electrodes are mounted. A setup capable to perform test on only a drop of liquid [Ivanov & Konstantinov, 2002] is also possible. The signals measured are in the nano- and microvolt scale and were amplified by 20 dB by the preamplifier. The detected signal had very low amplitude, thus a lock-in nanovoltmeter, capable of extracting the signal from the background noise, was utilized. The nanovoltmeter was coupled to a recording device to follow the time evolution of signals. The reference signal to the lock-in was supplied by the modulator. The measured signal is formed by the liquid-solid interface as discussed above when the irradiated solid surface is put in contact with the milk under investigation. Most probably, the presence of a liquid affects strongly the SPCE at the illuminated solid-milk interface and thus - the capacity of the measuring structure. Correspondingly, any minor changes in the milk (concentration, contaminations, pretreatment, etc.) change the SPCE signal, indicating that the processes at the interface are strongly dependent on its properties (Fig. 21).

The required information can be obtained either by direct observation of the signal amplitude or by using appropriate reagents (testing liquids) modifying the signal. This was demonstrated by the investigations in the case of hydrogen peroxide as an admixture (Fig. 22 a).

The milk samples (10 ml each) were characterized by measuring the amplitude of the generated potential difference and its variation after a droplet (0.04 ml) of testing liquid was added to the milk. The testing liquid was introduced both in the incident spot of the laser beam and at a certain distance (1 – 3 cm) away from it. Figures 21 and 22 demonstrate the opportunity for detecting changes in milk due to the presence of extraneous substances. The arrow signs indicate the moment of time at which the testing liquid was dripped in the milk sample. Variations in the signal response, similar to those presented in Fig. 22, were also observed in the presence of antibiotics/inhibitors in the milk samples.

The results described above demonstrate the opportunity for quality control of milk as well as for recognition of milk samples produced by different animal species since they generate signals with different amplitudes. The following types of milk were analyzed: cow, sheep, goat and buffalo. The amplitude of the signal generated by sheep milk was reduced by 15% compared to the signal, generated by cow milk. The amplitude of the signal, generated by the buffalo milk sample, was 50% smaller than the one generated by cow milk.

It should be noted that at the present stage of work the investigations are mostly qualitative ones. They are unable to identify the admixture type and its quantity in the milk. Considerable work is necessary to make possible quantitative estimations. Nevertheless, a qualitative evaluation of milk purity could be very useful for practical applications, if performed in a fast way, in real working environment, and without considerable expenses; these features are typical for the techniques proposed here.

Besides milk, SPCE can be applied for characterization of other foods (e.g. bee honey) as well.

## 5. Conclusion

The transverse acoustoelectric effect is considered promising for characterization of the electric properties of semiconductors. The TAV method is contactless, very sensitive and the measuring equipment is relatively simple. In addition, there are no special requirements to the exciting electrode, deposited on top of the semiconductor.

The most important advantages of SPCE-based methods include: high accuracy, low cost, instantaneous results, and possibilities for field measurements in real time, no complex equipment is required and no metal contact has to be deposited on the sample. No power supplies are required and the measuring technique doesn't pose any additional risks. This analytical method gives also great possibilities because it combines optical probing of the sample with electrical detection of the generated signal. The main advantage of SPCE is its universal nature.

The variety of possible applications of TAV and SPCE, described in this section, is promising enough to attract the attention of experts to the design and construction of electromagnetic field-matter- interactions-based devices for quality control.

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The rich palette of topics set out in this book provides a sufficiently broad overview of the developments in the field of quality control. By providing detailed information on various aspects of quality control, this book can serve as a basis for starting interdisciplinary cooperation, which has increasingly become an integral part of scientific and applied research.

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