Sensitization and Charge Carrier Kinetics in ZnO Powders

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The influence of the excess charge carrier injection mechanism on the excess charge carrier dynamics in ZnO powder is investigated by contactless transient photoconductivity measurements. Excess charge carriers were produced by above bandgap light, subbandgap light and by injection from an adsorbed dye (Rhodamine B) after excitation of this dye. In all these cases the transient photoconductivity decay extends over a large time range but only after band-to-band excitation an appreciable decay is observed in the microsecond time range. The experimental results are discussed in particular with respect to photocatalysis.

Keywords: Transient photoconductivity, sensitization, charge carrier kinetics, ZnO, photocatalysis.

Introduction

During the last years the interest in the electronic properties of semiconductor powders has increased [1], mostly because of the applicability of these materials in (photo-) catalysis [2]. However, the microscopic details of many photocatalytic mechanisms are not completely understood. Investigation of these mechanisms is usually performed by reaction product analysis [1]. In this context investigations of photoinduced charge carrier kinetics in semiconductor powders seem to be useful to complement the kinetic studies of charge transfer reactions [3]. In this work transient photoconductivity measurements are chosen as a tool for the investigation of charge carrier kinetics. A contactless transient photoconductivity method, the time-resolved microwave conductivity (TRMC) method, is used to avoid contact problems. The transient photoconductivity reflects the kinetics of mobile charge carriers induced by a light pulse. The interpretation of the decay behaviour is not simple as semiconductor powders are essentially heterogeneous. Complex kinetics is observed [4, 10], and a detailed microscopic interpretation will in general not be possible. For this reason it is preferred to study charge carrier kinetics in a relatively well known system under small variations of the experimental conditions. An interesting topic to be studied by transient photoconductivity measurements is the influence of different excitation processes on excess charge carrier kinetics. In this work ZnO powder is chosen as a model system to investigate this influence. Band-to-band excitation can be induced in this compound by light exceeding the band gap energy of about 3.2 eV, producing initially mobile electrons and mobile holes. Light of lower energy induces transitions from states in the bandgap to the bands producing mobile and localized charge carriers. A third possibility is given by adsorption of a dye on ZnO powder surfaces and charge carrier injection from the excited dye. ZnO treated with Rhodamine B is a well studied system [5, 6, 7] in which electrons are injected from the excited dye molecules to the conduction band [7].

Experimental

The time-resolved microwave conductivity (TRMC) method is based on the measurement of the relative change $\Delta P(t)/P$ of the microwave power reflected from a sample caused by a change $\Delta\sigma$ of the conductivity of the sample which is induced by a laser flash. In a small perturbation approximation a proportionality between $\Delta P(t)/P$ and $\Delta\sigma$ was derived [8]:

$$\Delta P(t)/P = A\,\Delta\sigma(t), \tag{1}$$

where A is a time independent proportionality factor. the signal $\Delta P(t)/P$ obtained with this technique will be called microwave photoconductivity. Because the electron mobility μ_e in ZnO is much larger than the hole mobility [9], $\Delta\sigma(t)$ can be attributed to excess electrons:

$$\Delta\sigma(t) \approx \Delta n(t)\, e\, \mu_e \tag{2}$$

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where $\Delta n(t)$ is the concentration of the excess electrons and μ_e their mobility.

The transient photoconductivity data will be displayed on double-logarithmic plots. Although this way of representation can obscure details of the decay processes, this is convenient because of the large signal and time range covered by the photoconductivity decay in ZnO powder. This way of representation is often used for transient photoconductivity measurements in amorphous semiconductors [11], where the extended decay of the transient photoconductivity is related to the presence of exponential band tails within the semiconductor bandgap (mobility gap). A convenient parameter used to discuss an extended decay in general is the decay rate defined as

$$k(t) = \frac{-1}{\Delta n(t)} \left(\frac{\partial \Delta n(t)}{\partial t} \right)_t . \tag{3}$$

The decay rate is in general time dependent but is independent of time for first order decay reactions.

Excess charge carriers were produced by illumination with 12 ns (Full Width a Half Maximum) pulses of a Nd:YAG laser at 532 nm and at 266 nm.

The TRMC experiments were performed in an X-band (8–12.4 GHz) home made equipment essentially identical to the K-band equipment described previously [8]. An increase in sensitivity is obtained by insertion of the sample into a microwave cavity. Measurements in the time range of seconds are possible by the use of a stabilized electronic circuitry and ZnO pellets. The pellets were pressed from a mixture of ZnO powder (Merck, p. A.) and a ten times greater amount of KBr (Merck, p. A.) after grinding in a mortar.

Sensitization of the ZnO powder was achieved by suspending the powder in a 10^{-4} M solution of Rhodamine B in methanol and subsequent evaporation at room temperature.

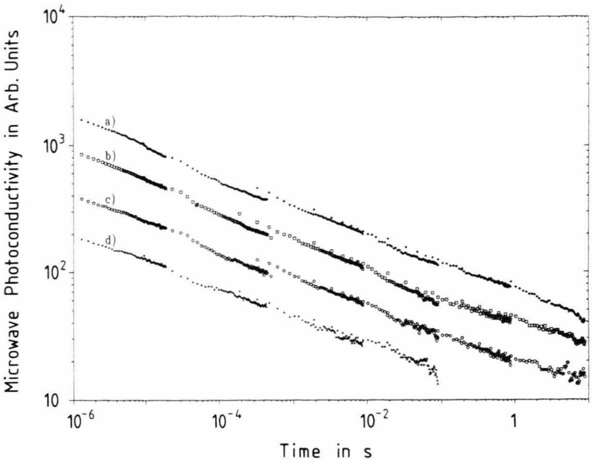

Fig. 1. Photoconductivity of ZnO powder after excitation with a 266 nm 12 ns (FWHM) laser pulse, Laser intensity: a) 10 mJ/cm^2 b) 3 mJ/cm^2 c) 1 mJ/cm^2 d) 0.3 mJ/cm^2.

Results

Transient Photoconductivity Induced by Band to Band Excitation

The transient photoconductivity induced by 266 nm light pulses in untreated ZnO powder is displayed in Figure 1. Initially mobile electrons and mobile holes are produced by light of this wavelength. The signal must be attributed to excess electrons because the electron mobility is much larger than the hole mobility in ZnO [9]. The initial signal height, i.e. the signal at 1 μs increases sublinearly with the excitation density. Decay processes depending on the excitation density must be assumed to be operative at a time scale faster than the time resolution of the present measurements. This is confirmed by measurements in the nanosecond time range where an initial fast decay was observed. The high absorption coefficient of ZnO at 266 nm and the short time scale localize these processes at the illuminated surfaces of the powder grains.

The excess electron decay extends over a very large time range with a decay rate decreasing with time. A slope $\alpha = -0.2$ is obtained on a double logarithmic plot over the whole time range, independent of the excitation density (Figure 1). This is described by an exponential time dependence of the excess electron density $\Delta n(t)$:

$$\Delta n(t) \propto t^{\alpha} = t^{-0.2} . \tag{4}$$

Transient Photoconductivity Induced by Subbandgap Excitation

The transient photoconductivity induced in ZnO powder by 532 nm light pulses decays initially slower than after UV-light excitation (Figure 2). Also after 532 nm light excitation the transient photoconductivity can be attributed to mobile electrons. However, it must be assumed that electron states in the bandgap are excited because the energy of the exciting photons at 532 nm (2.32 eV) is not sufficient to induce band-to-band transitions. Consequently mainly mobile electrons and localized holes are produced by 532 nm excitation.

Also after subbandgap excitation the decay rate decreases with time. The decay rate in the microsecond time range increases slightly with increasing excitation density (Figure 2). This indicates that the availability of excess holes at least partially controls the electron decay in this time range. This can also explain the slightly sublinear dependence of the initial signal height on the excitation density (Figure 2).

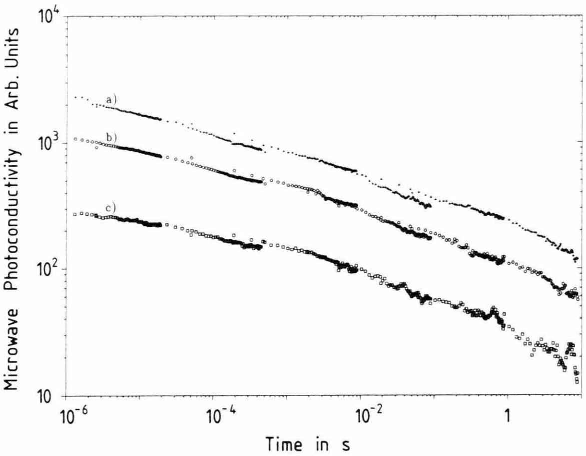

Fig. 2. Photoconductivity of ZnO powder after excitation with a 532 nm 12 ns (FWHM) laser pulse, Laser intensity: a) 1 mJ/cm^2 b) 0.25 mJ/cm^2 c) 0.05 mJ/cm^2.

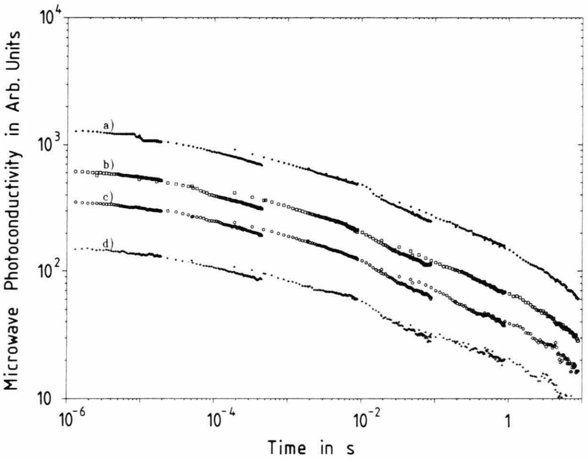

Fig. 3. Photoconductivity of ZnO powder sensitized by Rhodamine B after excitation with a 532 nm 12 ns (FWHM) laser pulse, Laser intensity: a) 10 μJ/cm^2 b) 5 μJ/cm^2 c) 2.5 μJ/cm^2 d) 1 μJ/cm^2.

Transient Photoconductivity Induced by Dye Sensitization

Excitation of adsorbed Rhodamine B at 532 nm leads to an efficient injection of electrons into the conduction band of ZnO. In the excitation density range covered, the transient photoconductivity is proportional to the excitation density (Figure 3). The signal height observed in the dye sensitized powder (Fig. 3) is at least one order of magnitude higher than in the untreated powder at the same excitation intensity (Figure 2). Therefore the signal in the sensitized powder refers to electrons injected from excited dye molecules and the contribution of excess charge carriers induced by direct excitation of states in the bandgap can be neglected at the excitation densities used in Figure 3. After electron injection the oxidized dye molecule relaxes where the positive excess charge is located at the semiconductor surface. Direct information on the time scale of the injection mechanism cannot be extracted from the present measurements and also preliminary measurements with 1 ns time resolution indicated identical rise times of the signals independent on the nature of the excitation process. Evidently the results are limited by the time resolution of the measurements, which gives an upper limit of 1 ns for the injection process. No decay of the signal in the nanosecond time range is observed, in contrast to the photoconductivity signals obtained by direct excitation of the semiconductor.

In the microsecond time range the excess electron population in the ZnO powder after sensitization (Fig. 3) decays initially slower than in the non-sensitized case (Figures 1, 2). The shape of the transients indicates again a decay rate that decreases with time. The most probable decay channel is the reaction of electrons with the excess positive charges located at the surface. This is obviously a very inefficient decay channel because of the relatively slow decay observed experimentally (Figure 3).

Discussion

The slower decay of the transient photoconductivity after 532 nm excitation (Fig. 2) than after 266 nm excitation (Fig. 1) excludes the decay of photoinduced excess electrons solely via intrinsic states in the bandgap as the main decay channel after band-to-band excitation. Mobile holes must be involved in some stage of the decay process. Homogeneous second order recombination can be excluded because of the decay behaviour observed (Figure 1). Equation (4) points to a thermally activated process as the rate determining step of the decay. A model fitting the experimental data (Fig. 1) is a reaction between excess conduction band electrons and holes emitted from a broad exponential distribution of states above the valence band. A similar mechansim of excess charge carrier recombination was proposed in amorphous silicon, which leads to similar photoconductivity decay curves [12, 13].

An important question that cannot be answered by the present experiments is whether 532 nm light excites mainly surface states. In this case the decay of the transients displayed in Fig. 2 reflects a reaction between mobile electrons and positive charges located at the surface, as those in Figure 3. The different decay behaviour in Figs. 2 and 3 then reflects the different reactivity of the two kinds of localized holes to electrons. If, on the contrary, 532 nm light excites mainly states in the bulk of the powder grains, the decay of the transients in Fig. 2 is due to slow recombination processes probably controlled by thermal emission of excess localized holes to a recombinative state. As the decay rate after 532 nm excitation approaches the decay rate after 266 nm excitation in the long time range (> ms) a similar process is suggested in this time range. Probably the excess holes have established a similar distribution in this time range.

The slow decay of the transient photoconductivity in the sensitized sample in the microsecond time range (Fig. 3) reflects a highly efficient charge carrier separation. The positive charge localized at the surface is available even for relatively slow catalytic reactions because the concurrent recombination reaction with electrons is slow. The photocatalytic activity of ZnO powder depends evidently on the possibility of a definitive separation of excess electrons and holes. This is determined by the exchange probability of the localized positive charge. An efficient hole trapping increases the life time of the reductive electrons. Our results indicate that efficient photocatalytic reactions can be expected for holes trapped by an adsorbed redox system (hole scavengers, sacrificial donors) located in the bandgap of the semiconductor. Reinjection of these holes is highly improbable, which strongly increases the lifetime of the photoelectrons. The extended time range of the transient photoconductivity decay in ZnO powder is remarkable. This does not seem to be a particular property of this compound, because it is also noted in the case of other semiconductor powders [4]. It is obvious that this phenomenon is related to the large density of states in the bandgap present in these systems. If emission from these states controls the decay of the mobile charge carriers, a broad energy distribution of these states leads to an extended decay of the transient photoconductivity.

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