

# Physics and applications of wide band gap semiconductors

V S Vavilov

## Contents

|  |            |
|--|------------|
| <b>1. Introduction</b>   | <b>269</b> |
| <b>2. Wide band-gap semiconductors (WS) as the object of physical experimentation and as materials for technical applications</b>      | <b>270</b> |
| <b>3. Generation of excess carriers. Hot electrons and holes and their thermalisation. Carrier transport phenomena</b>                 | <b>271</b> |
| <b>4. Transport phenomena and recombination of excess carriers</b>   | <b>272</b> |
| <b>5. Nonradiative recombination processes</b>   | <b>273</b> |
| <b>6. Photochromic reactions</b>   | <b>273</b> |
| <b>7. The photohardening effect</b>  | <b>273</b> |
| <b>8. Radiation control of the properties of WS</b>  | <b>274</b> |
| <b>9. Effect of point defects and extended defects on the energy levels of the local states and on non-equilibrium processes in WS</b> | <b>274</b> |
| <b>10. Methods of experimental studies of defects in the WS</b>  | <b>274</b> |
| <b>11. Radiation defects</b>   | <b>275</b> |
| <b>12. Luminescence in the porous silicon</b>  | <b>275</b> |
| <b>13. Practical applications of wide band semiconductor</b>   | <b>275</b> |
| <b>14. Conclusions</b>   | <b>276</b> |
| <b>References</b>  | <b>276</b> |

**Abstract.** Wide band gap semiconductors are electronic materials in which the energy of the band-to-band electronic transitions exceeds approximately 2 eV. These materials have different kinds of chemical bonds and of crystal lattice structures, but the electronic and optical processes taking place in them have a great deal in common. Diamond, silicon carbide SiC, gallium phosphide GaP, cadmium sulfide CdS, and some other related compounds of the  $A^{II}B^{VI}$  type occupy a special place among the wide-gap semiconductors. Recent developments in optoelectronics and other fields of practical applications (in particular, high-temperature devices and methods of detecting photons and charged particles) have stimulated a wide interest in wide band gap semiconductors. The data available for some of the most widely studied members of the very large family of wide gap semi-conductors have been used to analyse the most characteristic properties of the processes taking place in these materials, and especially those induced by the strong excitation of their electronic subsystem and by the phenomena associated with the always present carrier localisation centres.

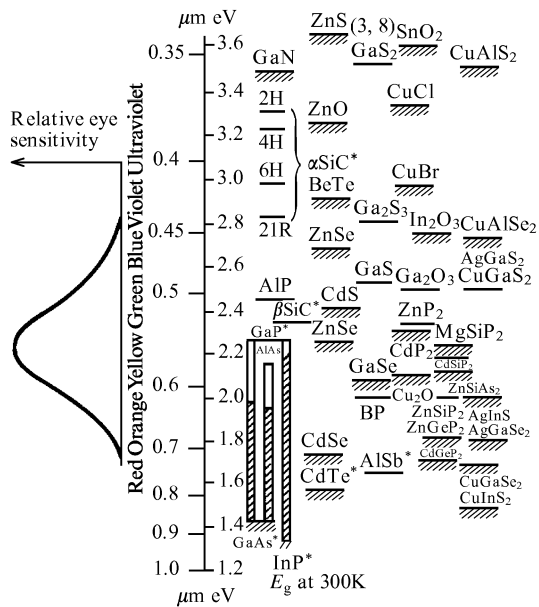
V S Vavilov P N Lebedev Institute of Physics, Russian Academy of Sciences, 53 Leninskii prosp., 117924, Moscow, Russia.  
Tel. (7-095) 135 05 51

Received 10 December 1993  
*Uspekhi Fizicheskikh Nauk* 37 (3) 000–000 (1994)  
Translated by J I Carasso

## 1. Introduction

The term wide band gap semiconductor (WS) is applied to substances whose electric conductivity at room temperature is vanishingly small in the absence of electrically active impurities with a small ionisation energy. The term WS has been generally used for many years, though strictly speaking it should not be forgotten that the wide band gap is the forbidden energy gap (wider than approximately 2 eV), and not the band of permitted energies of the charge carriers. Unlike the alkali halide crystals, in which the width of the forbidden gap is 7–10 eV, the WS may contain chemical impurities or defects with small or moderately high ionisation energies (0.05–0.5 eV). Another typical feature of these materials is their strong luminescence in the visible region of the spectrum in response to the generation of a high concentration of excess charge carriers. Some practically important and extensively studied materials (like gallium arsenide and cadmium telluride) have a band gap  $E_g$  close to 1.5 eV and are not included in the WS group. According to the ideas developed by A F Ioffe in the 1950s the term semiconductor can be applied to any condensed medium which displays phenomena induced by the presence of free charge carriers (electrons and holes).

At present any substance, whatever its  $E_g$  value, can be made a semiconductor for short times by using radiation ionisation (strong laser irradiation with  $h\nu > E_g$ , multiphoton excitation, or high energy pulses [1]). However, when excess carriers are excited by high-energy electrons or



**Figure 1.** Semiconductors suitable for fabrication of visible light sources [9].

photons ( $h\nu \gg E_g$ ) the ‘cost of an electron-ion pair’† is approximately  $(2.5-3)E_g$ , i.e. two-thirds of the energy is converted into excitation of the atomic vibrations in each ionisation act lasting approximately  $10^{-10}$  s. Therefore a longer interaction with a strong beam of radiation must cause heating of the sample, which may result in irreversible changes in the properties of the semiconductor [2, 3]. It follows that in order to establish longer (or steady-state) processes we must resort to doping the WS with electrically active impurities or to injection of charge carriers through p-n junctions, heterojunctions, or Schottky barriers. However, these approaches are not always realisable.

## 2. Wide band gap semiconductors (WS) as the object of physical experimentation and as materials for technical applications

From the very large number of materials with a large energy gap,  $E_g$ , which can be classified as WS we shall choose for detailed discussion a relatively narrow set and exploit the latest information on their electrophysical parameters and the modern technologies available for their production. Approximate data on the width of their forbidden gap, the mobility of their charge carriers, and on their strongest luminescence band are given in Table 1 and in Fig. 1.

The present writer, who has contributed for many years to the development of the physics and technology of WS, must accept his share of any criticism for the inclusion of such a limited number of substances in the review. The reference handbook by Landolt-Bornstein [4] contains detailed information on many tens of crystalline substances which can be classified as WS. Several modern monographs (see, for example, Ref. [5]) are devoted to families of substances defined by having a common chemical nature in accordance with the Periodic Table: in the case of Ref. [5] the feature

common to every member of the chosen class is its complying with the physics of compounds of the  $A^{II}B^{VI}$  family. However, these chemical families may include semiconductors characterised by very strongly different properties: the aim of the present review is to analyse phenomena typical of WS.

Two initially independent approaches to the study of WS are now available: the ‘luminescence’ technique [6]; in which the WS are referred to as crystal phosphors, and the ‘semiconductor’ approach. But by using both techniques over a period of time total consistency in terminology and in the fundamental concepts of the basic phenomena in WS have now been achieved.

One of the main characteristics of crystalline semiconductors (in the ideal case) is the unhindered transport of the charge carriers within the allowed energy bands. In real crystals some scattering of the charge carriers (electrons and holes) always takes place, and produces a marked lowering of the carrier mobility.

It can be seen from Table 1 that the mobility of diamond exceed those of all the other selected WS. Judging from data available [4] but not included in Table 1 the same applies to all the other WS.

The choice of a small group of substances for further study is consistent with current teaching trends in the development of semiconductor physics, reflected in particular in Queisser’s monograph *Kristallene Krisen* [7], available (in addition to the Germinal original) in English and in Chinese translations but not in Russian. It is now generally agreed that the invention of the transistor by Bardeen, Brattain, and Shockley (all Nobel Prize winners) has had the most powerful influence on the development of solid-state electronics. However, the formation of p-n junctions, the electroluminescence, and the generation of electric oscillations in silicon carbide (SiC) crystals were all discovered in the 1920s by O V Losev in Petrograd (Leningrad) [8]. The present author’s purpose in referring to that pioneering work is to underline the importance of having available an adequate supply of research samples: sufficiently perfect crystals with reproducible properties. Losev’s claim to priority is recognised in books on electroluminescence and light-emitting diodes [9] (Fig. 1). However, Losev had to work with individually selected carborundum crystallites, and his results were therefore treated as inexplicable.

Unlike the devices studied by Losev, even the earliest transistors were prepared from perfect single crystals of germanium. The present writer is well aware, from his own experience, that the requisite technology could be set up by groups of workers having only moderate resources. The

**Table 1.** Some parameters of the WS (300 K) [4, 5, 9, 47].

| Valence of component | WS       | $E_g$ /eV | $\mu_n$ /cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> | $\mu_p$ /cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> |
|----------------------|----------|-----------|--|--|
| IV                   | Si       | 1.12      | 1300   | 470  |
| IV                   | Diamond  | 5.5       | 2500   | 1800   |
| IV-IV                | SiC (6H) | 2.9       | $\cong 1000$   | $\cong 100$  |
| IV-IV                | SiC (4H) | 3.26      |  |  |
| III-V                | GaP      | 2.25      | 110  | 75   |
| II-VI                | ZnS      | 3.58      | 120  |  |
| II-VI                | ZnSe     | 2.67      | 530  | 16   |
| II-VI                | ZnTe     | 2.26      | 530  | 30   |
| II-VI                | CdS      | 2.59      | 340  | 18   |

†This definition was suggested by V L Ginzburg in 1959.

much more difficult technology needed to grow silicon crystals also reached (quite rapidly) a high level of development. This change in objective was stimulated by the much greater width of the forbidden gap in silicon than in germanium, which allowed operating temperature ranges consistent with military requirements to be expected from silicon devices. The leading experimenters of the 1950s turned their attention to silicon: they received adequate support and achieved important successes. American economists now believe that each dollar invested in silicon technology has already produced a hundred-fold profit, and that the revenue from the silicon industry at the end of the century will be comparable to the revenue from the car industry.

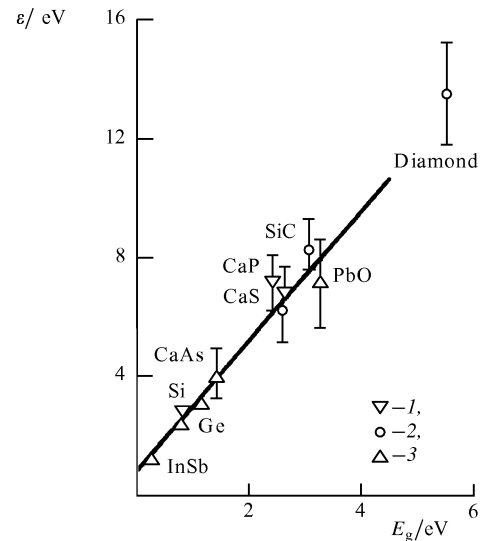
The ‘fate’ of the wide band-gap semiconductors, beginning with silicon carbide, was much less brilliant, though the WS had become an attractive research topic and a material widely used in practical applications long before the invention of the transistor (Table 2).

The WS group includes amorphous modifications of some substances which have been intensively studied in their crystalline modifications. It has been convincingly established that amorphous carbon (but not graphite!) can be prepared as thin films having a large area. It is possible to grow amorphous films of GaP, and probably also of other  $A^{III}B^V$  compounds. However, their study is only beginning, and it may be better not to embark on premature discussions.

To conclude this section we shall mention the visible luminescence observed in the so-called porous silicon, which has attracted great interest from technologists. The phenomenon is probably due to substantial changes in the band structure produced by quantum size effects (see below).

### 3. The generation of excess carriers. Hot electrons and holes and their thermalisation. Carrier transport phenomena

The phenomena which we shall now consider are among the most fundamental problems in semiconductor physics and technology [2]. As was said above, in order to excite large deviations from equilibrium into the electronic subsystem of a semiconductor we must supply an excess of energy. The first reported interaction of this type was the excitation



**Figure 2.** Mean ionisation energy against the band gap in some semiconductors. (1)  $\alpha$ -particles, (2) electrons, (3) photons [10].

by fast electrons, originally known as cathode rays: this gave rise to the term ‘cathodoluminescence’, which is now widely used. The internal ionisation energy, i.e. the energy of formation of pairs of nonequilibrium charge carriers (NCC) in nonmetallic substances, is related to the width of the forbidden gap, and exceeds it by a factor of 2.5–3, mainly as a result of energy transfer to the photons during the thermalisation of the primary electrons. Experimental data [10] on the mean ionisation energies in various semiconductors are shown in Fig. 2. Impact ionisation models of this process were developed by Popov, Shockley, and also by Antoncik [12], and later extended by other workers. Evidently, effects such as the ‘direct’ generation of excitons and the impact ionisation of impurity centres (which are usually present in WS in high concentrations) do not contribute significantly to the generation of NCC by beams of fast electrons.

Table 2. Some Applications of the WSs (see also Ref. [47])

| Material                          | Opto-electronics             | Electron beam pumped lasers | Injection lasers | Microwave generators  | High-temperature diodes and transistors | Radiation counters and dosimeters | Photo-detectors       |
|-----------------------------------|------------------------------|-----------------------------|------------------|-----------------------|---|-----------------------------------|-----------------------|
| Diamond                           | Application expected         |                             |                  | Applications expected | Used under laboratory conditions        | In use                            | Applications expected |
| Silicon Carbide<br>6H.SiC, 4H.SiC | Photodiodes (green, blue)    |                             |                  | Applications expected | In use                                  | In use                            | In use                |
| GaP                               | Photodiodes (mainly visible) |                             |                  |                       |   |                                   |                       |
| ZnS                               | In use                       |                             | First results    |                       |   |                                   |                       |
| ZnSe                              | In use                       |                             |                  |                       |   |                                   |                       |
| ZnTe                              | In use                       | In use                      | First results    |                       |   |                                   |                       |
| CdS                               | In use                       | In use                      |                  |                       |   |                                   | Widely used           |
| Porous silicon                    | Applications expected        |                             |                  |                       |   |                                   |                       |

The loss of energy by an electron resulting from all types of inelastic interaction is described by the Bethe equation

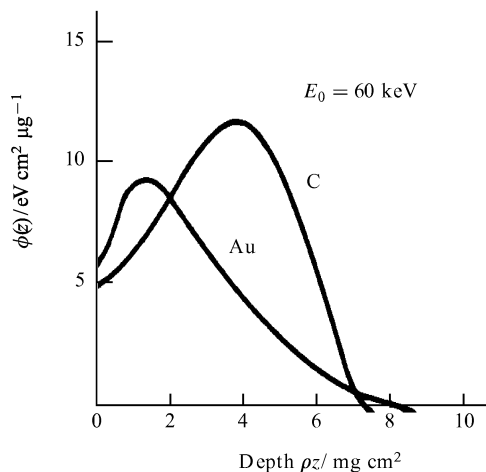
$$\frac{dE}{ds} = \frac{N_A e^4 Z \rho}{2\pi\epsilon_0^2 A E} \ln \frac{1.66E}{J}$$

$$= -7.85 \times 10^4 \frac{\rho Z}{AE} \ln \frac{1.66E}{J} \text{ keV sm}^{-1}, \quad (1)$$

where  $dE$  is the change in the energy of an electron having an energy  $E$  (keV) after travelling a path  $ds$  (cm),  $Z$  is the atomic number,  $A$  is the atomic mass,  $\rho$  is the density, and  $\epsilon_0 \approx 8.85 \times 10^{12}$ . The potential  $J$  increases monotonically with the atomic number, and can be described approximately by the formula

$$J = 1.15 \times 10^{-2} Z \text{ keV} \quad (2)$$

Thus the energy losses  $dE/ds$  are also an increasing function of  $Z$ , especially in the low-energy region, since the denominator in Eqn (1) is predominant over  $\ln E$  in the numerator.



**Figure 3.** Distribution of the dose over the depth  $\phi(z)$  for electrons having an energy of 60 keV in gold and carbon targets [13].

In addition to inelastic energy losses we have a strong scattering of the fast electrons due to elastic interactions with the electrons and atoms of the material. This effect influences the distribution of the ionisation density (dose) produced by a focussed beam of electrons over the penetration depth. The distribution curves of the dose as a function of depth are shown in Fig. 3 for electrons having an energy of 60 keV in gold and carbon targets.

In principle this method of exciting the NCC is quite universal, the only limitation being set by the acceptable level of heating of the WS. Thus by using short pulses at sufficiently long intervals we can achieve excitation levels high enough to produce population inversion of the levels and to generate coherent radiation, as was suggested by Basov et al.<sup>11</sup> and experimentally achieved in CdS and (later) in other semi-conductors. The probability of rearrangement of complexes of point defects and of chemical impurities increases rapidly with the level of excitation of the electronic subsystem of the crystal, leading to a change in the energy spectrum of the localised electronic

states. This phenomenon has been studied in detail in the  $A^{II}B^{VI}$  family of WS (and in particular in CdS) by Sheinkman et al., and an extensive analysis of the results has been published [24]. Similar processes, often called photochemical reactions, take place also under strong generation of NCC by light during interband or multi-photon absorption. At present the choice of lasers available to many laboratories is insufficient to allow the excitation of practically all the WS with high rates of generation of NCC.

However, present and future optoelectronic and other devices based on WS are likely to continue using processes in which nonequilibrium charge carriers are created by electric injection through p-n junctions, heterojunctions, or metal-semiconductor junctions (Schottky barriers). Structures in which electric injection can take place and having near-ideal properties have been analysed in depth by many workers. Unfortunately, in all the WS so far selected for discussion (except GaP and SiC) the injecting structures contain many centres located near the interface and able to stimulate the recombination of the nonequilibrium carriers. Another special feature is the relatively low equilibrium conductivity of most of the WS, resulting from the absence (or the compensation) of shallow donor and acceptor impurity levels. As a result, only a small fraction of these shallow centres can contribute equilibrium carriers to the allowed energy bands at room temperature. Thus, in semiconducting diamond the principal shallow acceptor impurity (boron) has an ionisation energy of 0.37 eV, and theoretical estimates for the donor impurities (Li, Na, and P) are approximately 0.15, 0.2, and 0.1 eV, respectively. Experimental data for Li are close to 0.1 eV.

The problem of introducing into WS electrically active impurities with energy levels low enough to produce thermal ionisation is still far from solved in spite of the intensive effort devoted to it. Traditional methods of doping during the growth of monocrystals or of epitaxial layers, or by thermal diffusion from the surface, gave good results with gallium phosphide and (to some extent) with silicon carbide. However, the thermal diffusion of impurities such as B and Al in SiC requires temperatures close to 2000 °C. Wide-band semiconductors of the  $A^{II}B^{VI}$  type show marked photoluminescence, and some of them can easily be grown as platelet crystals from the gas phase. In recent years some success has been reported in the fabrication of p-n junctions in ZnS, and laboratory versions of injection lasers based on this compound have been produced. Detailed information on the stability of p-n junctions and lasers of this type is not yet available.

#### 4. Transport phenomena and recombination of excess carriers

As can be seen from Table 1 the mobility of excess carriers is small in all the WS except diamond. In many cases the available data are unreliable. It is well known that the progress made (especially in the early stages) in the development of the technology of germanium and silicon, leading to the production of increasingly perfect crystals with a gradually lower concentration of uncontrolled impurities, made available materials with much improved carrier mobilities. In Ge, Si, and GaAs the mobility is now limited only by scattering on lattice vibrations at free surfaces or at interfaces. There is no doubt that further progress in the method of growing WS crystals will lower the contribution from typical mechanisms

for these materials, including scattering by charged centres and by dislocations.

Processes of radiative and nonradiative recombination of NCC have been subjected to detailed analyses since the pioneering work of Shockley and van Roosbroeck (see Ref. [18]), in which the probability of direct radiative recombination was calculated from the principle of detailed balancing applied to events leading to the absorption and to the emission of photons. The rate of the radiative recombination is strongly dependent on the character of the band structure near the edge of the principal absorption band. In semiconductors for which indirect phonon-assisted transitions are the most probable the NCC lifetimes with respect to direct radiative recombination can be very high. Among the materials considered here a direct band structure is found only in cadmium sulfide, zinc sulfide, and other substances of the  $A^{II}B^{VI}$  type (see Fig. 1). Radiative transitions accompanying the formation of excitons, and especially of excitons localised on impurity centres or on crystal lattice defects [9], are much more probable. Processes associated with excitons, exciton molecules, and the electron–hole ‘liquid’ (predicted by Keldysh) now constitute a very large field of study in solid–state optics [19], but they lie outside the scope of the present review.

## 5. Nonradiative recombination processes

In almost all the cases examined the transition of the electronic subsystem of a semiconductor from the excited to the initial state involves a number of competing processes (channels) whose nature can be inferred from indirect evidence, and mainly from the kinetics describing the lifetimes of the NCC. Phenomena such as the Auger effect, the surface recombination, and the trapping of carriers by deep centres with energy transfer to phonons have been examined in detail [2, 9, 10], but to study these effects experimentally we require an analysis of the data for each individual case. The Auger effect is often called impact recombination, since the energy released by a recombining electron is absorbed by a neighbouring electron which then loses it by emitting phonons. In this three-carrier process photon emission does not take place. Many variants of the process are possible: Pankove lists 12 types, according to the predominant carrier transport mechanism, in intrinsic and in impurity semiconductors [20]. Experimental data on the Auger effect for Ge, Si, InAs, and GaAs at high excitation levels were obtained and analysed by Galkin [21] and others [22]. According to Bergh and Dean [9] the Auger effect plays a dominant role in the recombination of an exciton localised on an atom in gallium phosphide at temperatures above 100 K: the probability of this non-radiative process is approximately 500 times greater than the same probability for the radiative transition. The Auger effect should also play an important role in strongly excited WS, probably because of the relative instability of a system of point defects and complexes towards the strong excitation of its electronic subsystem, especially in the WS and of  $A^{II}B^{VI}$  family [5]. Other forms of nonradiative recombination involving the localisation centres of charge carriers with deep levels can be predominant in determining the overall rate of recombination of NCC, mainly because the concentration of these centres (which is often not deliberately controlled) is relatively high [3, 5]. Thus, in a series a crystal of nitrogen-free diamond excited by short pulses of fast elec-

trons the lifetimes of NCC pairs were less than  $10^{-9}$  s [23]. Surface recombination in WS has not yet been adequately studied, but recent advances in growing thin-film structures of these materials suggest that a successful outcome may be expected very soon.

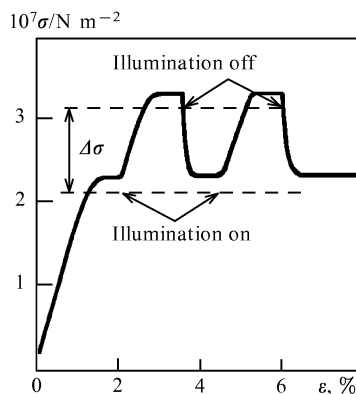
## 6. Photochromic reactions

This term is used for one of the types of process contributing to the formation and rearrangement of complexes (aggregates) of point defects (PD) and chemical impurities often stimulated by the excitation of the electronic subsystem, as was shown by the experimental studies of  $A^{II}B^{VI}$  compounds by Sheinkman and coworkers [5, 24]. The term ‘PCR’, now widely used, was first proposed by Beer and Borchardt [25] in 1953 to describe the ‘photoexhaustion’ effect which they had discovered in CdS crystals. It was also shown that the change in properties of the semiconductor stimulated by illumination are due to the generation (or the disappearance) of recombination centres. Under these conditions the important effect is not the absorption of the photon energy by the crystals but the action of the excess charge carriers generated by the light. Thus processes of the PCR type are one form of the general phenomena of the generation, rearrangement, or annihilation of defects and complexes initiated by ionising radiation, which also take place under the influence of fast electrons. Furthermore, whereas in PCR processes the presence of a high concentration of excess carriers is a necessary and sufficient condition, the PCR should take place also in the absence of an external ionising radiation under conditions of electric injection or avalanche breakdown. This observation is relevant to well known aspects of ageing and degradation of semiconductor devices.

## 7. The photohardening effect

This process, associated with the motion of dislocations in  $A^{II}B^{VI}$  compounds, was discovered in 1968 by Osip’yan and Savchenko [26]. It was found that the irradiation of CdS (and other) single crystals by light of a given wavelength causes a strong hardening, i.e. an increased resistance to plastic deformation. A typical deformation diagram illustrating the PHE is shown in Fig. 4. Illuminating the sample in the region of easy plastic flow ( $\sigma = \text{const}$ ) produces a marked mechanical strengthening, so that beyond this point the sample deforms elastically, and plastic flow begins again only at a stress  $\sigma_{TC}$  well in excess of the threshold stress in the darkness  $\sigma_{TT}$ . The relative hardening effect,  $(\sigma_{TC} - \sigma_{TT})/\sigma_{TT}$ , can be as high as 100% or more, while the rate of plastic deformation  $\epsilon_n$  under illumination decreases by several orders of magnitude for the same value of  $\sigma$ . Switching off the illumination restores the original plastic properties of the sample, as can be seen from Fig. 4. The PHE is usually observed with the sample under a uniaxial stress; however, strengthening by illumination can be achieved also under deformation of other types (such as torque, bending, etc.) provided that plastic deformation can be induced in this way. The PHE has been observed in almost all the  $A^{II}B^{VI}$  wide-band semiconductors, including polycrystalline samples. The PHE is excited most effectively by light which produces interband transitions: it is undoubtedly similar in nature to the photochromic reaction in WS. Its manifestations are associated with the type of electric field

near dislocations of various types. A negative PHE (the plastic softening effect) has been observed in some cases for excitation in a narrow spectral range. The first microscopic models of the PHE stipulate the accumulation of electrons from their trapping levels by moving dislocations: increasing the number of these electrons increases the charge on the dislocation and therefore lowers its mobility. As far as the present writer knows the PHE has not been studied in other wide-band semiconductors including SiC or diamond. According to a private communication Hall made an unsuccessful attempt to observe the PHE in Ge monocrystals.



**Figure 4.** Photohardening effect in CdS.  $\sigma$  is the applied stress,  $\epsilon$  is the deformation of the sample,  $T = 100^\circ\text{C}$ ,  $v_g = 10 \mu\text{m min}^{-1}$ ,  $\lambda = 550 \text{ nm}$  [5].

## 8. Radiation control of the properties of WS

The special properties of WS, induced by the presence of electron localisation centres with deep levels, are not always controllable by traditional methods of crystal growth. Methods of doping the WS under strongly nonequilibrium conditions therefore had to be found. These methods consist in introducing the required impurities during the growth of the crystal from a gas plasma or by ion implantation under conditions such that the addition of impurities, leading to the breakdown of the initial structure, is accompanied by reduction (usually during an annealing process, i.e. a heat treatment of prescribed length). During the last few years the implantation of high-energy ions (50–1000 keV) has become an essential part of the technology of solid-state electronics [13]. Thousands of ion accelerators are currently used in industrial countries, mostly in the production of silicon planar devices. As is well known, reliable tabulations of data on the penetration depth of ions of different masses in different solids are now available for experimental scientists and engineers. However, problems on the nature of the accompanying radiation damage and on the possibility of eliminating it still have to be solved individually. In recent years special attention has been devoted to the ion implantation of impurities in diamond [14, 17]. Workers engaged in the production of light-emitting diodes and other devices based on WS are increasingly turning to ion implantation and other methods of radiation interaction to control the energy spectrum of centres with deep levels, and in particular the irradiation of SiC with fast electrons [37]. The use of neutron transmutation doping, as now practised

in silicon technology [10], is a likely future development in the control of the properties of WS such as CdS.

## 9. Effect of point defects and extended defects on the energy levels of the local states and of non-equilibrium processes in WS

The analysis of the effect of point defects (PD) and of extended defects on the properties of semiconductors and the rational control of defect concentrations are among the most important problems in solid-state physics and technology. Many monographs and reviews have been written on these topics, and a biennial international conference has been established [27]. As was said above, the role of defects is specially important in all members of the very large class of WS, mainly because of the large binding energy of localised carriers and of the (so far) invariably high concentrations ( $\sim 10^{17} \text{ cm}^{-3}$ ) of the PD and of the uncontrolled impurities. The thermal generation of PD in compound semiconductors has been discussed extensively by Sakalas and Yanushkyavichus in their monograph<sup>28</sup> and also in Ref. [5] (for  $A^{II}B^{VI}$  compounds). Detailed information on PD in diamond can be found in the monograph [14] edited by Field in 1992, and considered among specialists as the Bible of Diamond. And yet, the problem of defects in diamond layers deposited from the gas phase, whose technology is being rapidly developed, is still far from being solved. The same is true of silicon carbide, in which the polytypism of the crystal structure has serious hindered, for many years, the interpretation of available data.

## 10. Methods of experimental study of defects in WS

The wide band gap of the WS was an obvious reason for the general adoption by workers in this field (as had been done earlier for alkali halide crystals) of optical methods, i.e. of the analysis of absorption, luminescence, and photoconductivity spectra [29], and also of electron paramagnetic resonance (EPR) spectra. Most of the PD (and their complexes with chemical impurities) in crystalline Si were unambiguously identified by Watkins, Corbett, and their coworkers using the EPR method. These results are of fundamental value in the technology as well as the physics of this material [31, 32]. In the case of silicon extraordinarily favourable conditions were created by combining the EPR procedures with electro-physical measurements, by virtue of the possibility of controlling the Fermi level and of obtaining (in most cases, with great ease) data on the energy levels of impurities and defects.

In WS comprehensive studies of this type are possible only exceptionally, as can be seen from the contents of recent monographs [5, 28] and original papers. On the other hand the optical method, and especially the analysis of the luminescence [33] and the EPR spectra, often allow us to determine the symmetry of the defects from the fine structure produced by an isotopic shift of the lines. Alternatively we can use rare-earth impurities introduced by various methods (in particular, by ion implantation): these are characterised by radiative transitions within the centres, and they can be used as probes acting on factors such as the lattice strains produced by defects close to the emitter [30].

## 11. Radiation defects

In addition to the grown-in point defects, [31] the interaction of the penetrating radiation with high-energy photons plays an important role in the generation and stabilisation of these defects. Since Seit<sup>34</sup> published an estimate of the energy needed for the impact (athermal) transfer of one of the regularly positioned atoms from its lattice site to one of the nearest interstitials (25 eV) experimental values of the threshold energy varying between 5 and 80 eV were obtained for many semiconductors. These experimental values are often used to calculate the upper limit of the concentration of displaced atoms [10]. Important corrections which were later applied to these calculations were discussed by Emtsev and Mashovets [35]. The principal consideration underlying these corrections is that a well defined threshold cannot be expected: we have a range (band) of threshold energies, so that at least in the classical semiconductors (Ge and Si) the components of Frenkel pairs are very mobile and closely spaced pairs are unstable.

However (and this is specially important in WS) the impact displacements of atoms from the lattice sites are not the only important processes in these materials. An equally important role is played by the interaction of the excited electronic subsystem with point defects and impurity centres [36]. Phenomena which were conveniently observed in alkali halide crystals as changes in optical absorption and in the luminescence spectra in the visible region were also observed in semiconductors, and termed subthreshold defect generation. These processes are basically similar to photochromic reactions (see Section. 6).

## 12. Luminescence in porous silicon

A fairly strong luminescence of silicon in the visible region of the spectrum was recently reported (in 1991) by Cullis and Canham [38]. Their observation, confirmed by many workers, stimulated great interest because the possibility of fabricating electroluminescent devices on the basis of a technologically well understood material like crystalline silicon was irresistibly attractive. It has long been known that some methods of chemical treatment (etching) of silicon monocrystals lead to the formation of spongy or partially tube-like structures to a depth of several micrometres from the etched surface of the crystal [39, 40]. According to numerous studies by electron microscopy these structures resemble a dendritic coral with irregularly spaced bridges between the individual branches. Methods of preparing porous silicon have long been known to specialists in 'silicon electronics', though differences in detail were evident between the techniques used by workers in England [39], in the USA (IBM) [41], and Germany (Technical University of Munich) [42], and in many other laboratories. There is little doubt that the discovery of visible radiation in porous silicon will ultimately lead to technologically important developments, but the physics of these devices will not benefit to the same extent. Most of the workers who published data on the photoluminescence and electroluminescence of this material (or, more precisely, on the whole family of heterogeneous materials, which include a wide variety of microcircuit elements based on crystalline Si), have been inclined to the conclusion that a 'quantum confinement' effect takes place and leads to radiative transmissions within the strongly modified system of energy

levels.<sup>43</sup> Theoretical studies have been aimed at a quantitative description of the reported emission spectra. However, it is legitimate to ask whether a porous structure is essential to the emission of visible radiation in silicon. V D Tkachev, of Minsk, thought that the same effect could be achieved by doping the silicon with rare-earth elements and by developing improved methods of exciting 'intracentre' optical transmissions. However he did not support his suggestion with experimental results. Michel and coworkers (USA) claimed [44] to have detected photo-luminescence (as well as electroluminescence) in the IR region (1.54  $\mu\text{m}$ ) in silicon monocrystals doped with Er by ion implantation. A theoretical explanation of the effect was put forward by I N Yassievich (St. Petersburg) at the same conference [45].

Reports by H Fuchs and coworkers [45] (Germany) of the preparation of free (substrate-free) thin layers of crystalline silicon by anodic oxidation are of interest: according to optical absorption results these films had a forbidden band gap of approximately 2 eV and showed photoluminescence. According to the published results the following observations are noteworthy.

(a) The photoluminescence seen in porous silicon is the most effective. However, many workers stress the 'ageing' effects found in this material, i.e. the change in the spectral composition and the decrease in the luminescence effectiveness with time, and their dependence on the excitation level. This is not surprising in view of the complicated geometry and of the marked irregularity of the structures so far produced.

(b) The methods of electric excitation most important for practical purposes (like the electron beam excitation method) have not yet been adequately studied.

(c) If the concept of 'quantum confinement' are valid it should be possible to preserve the pore structure by filling the pores with a suitable neutral medium. Work in this direction began towards the end of 1991, and rapid progress can be expected shortly.

## 13. Practical application of wide band semiconductors

A rational judgment of the contribution made by advances in physics to social progress will be made by our descendents in the next century. Though the present writer would not presume to compare the social effect of semiconductors with that of (say) the application of nuclear physics he is ready to support the widely held belief that since the 1950s solid-state electronics and its associated computer technology have played a direct role in the development of modern civilisation.

Within the scope of the present review we should confine our comments to the applications of the WS. As has already been stated in the Introduction their partial applications will be found, in the first instance, in the field of optoelectronics, including the universally familiar colour television sets, indicator lamps used in household appliances, and electroluminescent panels. We could mention an example familiar to the citizens of St. Petersburg (then called Leningrad, 15 years ago). Very pleasing electroluminescent lights were fitted all over the city to illuminate the house number plates. Unfortunately, within 2–4 years the intensity of their radiation had fallen sharply as a result of physical changes of the photochemical reaction type similar to those briefly mentioned above. Specialists in the field of silicon

electronics and helioenergetics know very well the extent to which the practical application of semiconductor devices depends on their reliability and service life. As a concrete example, users of solar batteries expect a service life of at least 10 years, and similar criteria are specified for devices in communications by fibre optics based on generators and detectors of the luminescence type. In the light of the facts and concepts discussed above the closing part of this review will be devoted to a brief examination of the prospects of further developments in technology and of new applications of physical phenomena typical of WS (Table 2).

(1) The broadest (and most profitable) field of application of the WS is their use in colour television as crystalline phosphors excited by fast electrons.

(2) Next in order of importance is the use of WS in injection excitation applications exploiting the energy of the outer electric field in indicators and in electroluminescence panels, and also (in the near future) as flat television screens to replace the vacuum tubes. On the basis of already available data these screens are expected to become serious competitors of the modern devices (based on scanning beams of fast electrons) during the next 5–10 years.

(3) The WS (mostly cadmium sulfide) are already widely used as photoresistors in automation and other conventional fields (exposure meters in cameras and cine-photography apparatus).

(4) The special features of human visual perception have been used for many decades in traffic lights and in the control panels of aircraft (and also, more recently, of motor cars). Electroluminescence devices will probably replace the less reliable traditional systems (based on filament lamps) during the next few years.

(5) The semiconductors most widely used at present (silicon and gallium arsenide) cannot be operated at temperatures above 100 °C. However, devices operating at higher temperatures are required in some areas of technology. Diamond and silicon carbide are the among the WS most likely to be used in these cases. According to recently published data these two materials have only each other as competitor for several of the important parameters (leaving out of consideration cubic boron nitride, BN, whose technology is at a less advanced stage). Now and in the foreseeable future the field of application of high-temperature devices will remain limited but important. We note that in addition to a wide working range (extending from 300 to 500 °C) both competitors (diamond and silicon carbide) offer a high stability against nuclear radiation damage.

## 14. Conclusions

During the last 50 years the fundamental and the applied studies in the physics of nonmetallic solids have achieved successes widely recognised outside the field of specialists in these materials. After the invention of the transistor and the development of silicon device technology we witnessed the appearance of many interesting new ideas and new concepts in many related areas of semiconductor physics, but their social effect is still not comparable with that of the main achievement: modern solid-state electronics. The present writer is confident that new development lines of great importance to mankind will very shortly be identified in the physics of wide band gap semiconductors. This belief stems, in the first instance, from the ability of this class of materials

to act as a 'bridge' between the human eye (limited by nature to a given region of spectral sensitivity) and the controlling signals used in solid-state electronic devices.

The writer is grateful to A N Georgobiani and Yu A Vodakov for helpful remarks.

## References

- Shockley W, in Proceedings of the Prague Conference on Semiconductor Physics: *J. Phys. Chem. Sol.* (1961), suppl. 1 [Translated into Russian *Usp. Fiz. Nauk* **77** 161 (1962)]
- Bonch-Bruевич V L, Kalashnikov S G *Fizika Poluprovodnikov* (Physics of Semiconductors) (Moscow: Nauka, 1977; 2nd ed. 1990)
- Milvidskii M G, Osvenskii V B *Strukturnye Defekty v Monokristallakh Poluprovodnikov* (Structural Defects in Semiconducting Single Crystals) (Moscow: Metallurgiya, 1984)
- Landolt-Börnstein *Za hlenwerten und Funktionen in Naturwissenschaften und Technik. Neue Serie* (Ed. O Madelung) Band 17 *Halbleiter* (Eds M Schulz, H Weiss) (Berlin: Springer, 1982)
- Fizika Soedinenii A<sub>2</sub>B<sub>6</sub>* (Physics of A<sub>2</sub>B<sub>6</sub> Compounds) (Eds A N Georgobiani, M K Sheinkman) (Moscow: Nauka, 1986) p. 320
- Antonov-Romanovskii V V *Kinetika Fotoluminescentsii Kristallofosforov* (Kinetics of Photoluminescence in Crystal Phosphors) (Moscow: Nauka, 1966) p. 324
- Queisser H *Kristalline Krisen* (München: Piper, 1985) p. 350
- Losev O V *Telegrafiya i Telefoniya* (Telegraph and Telephone) (18) 61 (1923); *Philos. Mag.* **7** 1024 (1928)
- Bergh A A, Dean P J *Light Emitting Diodes* (Oxford: Clarendon Press, 1976) [Translated into Russian *Svetodiody* Ed. A E Yunovich (Moscow: Mir, 1979) p. 686]
- Vavilov V S, Kekelidze N P, Smirnov L S *Deistvie Izluchenii na Poluprovodniki* (Radiation Effects in Semiconductors) (Moscow: Nauka, 1988)
- Basov N G, Krokhin O N, Popov Yu M *Usp. Fiz. Nauk* **72** (2) 161 (1960) [*Sov. Phys. Usp.* **3** (5) 702 (1960)]
- Antoncik E *Czech. Ψas. Fis.* **7** 651 (1957)
- Broudy J, Muray J *The Physics of Microfabrication* (New York, London: Plenum Press, 1982) [Translated into Russian *Fizicheskie Osnovy Mikrotekhnologii* (Ed. A V Shalnov) (Moscow: Mir, 1985) p. 494]
- The Properties of Natural and Synthetic Diamond* (Ed. J Field) (London: Academic Press, 1992)
- Bernholz J et al. in *Proceedings of the XX International Conference on Semiconductor Physics, Thessaloniki, Greece, 1990* Vol. 1, p. 332
- Prins J *Mater. Sci. Rep.* **7** (7–8) 271 (1992)
- Vavilov V S *Usp. Fiz. Nauk* **164** (4) 429 (1994)
- van Roosbroeck W, Shockley W *Phys. Rev.* **94** 1558 (1954)
- Modern Problems in Condensed Matter Sciences* (Amsterdam: North-Holland, 1986) Vol. 16
- Pankove J I *Optical Processes in Semiconductors* (Englewood Cliffs, N. J.: Prentice-Hall, 1971) [Translated into Russian *Opticheskie Protssy v Poluprovodnikakh* (Eds Zh I Alferov, V S Vavilov) (Moscow: Mir, 1973)]
- Galkin G N *Tr. Fiz. Inst. Akad. Nauk SSSR* **127** 3 (1981) (based on Doctoral Thesis)
- Blinov L M, Vavilov V S, Galkin G N *Fiz. Tverdogo Tela* **9** 884 (1967) [*Sov. Solid State Phys.* (1967)]
- Vavilov V S, Gippius A A, Konorova E A *Elektronnyye i Opticheskie Protssy v Almaze* (Electron and Optical Processes in Diamond) (Moscow: Nauka, 1985)
- Sheinkman M K, Korsunskaya N E in Ref. [5] ch. 4
- Beer K, Borhardt W *Fortschr. Phys.* **7** 184 (1953)
- Osip'yan Yu A, Savchenko in Ref [5] ch. 2
- Defects in Semiconductors — 16*. Proceedings of the 16th Conference (Lehigh Univ. USA: Trans Tech Publications, 1991)
- Sakalas A, Janushkevichus Z *To chechnye Defekty v Poluprovodnikovykh Soedineniyakh* (Point Defects in Semiconductor Compounds) (Vilnius: Mokslas, 1988) p. 155



29. Ryvkin S M *Fotoelektricheskie Ya vleniya v Poluprovodnikakh* (Photoelectric Phenomena in Semiconductors) (Moscow: Fizmatgiz, 1963)
30. Gippius A A Doctoral Thesis Fiz. Inst. Akad. Nauk SSSR (Moscow: FIAN, 1985)
31. Corbett J W, Bourgoin J-C in *Point Defects in Solids* Vol. 2: *Semiconductors and Molecular Crystals* (Eds J H Crawford, Slifkin) (New York, London: Plenum Press, 1975) [Translated into Russian *Tochechnye Defekty v Poluprovodnikakh* (Eds B I Boltaks, T V Mashovets ) (Moscow: Mir, 1979)]
32. Vavilov V S, Kiselev V F, Mukashev B N *Defekty v Kremnii i na Ego Poverkhnosti* (Defects in the Bulk and at the Surface of Silicon) (Moscow: Nauka, 1990)
33. Gippius A A, Vavilov V S in *Trudy VII Mezhdunarodnoi Konferentsii "Ionnaya Implantatsiya v Poluprovodnikakh", Vilnius, 1983* (Proceedings of the VII International Conference "Ion Implantation in Semiconductors", Vilnius, 1983) (Vilnius: Vilnius State University, 1985) p. 59
34. Seitz F *Discuss. Faraday Soc.* **5** 271 (1949) [Translated into Russian, in *Deistvie Izlucheniya na Poluprovodniki* (Radiation Effects in Semiconductors) (Ed. S M Ryvkin ) (Moscow: Inostr. Lit., 1954) p. 9]
35. Emtsev V V, Mashovets T B *Primesi i Tochechnye Defekty v Poluprovodnikakh* (Impurities and Point Defects in Semiconductors) (Moscow: Radio i Svyaz, 1982)
36. Vavilov V S, Kiv A E, Niyazova O R *Mekhanizmy Obrazovaniya i Miigratsii Defekto v v Poluprovodnikakh* (Mechanisms of Defect Formation and Migration in Semiconductors) (Moscow: Nauka, 1981)
37. Vodakov Yu A et al. *Fiz. Tekhn. Poluprovod.* **26** (11) 1857 (1992)
38. Cullis A, Canham L *Nature (London)* **353** 335 (1991)
39. Cullis A, Canham L, Dosser O *MRS Fall Meeting. Abstracts of Symposium AA* (Boston) p. 4
40. Kachalov M A et al. in *Rossiiskaya Konferentsiya po Fizike Poluprovodnikov, Nizhnii Novgorod, 1993, Tezisy Dokladov* (All-Russia Conference on Semiconductor Physics, Nizhny Novgorod, 1993), Abstracts, Vol. 2, p. 257
41. Bassons E, in Ref. [39] p. 4
42. Petrova-Koch V et al., in Ref. [40] p. 6
43. Asnin V M, Stepanov V I, in Ref. [39] p. 7.
44. Michel J, Kimmerling L et al., in Ref. [39] p. 7
45. Yassievich I N, in Ref. [40] p. 9
46. Fuchs H, in Ref. [40] p. 12
47. Vikulin J M, Stafeev V I *Fizika Poluprovodnikovykh Priborov* (Physics of Semiconductor Devices) (Moscow: Radio i Svyaz, 1990)