Кинетика процессов в конденсированных фазах и на межфазных границах.

Границы раздела и кинетика реакций на полупроводниковых электродах.

Lecture 3. Dark and Light Processes. Photogeneration of Electron-Hole Pairs. Quasi-Fermi Energies. Gaertner Equation.

Dr. O.A. Semenikhin

МГУ-2017

Elementary Steps of a Photoprocess

1. Light absorption, creation of electron-hole pairs or excitons.
2. Separation of the electron-hole pairs; exciton dissociation.
3. Bulk or surface recombination of photoexcited carriers.
4. Transport of photogenerated carriers in the bulk of a semiconductor.
5. Extraction of carriers at contacts/photoelectrochemical reactions at the interfaces. Reactions through surface states or directly through a corresponding bands.

Quasi-Fermi Energies

- The electrons and holes in a semiconductor can be involved in three different equilibria.
- Two first ones are the ones between electrons in the conduction band and between holes in the valence band separately. The process involved is called thermalization (essentially, collisions between cariers).
- The third one is between the electrons and holes in their respective bands and involves interband generation/refombination
- The overall (final) equilibrium involves all three components.
- However, the times of establishing the first two equilibria and the third one are very different, especially in indirect semiconductors where recombination and interband transitions in general are relatively slow (ps vs. ns).

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Quasi-Fermi Energies

- As a result, the electrons or holes can be in equilibrium within their corresponding bands, but not in equilibrium between each other.
- This would mean that in each band the electron/hole concentrations can be described by Fermi-Dirak statistics, but with the corresponding energies that are different from the true Fermi energy which are established after all the internband processes had time to occur.
- These energies are called quasi-Fermi energies.
- In many practical cases when a semiconductor is not in equilibrium, such as carrier photogeneration and extraction, carrier injection, current flow, etc., the electrons and holes still can be considered as being in equilibrium within corresponding zones and quasi-Fermi energies can be used.

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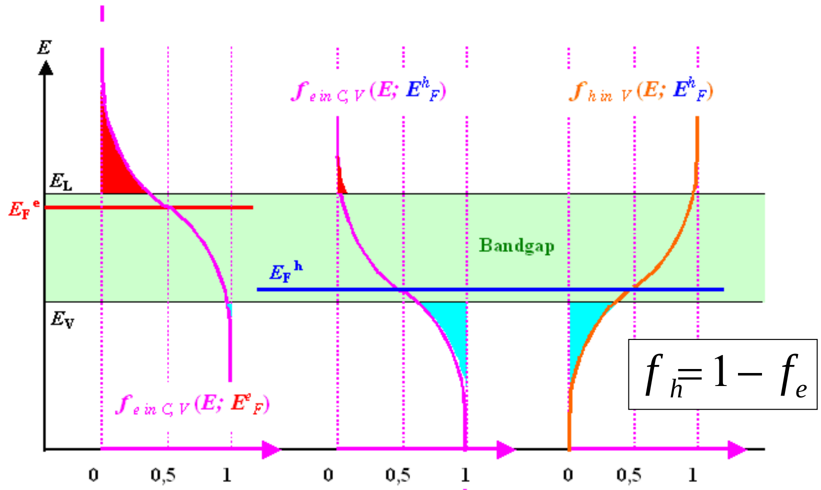
Quasi-Fermi Energies

$$n_e = N_{eff}^{\,e} \cdot \exp -\frac{E_C - E_F}{kT} \qquad n_h = N_{eff}^{\,h} \cdot \exp -\frac{E_F - E_V}{kT}$$

$$n_e^* = N_{eff}^{\,e} \cdot \exp -\frac{E_C - E_F^{\,e}}{kT} \qquad n_h^* = N_{eff}^{\,h} \cdot \exp -\frac{E_F^{\,h} - E_V}{kT}$$

Image: http://www.tf.uni-kiel.de/matwis/amat/semi_en/kap_2/backbone/r2_3_2.html

Quasi-Fermi Energies



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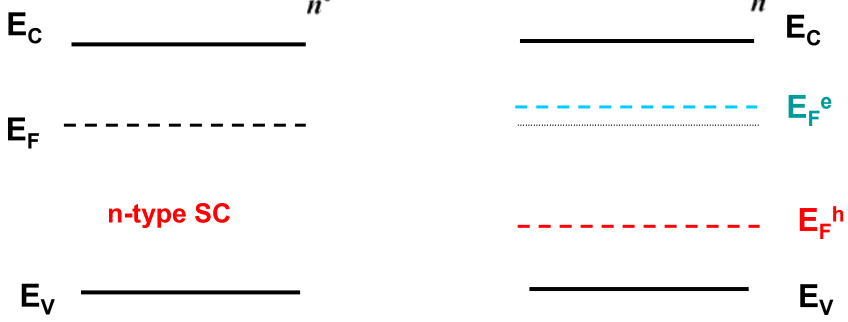
Quasi-Fermi Energies

$$E_F^e = E_C - kT \cdot \ln \frac{N_{eff}^{\,e}}{n^{e*}} \qquad E_F^h = E_V + kT \cdot \ln \frac{N_{eff}^{\,h}}{n^{h*}}$$



The changes in the carrier concentration and hence in the position of the quasi-Fermi energy is most pronounced for minority carriers (there were a lot of majority carriers even before illumination). So are photocurrents, which are therefore currents or minority carriers!

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Quasi-Fermi Energies

$$E_F^h = E_V + kT \cdot \ln \frac{N_{eff}^h}{n^{h,*}} \qquad E_F = E_V + kT \cdot \ln \frac{N_{eff}^h}{n^h}$$

$$E_F - E_F^h = kT \cdot \ln \frac{n^{h,*}}{n^h}$$

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Separation of electron-hole pairs and their reactions

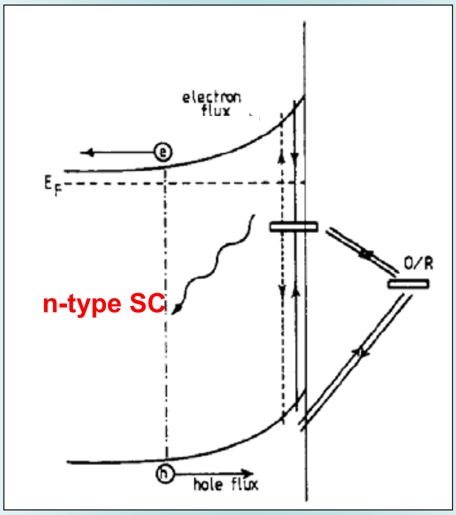

Image: L.M. Peter, Chem. Rev. 1990. 90, 753-769

Bulk and Surface Recombination

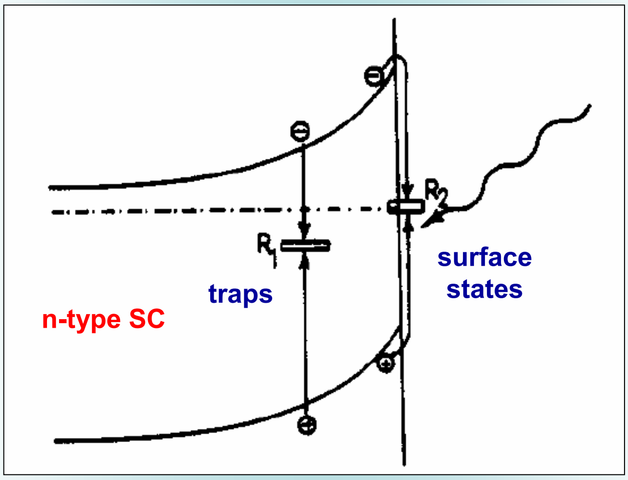

Image: L.M. Peter, Chem. Rev. 1990. 90, 753-769

Types of Bulk Recombination

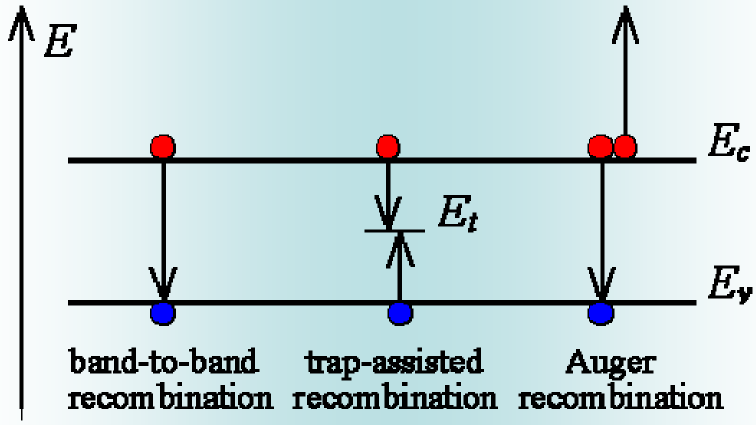

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Image: http://ecee.colorado.edu/~bart/book/book/chapter2/ch2_8.htm

Recombination Rate. Lifetime.

- The recombination rate is usually defined by a very important parameter called the lifetime of minority carriers. This parameter originates from kinetic treatment of the recombination process called Shockley-Hall-Read (SHR) statistics. It is broadly similar to the collision model used in chemical kinetics.
- The expression for the lifetime looks as follows:

$$\tau = \frac{1}{v \cdot s \cdot N}$$

- Here ***N*** is either the concentration of majority carriers (direct) or density of traps in the midgap (indirect recombination), ***v*** is the average thermal velocity of minority carriers in their band, and ***s*** is a scattering of capture cross section (a physicist's way of referring to a rate constant ☺).

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Recombination Rate. Lifetime.

➢For the trap-assisted recombination, the lifetime will depend on both the population of the midgap levels with the majority carriers and the probability of capture of minority carriers by the traps. Both these parameters depend on the position of the trap in the midgap…

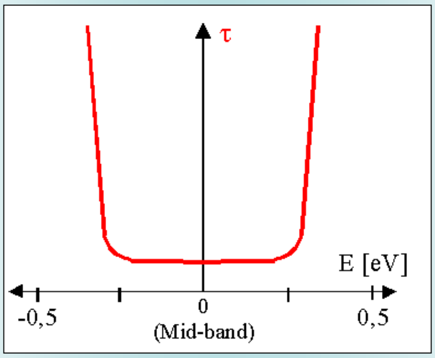

Image: http://www.tf.uni-kiel.de/matwis/amat/semi_en/kap_2/backbone/r2_3_3.html

Recombination Rate. Lifetime.

➢The lifetime is also inversely proportional to the trap concentration, as could be expected…

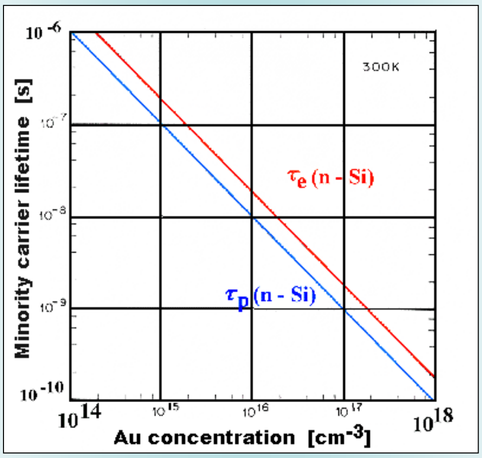

Image: http://www.tf.uni-kiel.de/matwis/amat/semi_en/kap_2/backbone/r2_3_3.html

Transport, Generation and Recombination in the Bulk

concentration of excess minority carriers

generation

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2} - \frac{n}{\tau} + \alpha I_0 e^{-\alpha x}$$

minority carrier diffusion

minority carrier lifetime defined by bulk recombination

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Gaertner's Model

PHYSICAL REVIEW VOLUME 116, NUMBER 1 OCTOBER 1, 1959

Depletion-Layer Photoeffects in Semiconductors

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(Received May 5, 1959)

The theory of photoconduction through the reverse-biased *p-n* junction in semiconductors is developed without the customary assumption that carrier generation in the junction depletion layer is negligible. Different from previous theories, the more general treatment leads to a voltage dependence of the photocurrent and its spectral distribution. When the incident light beam is modulated at frequencies comparable to the transit time through the depletion layer, a phase shift between the photon flux and photocurrent is noticed and transit-time rectification occurs.

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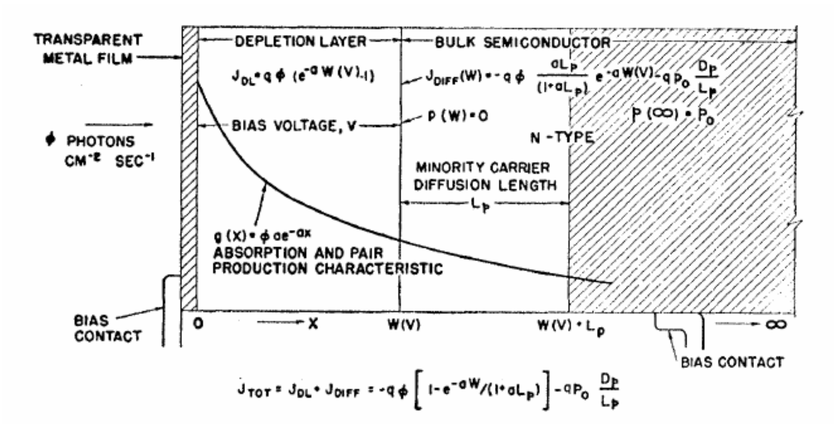
Gaertner’s Model



absorption coefficients of germanium and silicon. The photocurrent through the barrier will, therefore, consist of two contributions; one due to the carriers generated inside the depletion layer, and another due to carriers generated in the adjacent bulk material and diffusing into the junction. Since the thickness of the depletion layer, and thus the number of generated carriers which actually cross the junction, varies as a function of the voltage across the junction, deviations from the usual theory of the *p-n* junction photoeffect are observed, in particular, in the reverse biased condition.

Gaertner’s Model

The total current density through the reverse-biased depletion layer is given by

$$J_{TOT}=J_{DL}+J_{DIFF}, \qquad (A.1)$$

where J_{DL} is the drift current density due to carriers generated inside the depletion layer, and J_{DIFF} is the diffusion current density of minority carriers generated outside the depletion layer in the bulk of the semiconductor and diffusing into the reverse-biased junction. Recombination and thermal generation of carriers inside the junction will be neglected, but may be noticeable in material with a high concentration of recombination centers, and then would cause additional modifications of the theory. We consider monochromatic radiation only, in which case the absorption and pair production characteristic is given by

$$g(x)=\Phi a e^{-ax}. \qquad (A.2)$$

$g(x)$ and other pertinent quantities are shown in Fig. 1. $g(x)$ is the generation rate (density generated per unit time), Φ is the total incident photon flux, ($\Phi=\int_0^\infty g(x)dx$), and a is the monochromatic absorption coefficient.

J_{DL} is thus found to be equal to

$$J_{DL}=q\int_0^W g(x)dx=q\Phi(e^{-aW}-1). \qquad (A.3)$$

All light absorbed in the depletion layer gives rise to photocurrent!

Gaertner's Model

For definiteness let us consider an n-type semiconductor. In this case, the hole density in the bulk semiconductor region, $x > W$, is determined from the diffusion equation:

$$D_p p'' - (p - p_0)/\tau + g(x) = 0, \qquad \text{(A.4)}$$

no migration term, solution is easier

where D_p is the diffusion coefficient for holes, p is the hole density, p_0 is the equilibrium hole density, and τ is the lifetime of excess carriers. The solution of Eq. (A.4) under the boundary conditions

$$p = p_0 \quad \text{for} \quad x = \infty, \qquad \text{(A.5)}$$

no photoexcitation in the bulk, all light absorbed before reaching there

and

$$p = 0 \quad \text{for} \quad x = W \qquad \text{(A.6)}$$

all holes are extracted into the contact

is given by

$$p = p_0 - (p_0 + A e^{-aW}) e^{(W-x)/L_p} + A e^{-ax}, \qquad \text{(A.7)}$$

with $L_p = (D_p \tau)^{\frac{1}{2}}$ and

diffusion length for holes

$$A = (\Phi / D_p) \frac{a^2 L_p^2}{a(1 - a^2 L_p^2)}. \qquad \text{(A.8)}$$

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Gaertner's Model

The diffusion current density, $J_{DIFF} = qD_p p'$, at $x = W$ is thus obtained as

$$J_{DIFF} = -q\Phi \frac{aL_p}{(1 + aL_p)} e^{-aW} - q p_0 \frac{D_p}{L_p}. \qquad \text{(A.9)}$$

The last term is usually omitted since in an n-type semiconductor p_0 can be neglected

$$J_{TOT} = J_{DL} + J_{DIFF} = -q\phi \left[1 - e^{-aW}/(1 + aL_p) \right] - q p_0 \frac{D_p}{L_p}$$

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Gaertner's Model

Furthermore, if $\alpha^{-1} << W$ (weakly absorbed light), then

$$j_{photo} = -q\Phi(1 - \frac{1}{1+\alpha Lp}(1-\alpha W)) =$$

$$= -q\alpha\Phi \frac{Lp + W}{1+\alpha Lp}$$

If further Lp<<W (high recombination in the quasi-neutral region or low mobility), then

$$j_{photo} = -q\alpha\Phi W$$

The photocurrent is proportional to the width of the space-charge layer!

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Gaertner's Model

$$j_{photo} = -q\alpha\Phi W$$

We remember from earlier lectures that;

$$L_{sc} \equiv \Phi = \sqrt{\frac{2\varepsilon\varepsilon_0}{e_0 N_D}\left|\phi - \phi_{fb}\right|}$$

The photocurrent is proportional to the square root of the bias applied across the space-charge region and will also increase with a decrease in the donor density (wider SCR).

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Wilson's Model

A model for the current-voltage curve of photoexcited semiconductor electrodes

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(Received 6 May 1977; accepted for publication 1 June 1977)

A model to describe the behavior of photoexcited electrodes in an electrochemical cell is developed. In addition to the bulk semiconductor properties, the important parameters are a surface recombination parameter S_r and a surface electron transfer parameter S_t. It is the electron transfer process across the interface that leads to current in the external circuit. Using experimental curves for oxygen evolution at an n-type TiO_2 electrode and Hall-Shockley-Read recombination to determine S_r, it is shown that the I-V curve in anodic bias is controlled by the competition between S_r and S_t. The physical basis for S_t is discussed and experimental approaches to investigate surface reactions are suggested.

4292 Journal of Applied Physics, Vol. 48, No. 10, October 1977

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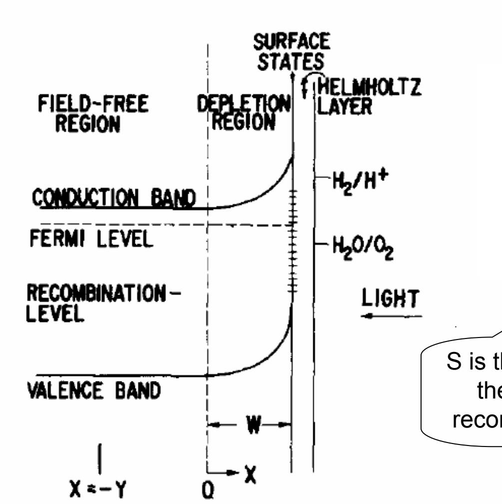
Wilson's Model



Using the boundary conditions

p finite at $x \to -\infty$,

p continuous at $x = -y$,

and

$$-D\frac{dp}{dx} = Sp, \quad \text{at } x = 0,$$

S is the kinetic parameter related to the rates of surface reactions, recombination and charge transfer

$$S = S_r + S_t$$

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Wilson’s Model

$$j_{photo} = -q\Phi \frac{S_t}{S_t + S_r}\left(1 - \exp(-\alpha W) + \exp(-\alpha W)\frac{L_p}{L_p + D/S}\frac{\alpha L_p}{\alpha L_p + 1}\right)$$

cf. (Gaertner’s model):

$$j_{photo} = -q\Phi\left(1 - \exp(-\alpha W)\frac{1}{\alpha L_p + 1}\right)$$

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Wilson’s Model

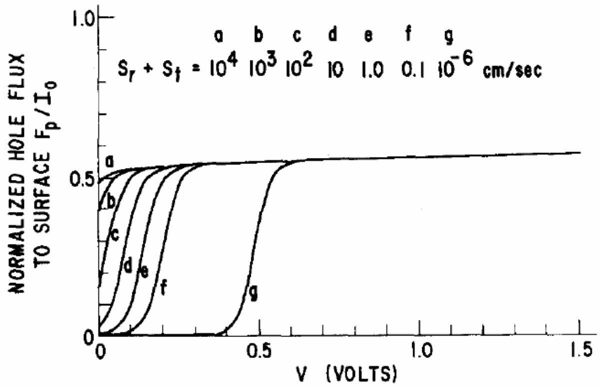

FIG. 2. Calculated hole flux to the surface with the surface reaction parameters indicated. Diffusion length $L = 10^{-4}$ cm; absorption coefficient $\alpha = 10^4$ cm^{-1}; doping density $N = 10^{18}$ cm^{-3}.

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Wilson's Model

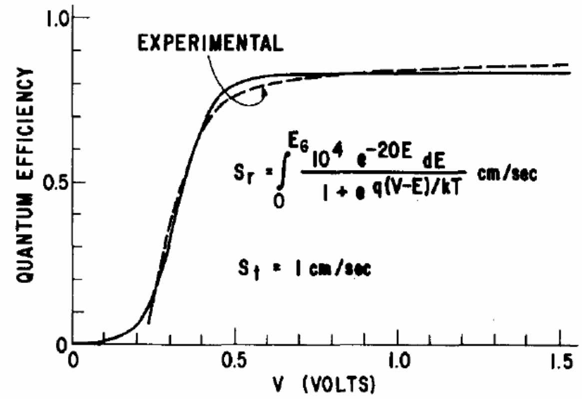

FIG. 6. Quantum efficiency versus voltage across the depletion layer. Dashed curve—experimental measurement on an etched TiO_2 crystal. Solid curve—calculated using $\alpha = 10^4$ cm^{-1}, $N = 6 \times 10^{17}$ cm^{-3}, $L = 4 \times 10^{-4}$ cm, $S_t = 1$ cm/sec, and S_r due to a distribution of surface states decreasing exponentially from the conduction band.

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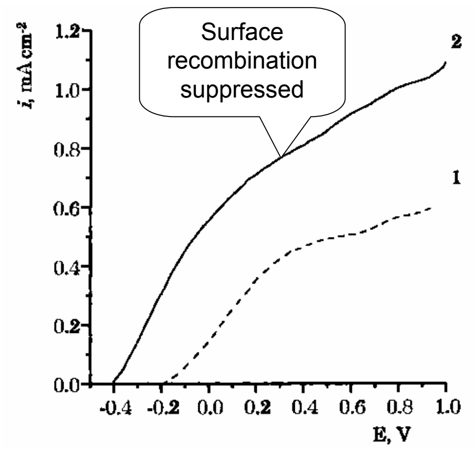
Experimental effect of surface recombination



Semenikhin et al Langmuir 15, 1999, 3731

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