Luminescent Processes Elucidated by Simple Experiments on ZnS

R. Schwankner and M. Eiswirth
Institut für Physikalische Chemie der Universität 8000 München, FRG
H. Venghaus[1]
Max-Planck-Institut für Festkörperforschung 7000 Stuttgart 80, FRG

Semiconductors represent a group of substances which over recent decades have attained enormous importance, both with respect to research and also for device fabrication, and the development is still going on. Many properties of semiconductors (their electrical or optical behavior, for example) are influenced strongly by impurities or other crystal imperfections, although the chemical concentration of impurities or defects may be fairly low. The purpose of the present paper is the description of some impurity-related optical properties of semiconductors, with special emphasis on luminescence of ZnS.

We will present several experiments which are easy to perform and require very little equipment. However, the understanding of the experiments is not straightforward, since it requires the knowledge of a number of rather complex properties of semiconductors. Nevertheless, the simple experiments can be used to explain rather subtle phenomena. Once these are understood qualitatively other phenomena such as age determination by luminescence measurements, for example, can be studied much more intelligently.

We start with a brief outline of the physical concepts necessary to understand the experiments presented in the second part of the paper. These experiments are performed on ZnS, but the phenomena observed are characteristic for many other semiconductors as well. The processes discussed are the basis for the importance which ZnS attained many years ago. For example, ZnS screens were widely used for the detection of X-rays in medical diagnosis or as oscilloscope screens. More recently it has been used as the host material for various rare-earth-doped powder phosphors for color television. It is also used for making luminescent dials for clocks.

Primarily we will be concerned with photoluminescence experiments. "Luminescence" is a general expression for light emission from solids as a consequence of an excitation process. The excitation may be achieved in a variety of ways, for example, by light (photoluminescence), fast electrons (cathodoluminescence), externally applied bias (electroluminescence) or by chemical reaction (chemiluminescence). The expressions "fluorescence" and "phosphorescence" were used in the past to distinguish between luminescence processes occurring within $\sim 10^{-8}$ s after excitation and processes occurring later, respectively. However, since there is no particular physical reason to make such a distinction, we will use the more general expression "luminescence" throughout. More details on the history of luminescence phenomena are given in Reference 1.

In the final section, we will discuss dating by luminescence measurements, pointing out the main ideas of this interesting and useful technique for estimating the age of ancient pottery and art objects.

Some Characteristics of Semiconductors

Interpretation of the experiments under consideration here requires the knowledge of some basic physical properties of semiconductors. These will be given in the following section. (see also Ref. 2). More detailed descriptions can be found in standard solid state physics textbooks. (*3*)

For the characterization of a given semiconductor the energy levels (eigenstates) which can be occupied by electrons are of fundamental importance. These levels are related to those of the components forming the crystal. However, they are not simply the eigenstates of the free atoms. Changes of the original atomic energy levels are due to an interatomic interaction which increases as the distance between the atoms becomes smaller. In particular, the highest occupied and the lowest unoccupied levels of the atoms forming the semiconductor are broadened into quasicontinua. These are called the valence band (VB) and the conduction band (CB), respectively, and they are separated by an energy gap E_g. This is often referred to as the "forbidden energy gap," since in a perfect crystal there are no one-electron states between the upper VB and the lower CB edges. (Cf. Fig. 1, below.) If a semiconductor is in its ground state, e.g. at zero degrees Kelvin, all CB states are unoccupied, while the VB is completely filled with electrons. The number of valence electrons, n, is typically of the order of $10^{22}/cm^3$.

The optical and the electrical properties of a semiconductor are closely related to the behavior of (1) a small number of electrons being in the CB and (2) the properties of an almost filled VB. The latter problem might appear extremely difficult to solve due to the large number of VB-electrons. However, it turns out that the behavior of $(n-1)$ electrons in the VB, i.e one electron is missing in an otherwise *filled* VB, is equivalent to the behavior of a single positively charged particle in an otherwise completely *empty* VB. This positively charged quasiparticle is called a "hole", since it represents a missing electron.

Typical examples of semiconductors, to which our considerations apply, are the following (in parentheses we have added the gap energy E_g in electron volts, (*4*)):

ZnS	(3.80 eV)	CdS	(2.52 eV)	GaAs	(1.54 eV)	Si	(1.11 eV)
ZnO	(3.43 eV)	CdSe	(1.77 eV)	GaP	(2.25 eV)	Ge	(0.66 eV)
ZnSe	(2.78 eV)	CdTe	(1.54 eV)	InP	(1.42 eV)		
ZnTe	(2.34 eV)						

In real crystals, imperfections such as impurities, atoms on improper lattice sites, or vacancies, for example, introduce energy levels within the forbidden energy gap E_g. Imperfections having excess electrons are called donors. The energy required to move a donor electron into the CB is the donor ionization energy E_D. On the other hand, imperfections capable of binding extra electrons are called acceptors. The acceptor ionization energy E_A is the energy required to lift an electron from the top of the VB to the acceptor ground state. Examples of donors[2] in ZnS are Al on a Zn site or Cl on a S site. Acceptors[2] would be Li, Ag, or Cu on Zn sites or P on S sites.

[1] All correspondence should be directed to this author at SIEMENS AG, FL OHL, D 8000 München 83.

[2] In the past, donors were called "coactivators." Acceptors in ZnS were called "activators." We will not use these expressions since they can be somewhat misleading and are not relevant to our discussion.

[3] e.g., A. Gutekunst KG, D 7220 Schwenningen, Germany.

[4] ZnS(Cu) and ZnS(Ag) typically emit green or blue light, respectively.

Reprinted from **Journal of Chemical Education**, Vol. 58, Page 806, October 1981.

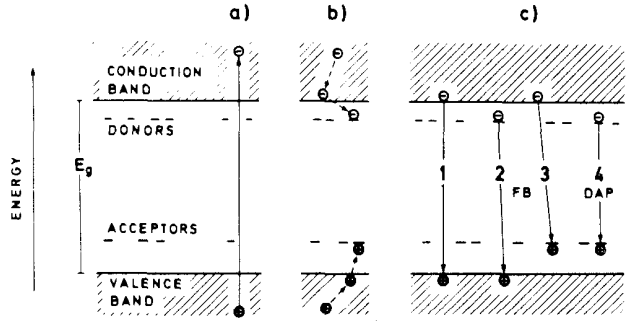

Figure 1. Excitation, relaxation, and recombination processes in a simplified energy level diagram for semiconductors. Donor and acceptor levels given by horizontal bars, charge of donor and acceptor cores *not* indicated (cf. text!) E_g: energy gap.

(a): Creation of electron-hole pair (incoming photon moves VB-electron into the CB)

(b): Relaxation of electron (hole) to the bottom (top) of CB (VB) and capture by ionized donor (acceptor)

(c): Radiative recombination processes. (1) band-to-band recombination. (2) recombination of donor bound electron with free hole. (3) recombination of free electron with acceptor bound hole. (4) donor acceptor pair transition.

Donors and acceptors are always present in real semiconductors, even if they are not intentionally doped. A semiconductor having more donors than acceptors is called n-type. If the semiconductor is in its ground state all acceptor levels are filled with donor electrons. A corresponding number of ionized donors is left. The excess donors are neutral, still having their electrons. On the other hand, if the number of acceptors exceeds that of the donors, the semiconductor is called p-type. In this case, all the donors are ionized after relaxation of the donor electrons to acceptor levels. The excess acceptors are neutral. In Figure 1, where excitation, relaxation and recombination processes are illustrated, these details are *not* shown. For the sake of simplicity we have used only horizontal bars to indicate the donor and acceptor levels. Electrons or holes bound to impurities are shown only if they are required to illustrate excitation or other processes. We also do *not* show the charge of the impurity cores, but it should be kept in mind, that a donor (acceptor) is neutral, if an electron (hole) is bound to the donor (acceptor), since the donor (acceptor) core is positive (negative) itself.

ZnS is always observed to be n-type (similar to CdS or ZnSe). On the other hand, ZnTe for example is always p-type. The reason for this behavior is related to some extent to the nature and type of native defects present in each material and is the subject of current research. (5)

If a semiconductor is irradiated with light, electrons can be moved from occupied states to higher lying unoccupied levels, provided the quantum energy $\hbar\omega$ of the incoming photons is sufficient. [Planck's constant $\hbar = h/2\pi = 1.05459 \times 10^{-34}$ Js; $\omega = 2\pi\nu$, where ν is the light frequency. The photon energy $\hbar\omega$ is related to the light wavelength λ in vacuum by the relation $\hbar\omega = 1239.85/\lambda$, where the expression yields $\hbar\omega$ in eV, if λ is inserted in nm. If the photon energy $\hbar\omega$ is larger than the band gap energy E_g, the predominant process is the excitation of electrons from the VB into the CB. This is equivalent to the creation of electron-hole pairs (cf. Fig. 1a).

Electrons excited higher into the CB relax down to the bottom of the CB by excitation of lattice vibrations, "phonons." Eventually the electrons are captured by donor states. Holes relax to the *top* of the VB and are eventually captured by acceptor states. (Relaxation of holes to the *top* of the VB and into acceptor states is understood easily by keeping in mind that holes correspond to missing electrons.)

Visible light may then be emitted by one of the following processes. (Cf. Fig. 1 c, the numbers in parentheses correspond to those in Fig. 1 c):

- recombination of a CB electron with an acceptor hole, i.e., transition of an electron from the CB to an unoccupied acceptor state (3)
- recombination of a donor electron with a hole in the VB (2)
- recombination of a donor electron with an acceptor hole (4)

The direct recombination process between CB electrons and VB holes (1) has very low probability because of the difficulty of simultaneously conserving both energy and momentum for these two particles. Processes (2) and (3) are often referred to in the literature as "free-to-bound" (FB) transitions, and process (4) is referred to as a "donor-acceptor-pair" (DAP) transition.

Recombination may occur also via exciton states. (An "exciton" is an electron-hole pair bound by the Coulomb attraction similar to the proton-electron pair of a hydrogen atom.) Exciton states will not be considered, since they are unimportant for the particular experiments discussed here. In general, however, exciton-related processes may be quite significant. Radiationless recombination processes will also not be discussed here, although they again may be important in many cases.

Experimental

For the performance of the experiments described below the following equipment is required: One ordinary ZnS screen, a ZnS screen containing a small amount of radioactive promethium ($^{147}_{61}$Pm), a lamp for UV excitation, a transparent (glass) dewar, liquid nitrogen, a He-Ne gas laser (output power 1 mW e.g.). One has to **make sure that the direct or the reflected laser beam does not hit the eye.** However, special goggles are not required.

ZnS screens suited for the experiments described here can be obtained from scientific supply houses or from manufacturers of luminescent dials for clocks.[3] ZnS screens with Pm content are generally supplied with a protective layer which prevents the rubbing off of radioactive material. Thus, the Pm-doped screen can be handled without special precautions.

As UV excitation source, a normal incandescent bulb can be used, where the radiation emitted in the visible and infrared spectral regions may be eliminated by a suitable filter.

Experiments and Interpretation

Experiment 1: A ZnS screen is illuminated with UV light. The screen luminesces and after switching off the UV source the light emission continues, typically for minutes or even for hours. The luminescence light is green or blue in general, depending on the impurities present in the ZnS.[4]

The following conclusion can be drawn immediately. Even if the luminescence is in the blue spectral region, the energy of the emitted photons is considerably smaller than the band gap energy E_g of ZnS. This indicates, that the recombination processes responsible for this light-emission are impurity-related. (More detailed investigations show, that the direct CB → VB transitions are negligible, as already mentioned above.) The transitions yielding visible light emission may either be DAP or FB transitions. Further information on the nature of the predominant recombination processes is provided by the following experiment.

Experiment 2: After UV excitation, the ZnS screen is put into a Dewar flask filled with liquid nitrogen ($T_N \sim 80$ K). The luminescence immediately stops. Finally, light emission starts anew if the screen temperature is raised again to room temperature.

Experiments 1 and 2 can be understood as follows: Both electrons and holes relax to the respective lowest available energy level and are most likely to be trapped by donors or acceptors, respectively. Consequently, one expects DAP transitions to be the predominant recombination process. However, the recombination probability between a donor electron and an acceptor hole is temperature *in*dependent. Thus, the observed strong temperature dependence of the emitted luminescence intensity seems to rule out this interpretation. The apparent contradiction is removed considering the following facts. The probability for a DAP transition decreases rapidly as the distance r_{DA} between the donor and the acceptor increases. DAP transitions are significant only as long as r_{DA} is comparable to the Bohr radius of the donor electron and that of the acceptor hole, (which are typically several nm). Although the principle of occupying the lowest possible energy level favors the electrons being bound to do-

nors, there is a small but finite probability W_{CB} for a donor electron to be in the CB. The electron then has some chance of recombining with an acceptor hole (FB transition process 3 in Fig. 1). Alternatively, the electron is captured again (after $\sim 10^{-12}$ s) by a donor. This donor may be closer to a neutral acceptor than the donor the electron was bound to before, and then the probability for radiative recombination via DAP transition is increased. The temperature dependence of W_{CB} is given by

$$W_{CB} \sim \exp(-E_D/kT) \qquad (1)$$

where E_D is the donor ionization energy and $k = 8.62 \times 10^{-5}$ eV K^{-1} is Boltzmann's constant. The exponential dependence given by eqn. (1) explains the strong decrease of luminescence as the ZnS screen is cooled down to liquid nitrogen temperature. Both processes, that of FB transition and that of transformation of distant DAP into closer DAP are reduced significantly at lower temperatures.

Considerations similar to those outlined here for electrons and donor states apply to holes and acceptor states. More detailed descriptions of the processes discussed here are given in References 6 and 7.

Another experiment is understood immediately on the basis of the foregoing.

Experiment 3: After irradiation of a ZnS screen with UV light, the screen is heated by a hot object placed onto the screen. Initially the luminescence from the hot parts of the screen increases, afterwards these areas appear dark. This is shown in Figure 2. The picture was taken 30 sec after putting a hot pair of tongs onto the screen.

The interpretation of the experiment is straightforward. According to eqn. 1, the radiative recombination probability is enhanced as the temperature of the screen is raised. This causes the increase of the luminescence but simultaneously de-excites the crystal.

The foregoing experiment can be modified using a He-Ne-laser to de-excite the crystal:

Experiment 4: The excited screen is irradiated with the 632.8 nm line of a He-Ne-laser (photon energy 1.959 eV). The areas irradiated with the laser initially luminesce brighter than the surrounding areas but appear dark afterwards. An example for this kind of experiment is shown in Figure 3.

The observations are interpreted as follows. Electrons trapped by donors are moved into the CB and then may recombine via FB transitions (cf. Fig. 1 c). Alternatively, an electron in the CB may be retrapped by a donor. If this donor is sufficiently close to a neutral acceptor, a DAP transition may occur, otherwise the electron is eventually moved again into the CB by a laser photon. (Again, similar considerations apply to holes.) The enhanced de-excitation of the ZnS by the He-Ne-laser radiation is in principle the same as in the case of de-excitation by raised temperature (cf. experiment 3).

It should be kept in mind that the energy of the laser radiation is too small to create electron-hole pairs or to lift electrons from acceptor into donor states. Thus, there is no more luminescence after all excited carriers have recombined. The He-Ne-laser radiation does not change the overall amount of luminescence emitted from the irradiated areas, but it causes the recombination to take place in a much shorter time.

Experiment 4a: If experiment 4 is performed while the screen is cooled to liquid nitrogen temperature (putting the screen into a transparent Dewar flask filled with liquid N_2), irradiation of the screen with the He-Ne-laser has the same effect as observed at room temperature. This result corresponds to what one would expect, since the important process of lifting electrons (holes) from the donors (acceptors) to the CB (VB) is essentially independent of the screen temperature.

Experiment 5: A ZnS screen containing a small amount of promethium ($^{147}_{61}$Pm, half life 2.6 years) luminesces without initial UV excitation. If the screen is irradiated with the He-Ne-laser similar effects as in experiment 4 occur. Initially the luminescence increases, then the irradiated areas get dark. However, in contrast to the situation observed on the screen without $^{147}_{61}$Pm contents, the dark areas start to emit light again, and thus disappear. If the ZnS screen containing $^{147}_{61}$Pm is put into liquid nitrogen (as in experiment 2) the luminescence intensity goes down; however, it does not drop to zero as in the case of the UV excited screen without $^{147}_{61}$Pm.

The interpretation of the observations is the following: $^{147}_{61}$Pm undergoes a β^--decay, i.e. emits fast electrons. Their maximum energy is 0.23 MeV. These high-energy electrons create electron-hole pairs, which relax and then may recombine radiatively by FB or alternatively by DAP transitions. Thus, there are two processes giving rise to luminescence in the case of a $^{147}_{61}$Pm doped screen, which was excited by UV irradiation: (a) the thermally induced transformation of distant excited DAP into closer pairs, and (b) the creation of (sufficiently close) excited DAP as a consequence of the β^--decay of the $^{147}_{61}$Pm. The latter process (b) is practically temperature independent, and it is the origin of the luminescence which persists even at liquid nitrogen temperature. On the other hand, the former process (a) ceases almost completely at low temperature and accordingly the luminescence intensity decreases, if the screen is cooled down. In the case of the undoped screen the former process (a) is the only one giving rise to luminescence after the end of UV excitation, thus the decrease of luminescence at low temperature is almost complete.

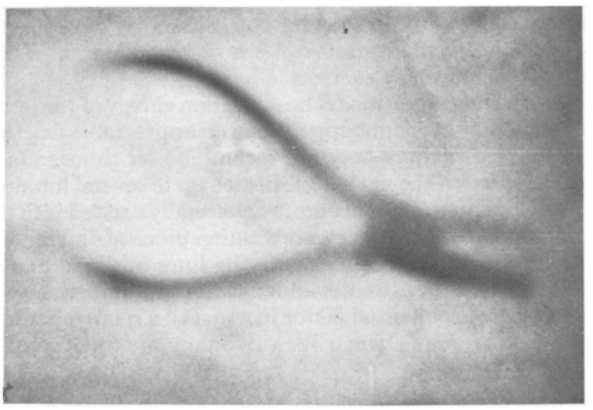

Figure 2. ZnS screen 30 sec after putting a hot pair of tongs onto a screen excited by UV irradiation before. Heated areas appear dark.

Figure 3. ZnS screen after UV excitation and subsequent irradiation with He-Ne gas laser. Dark lines forming "LASER" represent trace of laser beam on the screen.

The behavior of the $^{147}_{61}$Pm doped screen after UV excitation and subsequent irradiation with a He-Ne-laser is also explained easily. Areas which appear dark initially after stimulation of luminescence with the He-Ne-laser start to emit light again without additional UV excitation as a consequence of the continuous creation of electron-hole pairs all over the screen which is associated with the constant β^--decay of the $^{147}_{61}$Pm. On the other hand, dark areas remain dark in the screen *without* $^{147}_{61}$Pm content, since an excitation mechanism equivalent to the decay of $^{147}_{61}$Pm is lacking.

Application of Luminescence Measurements to Archeology

As mentioned in the introduction, the phenomena discussed here are not restricted to ZnS. Substances exist, where the time for excited carriers to remain trapped at impurities without recombining may be much longer than considered so far. It may amount to hundreds of thousands of years even at ambient temperature. Materials where such long trapping times are observed are loam and kaolin for example, and the age of pottery or other objects made from these materials can be determined by thermally stimulated luminescence ("thermoluminescence"). A detailed description of recent investigations of this type is given in Reference 8.

The principle of age determination by thermoluminescence is that kaolin or loam always contain a small amount of ra-

dioactive elements, in particular potassium ($^{40}_{19}K$) and several thorium ($_{90}Th$) and uranium ($_{92}U$) isotopes. When these elements decay, they may excite free carriers, which are trapped subsequently by impurities. The ionization energy of the latter is so large, that at room temperature an appreciable fraction of the excited carriers does not recombine for thousands of years. However, if the material is heated up to several hundred degrees Centigrade the carriers are thermally excited into the CB and undergo radiative recombination processes giving rise to observable luminescence along the lines outlined above. The strong temperature dependence of the luminescence is related to the exponential factor in eqn. (1): a relatively small increase of E_D may change W_{CB} by many orders of magnitude.

If the material having deep traps is heated, the total thermally excited luminescence intensity is (a) proportional to the contents of radioactive elements in the material, and (b) proportional to the time which has elapsed since a previous heating. Assuming that this former heating was that in the manufacturing process of the object under investigation, the measured luminescence intensity can be used to determine the age. In order to do this, the contents of radioactive isotopes and the effectiveness of exciting carriers in a decay process also must be determined.

Summary

We have shown how several simple experiments can illustrate many of the phenomena involved in the luminescence of a well known technologically important semiconductor, ZnS. The processes discussed apply to many other semiconductors as well. We use the experiments to help one understand the principles of age determination of ancient pottery and art objects using thermally stimulated luminescence.

The authors are indebted to S. Zierer for making the photographs, to G. H. Döhler and Don L. Kendall for helpful discussions and a critical reading of the manuscript, and to J. Voitländer for his continuous interest in the work.

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