PHOTOSENSITIZATION OF ELECTRONIC TRANSITIONS BY DYE MOLECULES IN SYSTEMS CONSISTING OF A SEMICONDUCTOR AND ADSORBED MOLECULES OF p-BENZOQUINONE

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Electrophysical methods and ESR measurements have been used to investigate the changes, photosensitized by molecules of rhodamine B (RB), in the charge states of electron traps created by molecules of p-benzoquinone (pBQ) in the Ge/GeO₂ system. The results obtained in studying the quenching of fluorescence of RB molecules indicate that the photodestruction of electron traps is due to transfer of electronic excitation energy from the RB molecules to charged complexes formed upon adsorption of the pBQ. In order to select optimal conditions for recharging of such complexes, a study has been made of the relationship between the relative change in ESR signal and the concentration of adsorbed RB molecules.

The phenomenon of photoadsorption and photocatalysis, in the opinion of most investigators, is related to recharging of adsorption centers upon photoexcitation of the electron subsystem of a semiconductor. As shown in [1], however, photoexcitation is a necessary but not sufficient condition for adsorption (desorption) or dissociation of adsorbed molecules. Realization of such processes requires additional vibrational or electronic excitation of the adsorbed complexes. We have established that this may be accomplished by utilization of the energy released in acts of capture or recombination of nonequilibrium charge carriers on deep centers (adsorption states [2]) or the energy of local phonons that are resonance-excited by an external source such as an IR laser [3].

There is still another possible path for controlling acts of adsorption and catalysis: supply of energy to the adsorption complexes for photoexcited molecules of dyes adsorbed on the same surface. This sort of approach is used extensively in the photosensitization of photoelectric processes on the surface of semiconductors [4]. Korotkov et al. [5] carried out the photosensitized dissociation of H₂O molecules adsorbed on a dielectric by electronic excitation of adjacent naphthalene molecules with subsequent resonance transfer of...
energy of the H₂O molecules. We have been successful in realizing a photosensitized change in population of various groups of surface states on real surfaces of semiconductors [3, 6].

Electrophysical measurements usually provide the main channel of information on recharging adsorption states – measurements of the change in total charge (Qₛ) and potential (Vₛ) of the surface, change in conductivity, etc. Under real conditions, however, owing to the mutual compensation of changes of different groups of surface states differing in capture cross section, it is not always possible to observe in pure form the changes in charge of the adsorption complexes themselves. For example, in the case of monatomic semiconductors (Ge and Si) coated with a dielectric oxide film, photosensitized by means of dye molecules, the destruction of electron and hole traps of the dielectric (TD) leads in turn to a change in charge of the slow states (SS) at the interface and in the charge of the fast states (FS) [6] (Fig. 1). The total surface charge in the semiconductor/dielectric structure is expressed by the relationship Qₛ = QTD + QSS + QFS. If the adsorption states are paramagnetic, their recharging can also be judged from the change in the ESR signal related to these states. A good system from this point of view is Ge/GeO₂/adsorbed molecules of p-benzoquinone (pBQ). As shown by data reported in [1, 7], adsorption of pBQ leads to the appearance, on the Ge surface, of an additional system of acceptor adsorption SS (recharged upon application of a transverse electric field to the sample) and electron paramagnetic traps of the dielectric TD⁻ that are recharged by photoinjection of electrons from Ge and GeO₂. In the work reported here, we investigated changes, photosensitized by dye molecules, in the charge state of electron traps created by molecules of pBQ in the Ge/GeO₂ system (Fig. 1), by the simultaneous application of electrophysical methods and ESR measurements.

**EXPERIMENTAL PROCEDURES**

For the measurement of electrophysical parameters of the surface and measuring the fluorescence of adsorbed dye molecules, we used a Ge single crystal of the n type (ρ = 36 Ω·cm), treated in a peroxide etchant. The Ge specimens for recording the ESR spectra were prepared in the form of microcrystals with a specific surface of approximately 5 m²/g. The adsorption of pBQ molecules and then the dye rhodamine B (RB) was carried out under vacuum conditions. The Ge specimens were first dehydrated at 670 K in this same vacuum unit. The concentration of adsorbed molecules was estimated by means of a piezoresonance quartz balance.

All change in the system of surface states were determined by the field effect method on a large sinusoidal signal. The fluorescence spectra of the adsorbed RB were registered by means of an automated spectrometer based on a KSVU-12 unit. Fluorescence of the adsorbed dye molecules was excited by light from a DKSSH-1000 xenon lamp through an MDR-2 monochromator. The ESR spectra were taken in a Sibir'-3 spectrometer.

**RESULTS AND DISCUSSION**

According to information reported in [1, 7], dehydration of the surface of germanium leads to the removal of most of the eigenstates SS and TD⁻ (Fig.1). The surface potential is shifted into the region of negative values, and there is no more slow relaxation of surface charge upon application of a transverse electric field. It is known that irradiation of the surface in the region of light quanta hνc from 2.5 to 4 eV, as a result of transitions of electrons from Ge to TD⁻ in GeO₂ (transitions hνc in Fig. 1), leads to negative charging of the surface. Dehydration results in practically complete disappearance of charging upon illumination (Fig. 2, curves 1 and 2).

Adsorption of pBQ at 300°C with a pBQ vapor pressure of approximately 13 Pa is accompanied by the appearance of new acceptor slow states at the Ge/GeO₂ interface and acceptor traps (TD⁻) in the GeO₂. The concentration of adsorbed pBQ molecules on the surface was found to be npBQ = 4.5 · 10¹⁴ molecules/cm², and the additional dark charge that appeared after adsorption in the SS that were formed Qd = 3.2 · 10⁻⁸ C/cm², a value close to that reported in [7]. As can be seen from Fig. 2 (curve 3), the illumination-caused charging of the surface that is related to the formation of the new TD⁻ of adsorption origin shows a sharp increase. The adsorption of pBQ on Ge single crystals leads to the appearance of an ESR signal with g = 2.0017 ± 0.0002 and a line width ΔH = 0.5 mT. The concentration of spin centers that are formed, Nₛ = (4 ± 1) · 10¹¹ spins/cm², is somewhat greater than the concentration of charged SS, equal to Qd/e, where e is the electron charge. The kinetics of establishing the equilibrium value of Nₛ correspond approximately to the kinetics of dark charging of the surface of a single-crystal specimen of germanium. Illumination of the surface in the region hνc ≥ 2.5 eV produces a 20% increase in the intensity of the ESR signal, owing to transition of part of the