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Use of vibronic phenomena in adsorption phase for developing of semiconductor gas sensors

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Semiconductor sensor selectivity is of the most importance for environment monitoring. The surface modifications and multi-sensor systems are widely used for the selectivity increasing in commercial sensors. The work presented is an experimental study aimed to show the use of fine vibrational phenomena on the semiconductor surface for the increase of the sensor selectivity. Our experiments showed that resonant vibrational energy transfer from the photoexcited adsorbed dye may occur if gas molecules have correspondent vibrational modes. This energy transfer controls both the luminescent signal from the dye and electrical response of the semiconductor substrate. The sensor selectivity in this case is due to the overlapping of rich vibrational spectra of the molecules. We have shown that isotopes can be distinguished from each other in this way since they have different vibrational frequencies. This could not be done with traditional ‘chemiresistors’. Selective sensors for specific gas molecules could be produced in this way by depositing organic dye molecules on the semiconductor surface with vibrational modes ‘tuned’ to the vibrations of those gas molecules.

Key words: *gas sensors; semiconductor surface; dye molecules; vibronic interactions; photoconductivity; vibrational energy transfer*

1. Introduction

Gas analysis has become a major issue for industry and government agencies concerned with public health and environment. Current methods based on sorbent traps or canisters [1] to collect samples to be analyzed in the laboratory do not provide rapid information. For this reason the development of highly sensitive gas sensors to provide continuous monitoring of the concentration of particular gases in the environment in a quantitative and selective way is of the most importance. Solid-state semiconductor-based sensors promise much more rapid results, but suffer from a lack of specificity [2]. The most common types of semiconductor gas sensors are based on

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recording of adsorption-induced changes in integral characteristics of the surface, such as dark- (σ_d) and photoconductivity (σ_p), or the surface potential Y. These integral characteristics are determined by equilibrium surface electron states (SES) that primary depend on the structure of terminal chemisorbed molecular groups [3]. In the case of van der Waals adsorption, the energy parameters of biographical SES change only insignificantly [4]. The energy spectrum of all the states on a real disordered surface has a quasi-continuous nature and barely reflects the specificity of adsorbed molecules. All these factors restrict the variety of molecules that can be detected and result in extremely low selectivity of these sensors. The fabrication of selective commercial sensors involves their surface modification or the use of catalysts [5].

The equilibrium response of the electronic semiconductor subsystem (variation of σ_d, σ_p, Y, etc.) to the adsorption process is traditionally believed to be a result of change in the occupation of its SES. This purely 'charge-controlled' approach can hardly solve the selectivity problem. In the present work, contrary to the 'traditional' semiconductor approach [2, 3], we try to solve this problem by encompassing our efforts towards the study of fine vibronic effects caused by adsorption. The issue can be successfully addressed, in our opinion, by the combination of traditional semiconductor sensor technique and fine vibronic effects caused by adsorption. The electron-vibrational coupling leads to a strong influence of gas environment on photosensitization of electronic processes in semiconductors. Vibrational and rotational spectra of a molecule, considered as its signature, determine the vibronic interactions.

Photo-induced singlet–singlet $S_0 \to S_1$ transitions in the adsorbed dye molecules are known to initiate electronic transitions in solids [6]. Two paths of such a spectral sensitization are feasible: (i) resonant transfer of the reverse $S_1 \to S_0$ transition energy from a molecule to charged SES and (ii) electron transition from an excited molecule to the solid conduction band. It was found that in the insulator–semiconductor structures based on Ge and Si, as well as ZnO and CdS, only the first mechanism takes place [6].

The overall deactivation rate constant (k) of the photo-excited molecule is known to be determined by energy transfer through the following five channels: (1) luminescence (k_l); (2) non-radiative energy transfer to near adsorbed molecules through the Förster–Dexter induction-resonance mechanism (k_{FD}); (3) intromolecular singlet –triplet transfer (k_{st}); (4) electron-vibrational coupling (internal energy conversion to vibrational modes) (k_{ic}); (5) non-radiative energy transfer to the solid (k_s), i.e.:

$$k = k_l + k_{FD} + k_{st} + k_{ic} + k_s \tag{1}$$

In semiconductors, k_s is determined by the charge exchange efficiency between the conductive band and different groups of SES and by band-to-band transitions.

Combined electrophysical measurements of the surface charge and spectral measurements of molecular luminescence provide unique possibilities between studying fine vibronic effects in the semiconductor–dielectric–dye structures. The semiconductor electronic subsystem may be very sensitive to any changes in the adsorbed phase due to strong competition of two energy transfer channels: 1) inside the molecular phase (channel M) and 2) into the semiconductor substrate (channel S). An intensive fluorescence quenching occurs and the SES emptying rate decreases, when molecules with overlapping luminescence and absorption bands are present on the surface. In this case there is no resonance between electron transitions in molecular phase, the energy migrates through other alternative pathways in channel M: reabsorption of emitted photons and electron-vibrational coupling. In the latter case, the energy of an excited electron of donor molecule transfers to vibrational modes of this molecule via internal conversion and then – to adjacent acceptor molecules if their vibrational spectra overlap [7].

2. Experimental

Experiments were performed with single crystal of germanium (Ge) and zinc oxide (ZnO) specimens as well as with polycrystalline ZnO and CdS films. ZnO films were prepared by oxidation of Zn films on an insulator substrate, and CdS films were deposited onto the insulator surface from water solution. Sapphire, quartz or glass substrates were used. Dye molecules of rhodamine B (RhB) or rhodamine 6G (Rh6G) were adsorbed on the surface of specimens from an ethanol solution. The surface concentration of rhodamine molecules was determined by means of a piezoresonance balance, and was chosen to be 2×10^{13} molecules/cm^2 that made the efficiency of the channel S greater than that of channel M. SES in germanium-oxide structure were first charged by exposition of specimens to light. A xenon lamp and a monochromator were used to obtain the proper wavelength.

The value of surface charge representing the electron subsystem response in Ge was measured by the field effect on a high sine wave signal – the standard method for measuring semiconductor surface potential. This field effect, first observed by Shockley and Pearson, consists essentially in the following. The sine wave voltage is applied to the capacitor having one metal plate and the other plate of semiconductor. The weak DC current is being measured along the semiconductor plate while modulated by the transverse voltage. This $I(V)$ dependence provides the information on the value of the surface charge [4]. In ZnO and CdS the electron subsystem response was detected as a change in photoconductivity. The conductivity of the samples is changing while they are illuminated, in the same way as it happens when these materials are used in industrial light sensors. In order to obtain photosensitized effects, the specimens were illuminated with monochromatic light to excite the dye molecules. After dye deposition the sample shows additional band of photoconductivity in the region where it was not sensitive to light before. This new band of photoconductivity corresponds to the dye absorption and it is due to the energy transfer from the dye molecules to the semiconductor [6]. To study the influence of ambient gases, the samples were exposed to a low-pressure vapour of naphthalene and ethanol, as well as deuterated naphthalene. The molecular electronic spectra of these species differ substantially from those of RhB, while vibrational spectra of CH groups in ethanol and naphthalene molecules partially overlap with some vibrational modes of RhB. The vibrational modes in deuterated molecules are shifted, thus no resonance transfer is expected.

3. Results and discussion

In general, the results were similar for all systems studied, being independent of the substrate type. Consider the effect of naphthalene molecules on the RhB fluorescence. In the presence of naphthalene, the RhB fluorescence was quenched. According to [1], this can be explained only in terms of electron-vibrational coupling in RhB molecule because the strong mismatch of the naphthalene and RhB electron spectra does not allow the direct electron energy transfer. The presence of the deuterated naphthalene molecules, with vibrational modes that differ from those of naphthalene, did not produce fluorescence quenching. This fact confirmed the resonant vibronic nature of the observed phenomenon.

In the case of GeO_2 samples after optical charging of SES, the surface charge relaxes for about 30 min in darkness before reaching a stable value. The surface charge relaxation rate increases if, after charging, the specimen were additionally illuminated in the RhB absorption band. This effect is related to the additional photosensitized emptying of traps in the dielectric at the expense of the electronic excitation energy of the RhB molecules. We apply the term ‘efficiency of SES photo-emptying’ to the quantity $\Phi = (Q_0 - Q)/Q_0$, where Q and Q_0 are the surface charge remaining after 10-minute relaxation under and without an additional illumination in the absorption band of the dye, respectively. Experiments showed that no photo-ejection happened if the structure, either with a dye or without, were exposed to light aside the absorption band.

Adsorption of the naphthalene molecules significantly reduces the value of Φ owing to vibrational deactivation of some RhB molecules. Figure 1 shows the decrease of the parameter Φ and the intensity of luminescence I versus naphthalene vapour pressure. No effect was observed in the presence of deuterated naphthalene molecules.

The observed quenching of RhB fluorescence and the change in the efficiency of the photo-ejection can only be attributed to the internal conversion of the electronic excitation of the RhB molecules to vibrational modes accompanied by subsequent energy transfer to the guest molecules. It is due to the fact that their vibrational mode energy comes very close to that of the RhB molecules interacting with them. The fact that the system shows no sensitivity to deuterated molecules indicates that the vibrational modes of the interacting molecules must be the same.

Of the two discussed parameters, I and Φ, the latter has proved to be more sensitive to the presence of guest molecules. This implies that the electrophysical method is more promising for gas detection than the optical one. It may well provide a basis for new high-performance, low-concentration sensors. Furthermore, this will substantially extend the class of detectable molecules, including isotopically substituted ones. We previously observed a similar effect with H_2O, D_2O.

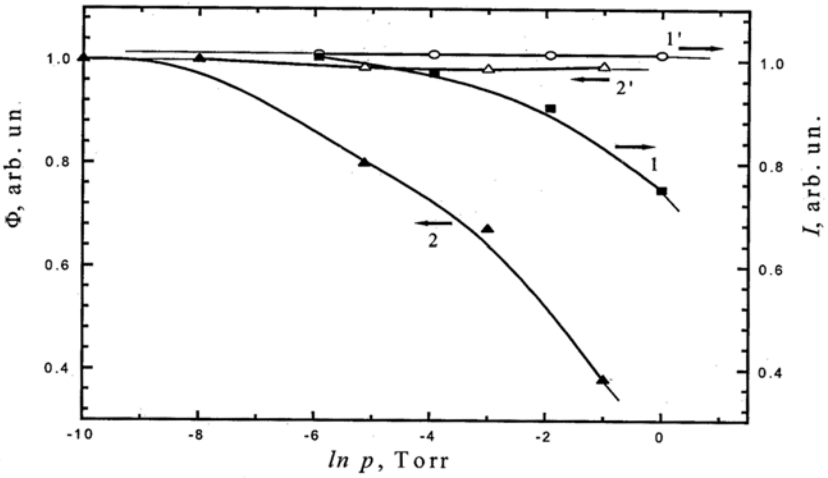

Fig.1. Fluorescence intensity of rhodamine B (1, 1′) and efficiency of SES photo discharge (2, 2′) in Ge–GeO_2–RhB system as functions of naphthalene (1, 2) and the deuterated naphthalene (1′, 2′) vapour pressure. The SES photo discharge data were extracted from the surface potential measurements

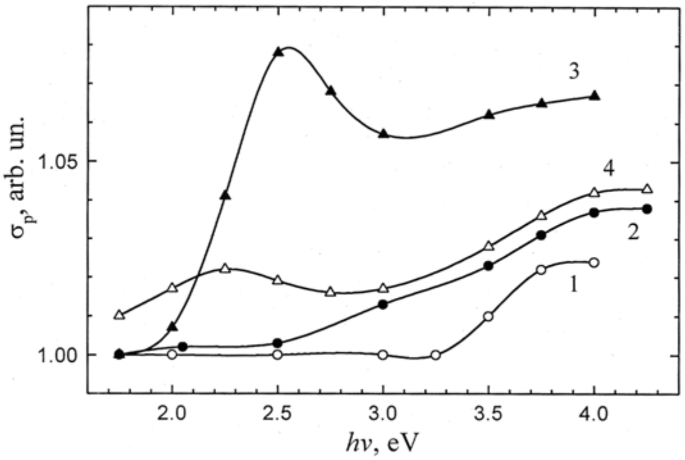

Fig. 2. Photoconductivity spectra of single crystal (1, 3) and polycrystalline (2, 4) ZnO: without dye (1, 2) and after RhB deposition (3, 4)

We have performed similar experiments using a popular material for photosensitization studies: zinc oxide single crystals and polycrystalline films with rhodamine B molecules adsorbed on the surface. Figure 2 shows spectral dependencies of the photoconductivity of ZnO specimens without and with adsorbed dye. The photoconductivity spectra of ZnO crystals represent a sharp edge of fundamental absorption at $h\nu = 3.3$ eV, i.e. at the energy corresponding to the gap of ZnO (Fig. 2, curve 1). Here

σ_p is the ratio of the photo- and dark conductivity. This edge smears out for the polycrystalline film.

When evacuated crystal with adsorbed dye was illuminated in the spectral range of RhB absorption, $h\nu = 2.3–2.5$ eV, we observed a typical spectral sensitization effect (Fig.2, curve 3), that is the steep increase in σ_p. This effect is less prominent for the polycrystalline film (Fig. 2, curve 2, 4).

Admission of naphthalene vapours to the surface reduced the sensitization efficiency. The effect was observed when the naphthalene vapour pressure exceeded the value of 0.1 Pa. Figure 3 demonstrates the pressure dependence of the ratio $\Phi = \sigma_p/\sigma_{p0}$, where σ_{p0} and σ_p are the values of photoconductivity at the maximum of the RhB absorption band before and after adsorption of the 'guest' naphthalene molecules, respectively.

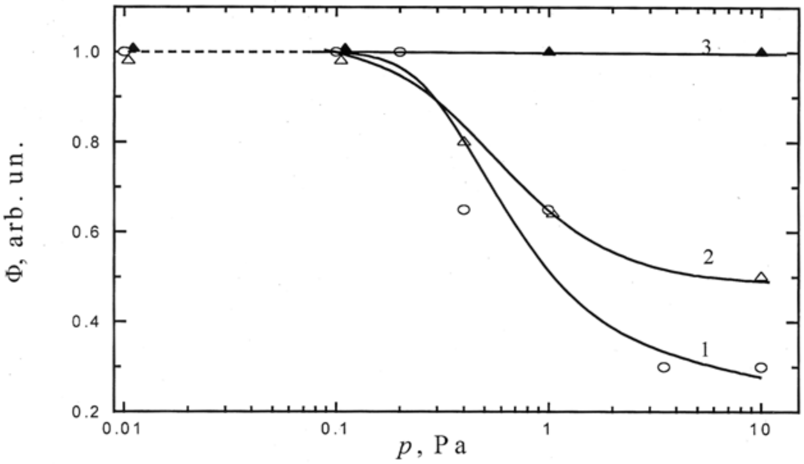

Fig. 3. Efficiency of conductivity photosensitization as a function of naphthalene vapour pressure for ZnO single crystal (1) and polycrystalline film (2) with adsorbed RhB molecules. The same with deuterated naphthalene (3)

As an attempt to build a sensor capable of detecting hydrocarbons in ambient conditions, we have chosen a system based on thin polycrystalline film of CdS with adsorbed dye molecules. Spectra of dark and photoconductivity of CdS films of different thickness and grain sizes are similar to those of ZnO shown in Fig. 2 and differ from the ZnO curves by specific for CdS main absorption band. The band of sensitized conductivity due to RhB molecules reaches a maximum at 2.3 eV. The conductivity of the films tested was slightly dependent on water vapour concentration allowing hydrocarbons measurements under real atmospheric conditions. Admission of naphthalene and ethanol vapours to a camera with the sensor has changed photoconductivity in a wide region of light energies. However, the system was much more sensitive to the ambient hydrocarbon concentration in the conductivity band photosensitized by RhB molecules, where the sensor is very selective because of abovementioned vibration resonance. An example of the system spectral response to naphthalene and ethanol vapour is shown in Fig. 4. The coefficient of photoconductivity reduction was taken as $K = \sigma_p/\sigma_{p0}$, where σ_{p0} and σ_p are the values of photoconductivity before and after adsorption of the 'guest' molecules, respectively. Figure 4 shows that system response at the RhB absorption band was 5–10 times higher than in the intrinsic photoconductivity band of CdS.

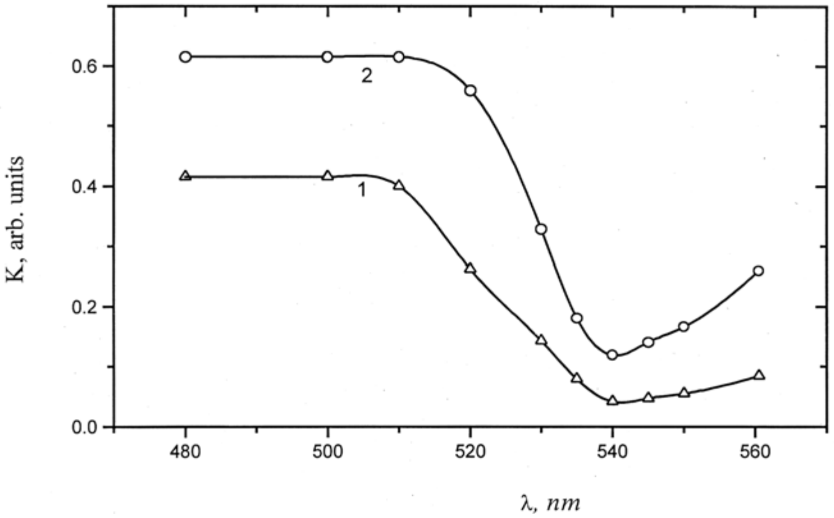

Fig. 4. Spectral dependence of the coefficient of photoconductivity reduction by ethanol vapour of pressure $p = 400$ Pa (1) and naphthalene vapour of $p = 1$ Pa (2) for CdS film with adsorbed RhB molecules

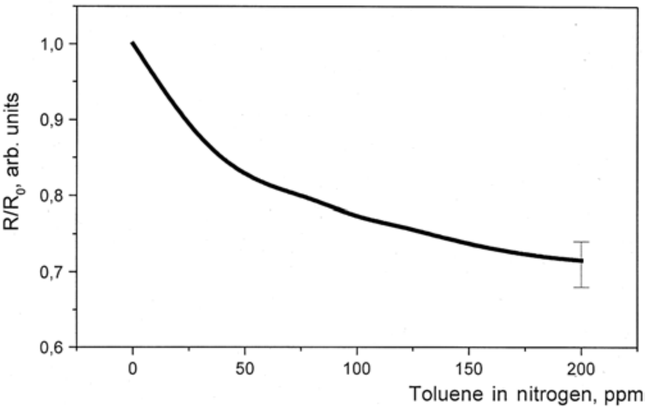

Fig. 5. Average response to toluene diluted by nitrogen at the atmospheric pressure. The resistance is normalized to that found with pure nitrogen or in vacuum

A specially designed vacuum system allowing the experiments to be done in static, as well as dynamic flow mode was used to evaluate CdS–RhB system efficiency for volatile hydrocarbons in air detection. Experiments were carried out by preparing mixtures of toluene in nitrogen or air in a stainless steel canister. Then the chamber was filled with the prepared gas mixture. For lower concentrations the chamber was partly filled with nitrogen and then brought to the final pressure with the gas mixture. The proportions for these dilutions were monitored by measuring the pressure within the chamber with an accurate pressure gauge. Between measurements the sensor was each time conditioned by several nitrogen purges with vacuum pumping between them.

The first results observed with the test toluene/nitrogen mixture at the atmospheric pressure are presented in Fig. 5. The plot indicates that the best sensitivity (largest slope) is reached at lower concentrations. In other experiments, the sensor was proved to show a clear response to toluene in nitrogen concentrations as low as 2.6 ppm.

4. Conclusions

We have investigated a new physical principle that can be used for building selective gas sensors. The sensor selectivity in this case is due to the overlapping of rich vibrational spectra of gas molecules with those of adsorbed dye. The selective sensor for specific gas molecules could be produced by depositing on the semiconductor surface organic dye molecules with vibrational modes ‘tuned’ to the vibration of those gas molecules. We have shown that isotopes can be distinguished in this way. This could not be done with traditional chemiresistors. The results obtained with a ‘CdS –adsorbed dye’ system are especially promising in terms of new design for gas sensors based on physical principles of selectivity. The other semiconductors could be used as well, such as SnO_2 – one of the most important semiconductor gas sensor materials. Modern organic synthesis offers ample scope of possibilities for building dye molecules with vibrational modes selective to specific gas molecules.

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