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Kinetics of the photoinduced phase transition at the surface of a semiconductor with renormalized bandgap

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Abstract

A unified approach to describing all the stages of a nonequilibrium first-order phase transition is proposed based on the analogy with the decomposition of a supersaturated solid solution without using the generalized thermodynamic potential. Expressions for the asymptotic particle size distribution function for the new phase at the late transition stages, as well as for the critical particle radius are obtained.

1. Introduction

Semiconductors with a renormalized bandgap present considerable theoretical and practical interest for optoelectronics applications [1–3]. The most remarkable feature in such a system is the photoinduced phase transition, that is a dramatic change in absorption coefficient, hence in the conduction band electron concentration for critical incident intensities [4]. The photoinduced phase transitions are expected to be observable in widegap cooled semiconductors such as CdS and ZnSe [2–4].

The essential feature of the photoinduced phase transition is its nonequilibrium nature, although it is similar to first-order phase transition. An adequate description of the kinetics of nonequilibrium phase transitions is a fundamental problem in physics. The evolution of a new phase is known to proceed in two stages. The initial stage involves growth of separate nuclei of a new phase, and is closely related to the mechanisms of their formation [5]. The late stage involves further growth of larger nuclei at the expense of smaller nuclei [6]. These two stages are usually treated separately, although the same kinetic equation is used in both cases.

The purpose of the present paper is to present an approach that would describe the above two stages in a unified manner, in terms of the photoinduced phase transition on the surface of a semiconductor with renormalized bandgap.

It is known that concentration fluctuations may result in formation of a nucleus of a new, strongly absorbing phase. It is shown that under certain conditions this nucleus will be in unstable equilibrium with the weakly absorbing environment. It is shown that at late stages of a nonequilibrium kinetic transition the behaviour of nuclei resembles that of Ostwald ripening.

2. Physical model and basic equations

Let the surface ($z = 0$) of a semiconductor wafer having thickness l be illuminated by a broad beam with photon energy just below bandgap and uniform intensity I_0. The radiative transfer equations for a laser beam with intensity I, photocarrier density $n(x, y, z, t)$ will be given by

$$\frac{\partial I}{\partial z} = -\alpha(\omega, n)I \tag{1}$$

$$\frac{\partial n}{\partial t} = D_\perp \left(\frac{\partial^2 n}{\partial x^2} + \frac{\partial^2 n}{\partial y^2} \right) - D_z \frac{\partial^2 n}{\partial z^2} + \alpha(\omega, n) I(z) - \frac{n}{\tau} \tag{2}$$

where $\alpha(\omega, n)$, $D_\perp$, D_z are the absorption coefficient and the carrier diffusion coefficients along and across the wafer, respectively, and τ is the photocarrier lifetime. The longitudinal inhomogeneity of carriers density distribution is associated with inhomogeneity of light absorption, and the cross inhomogeneity of carrier density distribution is associated to natural inhomogeneity of a semiconductor wafer. The absorption coefficient behaviour as a function of radiation frequency depends appreciably on the difference $(\hbar\omega - E_g^*)$, where E_g^* is the bandgap.

The intraband absorption is assumed to be constant,

$$\alpha(\omega, n) = \alpha_1 \tag{3}$$

and weak, $\alpha_1 \ll \alpha_0$. The frequency dependence of the absorption coefficient $\alpha(\omega, n)$ for direct interband transitions is given by

$$\alpha(\omega, n) = \alpha_2(\omega, n) = \alpha_0 \sqrt{\frac{\hbar\omega - E_g^*}{E_g}} \tag{4}$$

where α_0 is a constant. For beam intensities high enough to to give rise to correlation effects, the bandgap will be renormalized to

$$E_g^* = E_g(1 - cn) \tag{5}$$

where the concentration coefficient of the bandgap is given by $c = E_g^{-1} \partial |E_g| / \partial n$.

For sufficiently high intensities $I > I_c$, explicit incorporation of $E_g^* = E_g^*(n)$ into the absorption coefficient will result in concentration nonlinearity of absorption, i.e. in an abrupt absorption increase. This permits the absorption coefficient to be replaced by a step function in the sharp absorption edge limit [1]

$$\alpha(\omega, n) = \alpha_1 + \theta(n - n_c)(\alpha_2 - \alpha_1) \tag{6}$$

where n_c is the critical photoelectron concentration for the onset of correlation effects. Absorption will continue to increase until filling of states becomes significant.

The physical model of a semiconductor with a strongly nonlinear absorption due to bandgap narrowing with increasing density of photocarriers given by equations (1)–(5), has been used by the present authors [7] to evaluate the effect of laser fluctuations on multimodal electron and hole distributions. In the problem there are two reference lengths: the diffusion length $L_z = D_z \tau$ and length of light absorption $\Lambda(\omega, n) = \alpha^{-1}(\omega, n)$, for which is supposed the requirement $L_z \gg \Lambda \geqslant l$. Taking this into account, for the solution of combined equations (1) and (2) we search for an expansion on the small parameter $\Lambda/L \ll 1$

$$n(x, y, l/2 \pm z) = n(x, y, l/2) \pm (l/2 - z) \frac{\partial n}{\partial z}|_{(x,y,l/2)} \pm \ldots$$

where the quantity $n(x, y, l/2)$ is the mean photocarrier concentration on the wafer thickness and does not depend on coordinate z. Viewing only order zero in concentration and introducing

the intensity value averaged over the wafer thickness, we obtain a nonlinear equation for generation–recombination balance.

$$\frac{\mathrm{d}n}{\mathrm{d}t} = D\Delta n + I_0 l^{-1}\{1 - \exp[-\alpha(\omega, n)l]\} - \frac{n}{\tau} \tag{7}$$

where $\Delta = \partial^2/\partial x^2 + \partial^2/\partial y^2$, $D \equiv D_\perp$.

For a fixed incident light frequency, equation (7) becomes

$$\frac{\mathrm{d}\eta}{\mathrm{d}\theta} = \delta\Delta'\eta + \beta\{1 - \exp[-\lambda_1 - \theta(\eta - \eta_0)(\lambda(\Omega(1+\eta))^{1/2} - \lambda_1)]\} - \eta = \delta\Delta'\eta + f(\eta) \tag{8}$$

where $\eta = n/n_c$, $\theta = t/\tau$, $\beta = I_0\tau n_c^{-1}l^{-1}$, $\lambda = \alpha_0 l$, $\lambda_1 = \alpha_1 l$, $\Omega = (\hbar\omega - E_g)/E_g$, $\delta = D\tau n_c^{-1}l^2$, $\Delta' = \partial^2/\partial(x/l)^2 + \partial^2/\partial(y/l)^2 = \partial^2/\partial x'^2 + \partial^2/\partial y'^2$ are dimensionless variables.

3. Growth rate of a nucleus of a new phase

For a steady-state and uniform case, equation (8) can have one, two or three solutions, depending on the magnitude of the parameteric variable β (see figure 1). In the latter case, equation (8) has two stable steady-state uniform solutions η_1 and η_3, and an unstable intermediate solution. Physically, each stable solution can be related to a phase, and the unstable state to a transition point. This enables one to make use of the notions of the theory of phase transitions. Thus, only one phase will be present to the left of η_1 and to the right of η_3, while between these solutions, the two phases will coexist.

In the region where the two phases coexist, the low-absorption phase will be stable, and the high-absorption phase unstable to the left of the transition point, while to the right of this point, the reverse is true. In extended bistable systems, the stable steady-state uniform

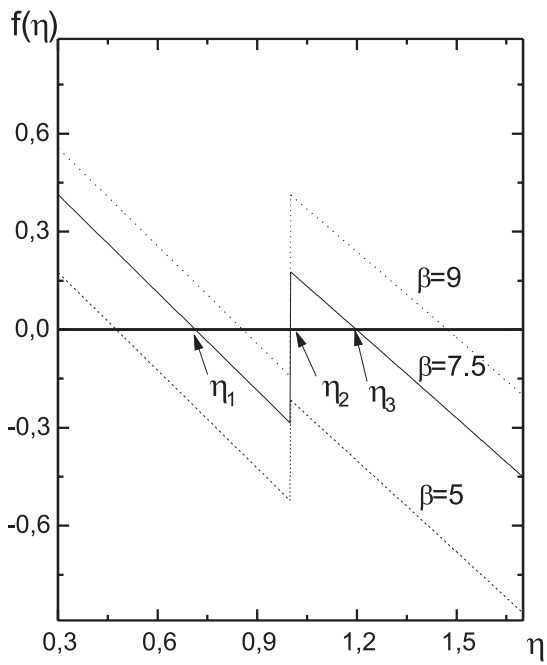

Figure 1. Plot of function $f(\eta)$ for various parameters β.

solutions (in this case, the low-absorption phase η_1 and the high-absorption phase η_3) are coupled through a switching wave which is a self-similar solution of a nonuniform equation (equation (8)). We now evaluate the velocity of a two-dimensional circular switching wave which we will view as a nucleus of a new phase on the semiconductor surface.

The position of the front boundary of the two-dimensional circular wave is determined by the coordinate r, for which the instantaneous concentration value n_2 will correspond to an unstable (intermediate) steady-state solution η_2,

$$n(r,t) = n_2. \tag{9}$$

Differentiating equation (9), one obtains

$$\frac{\mathrm{d}n}{\mathrm{d}r}\frac{\partial r}{\partial t} + \frac{\partial n}{\partial t} = 0. \tag{10}$$

Multiplying equation (10) by τ/n_0, we thus obtain from equation (10),

$$\frac{\partial \eta}{\partial R}\frac{\mathrm{d}R}{\mathrm{d}\theta} + \frac{\partial \eta}{\partial \theta} = 0 \tag{11}$$

where R stands for r/l.

In cylindrical coordinates, equation (8) will become

$$\frac{\mathrm{d}\eta}{\mathrm{d}\theta} = \frac{\delta}{\rho}\frac{\partial \eta}{\partial \rho} + \delta\frac{\partial^2 \eta}{\partial \rho^2} + \beta\{1 - \exp[-\lambda_1 - \theta(\eta - \eta_0)(\lambda(\Omega(1+\eta))^{1/2} - \lambda_1)]\} - \eta \tag{12}$$

where $\rho = \sqrt{x'^2 + y'^2}$ is the dimensionless space coordinate.

Multiplying equation (12) by $\partial\eta/\partial\rho$ and integrating between η_1 and η_3, we obtain [8]

$$\int_0^\infty \left[-\frac{\partial\eta/\partial\theta}{\partial\eta/\partial\rho} + \frac{\delta}{\rho}\right]\left(\frac{\partial\eta}{\partial\rho}\right)^2 \mathrm{d}\rho = \int_{\eta_1}^{\eta_3} (\beta\{1 - \exp[-\lambda_1 - \theta(\eta - \eta_0)(\lambda(\Omega(1+\eta))^{1/2} - \lambda_1)]\} - \eta)\,\mathrm{d}\eta. \tag{13}$$

The derivative $\partial\eta/\partial\rho$ gives a sharp peak near the wavefront boundary $\rho = R$, so that an approximate relation

$$\left[-\frac{\partial\eta/\partial\theta}{\partial\eta/\partial\rho} + \frac{\delta}{\rho}\right]\int_0^\infty \left(\frac{\partial\eta}{\partial\rho}\right)^2 \mathrm{d}\rho = \int_{\eta_1}^{\eta_3} (\beta\{1 - \exp[-\lambda_1 - \theta(\eta - \eta_0)(\lambda(\Omega(1+\eta))^{1/2} - \lambda_1)]\} - \eta)\,\mathrm{d}\eta \tag{14}$$

can be written. Using equation (10), one then obtains

$$\frac{\mathrm{d}R}{\mathrm{d}\theta} = \mu - \frac{\delta}{R}. \tag{15}$$

Equation (15) is valid under the thin wall approximation. Here, μ is assumed to be given by

$$\mu = \int_{\eta_1}^{\eta_3} (\beta\{1 - \exp[-\lambda_1 - \theta(\eta - \eta_0)(\lambda(\Omega(1+\eta))^{1/2} - \lambda_1)]\} - \eta)\,\mathrm{d}\eta \left(\int_{\rho_2}^\infty \left(\frac{\partial\eta}{\partial\rho}\right)^2 \mathrm{d}\rho\right)^{-1} \tag{16}$$

which stands for the velocity of the plane wave front of the switching wave ($R \to \infty$). It follows from the steady-state condition of the wavefront boundary R that

$$R_C = A^{-1}\delta \int_{\rho_2}^\infty \left(\frac{\partial\eta}{\partial\rho}\right)^2 \mathrm{d}\rho = \frac{\delta}{\mu} \tag{17}$$

where

$$A = \int_{\eta_1}^{\eta_3} (\beta\{1 - \exp[-\lambda_1 - \theta(\eta - \eta_0)(\lambda(\Omega(1+\eta))^{1/2} - \lambda_1)]\} - \eta)\,\mathrm{d}\eta \quad (18)$$

has the same meaning as the degree of supersaturation in semiconductor solid solutions. With equation (17) taken into account, equation (15) becomes

$$\frac{\mathrm{d}R}{\mathrm{d}\theta} = \delta\left(\frac{1}{R_C} - \frac{1}{R}\right). \quad (19)$$

For $R > R_C$, $\mathrm{d}R/\mathrm{d}\theta$, and the nuclei of the high-absorption phase of radius R will grow, while for $R < R_C$, $\mathrm{d}R/\mathrm{d}\theta < 0$, and the nuclei will dissolve. The nuclei of critical radius R_C, which are in equilibrium with the environment, will neither grow nor dissolve. Since no restrictions on A have been placed, equation (19) will be formally valid for both early and late stages of growth of the new phase.

4. Behaviour of nuclei of the new phase at late stages of a photoinduced phase transition

At late stages of the first-order phase transition the growth of larger nuclei of a new phase proceeds at the expense of dissolving smaller nuclei [10–12]. For the case in question, Ostwald ripening sets in when A tends to zero. In other words, a developed interface is generated in a nonequilibrium system which is related to the Ostwald ripening stage [6]. We note, however that at this stage the fluctuation mechanism of formation of a new phase is ruled out because the critical sizes of nuclei are too large.

Equation (19), which represents the growth rate of a strongly absorbing phase, can then be rewritten as

$$\frac{\mathrm{d}R}{\mathrm{d}\theta} = \frac{\delta}{R}\left[\frac{R}{R_C} - 1\right]. \quad (20)$$

It is identical to the expression for late stages of formation of a discontinuous film from a supersaturated solid solution of atoms, adsorbed on a substrate [13]. According to Wagner [12] and Vengrenovich [13], δ can be viewed as a constant describing the rate of particle arrival at the perimeter of a growing droplet. As can be easily seen, for the case in question, its magnitude is determined by the diffusion coefficient of electrons and their lifetime.

Following Vengrenovich [14, 15], we determine the maximum possible nucleus size R_g using the equation for specific growth rate.

$$\frac{\mathrm{d}}{\mathrm{d}R}\left(\frac{\dot{R}}{R}\right)\bigg|_{R=R_g} = 0 \quad (21)$$

where $\dot{R} \equiv \partial R/\partial\theta$.

It follows from equation (21) that $R_g = 2R_C$. Note that Lifshits–Slezhov theory gives $R_g = \frac{3}{2}R_C$ for particles growing by bulk diffusion. Using equation (20) one can easily obtain the time dependence of R_g

$$R_g^2 - R_{g0}^2 = 2\delta(\theta - \theta_0) \quad (22)$$

Assuming $\mathrm{d}R/\mathrm{d}\theta$ to be the velocity of a nucleus in the size space, we can write the continuity equation in this space as

$$\frac{\partial g}{\partial\theta} + \frac{\partial}{\partial R}\left(g\frac{\partial R}{\partial\theta}\right) = 0. \quad (23)$$

The nucleus size distribution function is normalized so that

$$N(\theta) = \int_0^{R_g} g(\theta, R)\,\mathrm{d}R \tag{24}$$

which is the number of nuclei per unit volume.

Finally, the law of conservation of the number of charge carriers is given by

$$A(\theta) + \pi \int_0^{R_g} R^2 g(\theta, R)\,\mathrm{d}R = A_0 \tag{25}$$

where A_0 has the same meaning as the initial supersaturation in semiconductor solid solutions.

The expressions (20), (23) and (25) make a complete set of equations for the problem in question. Substituting equation (20) into equation (23) we obtain a distribution function similar to that obtained earlier for a discontinuous film [13],

$$g(u) = Cu(2-u)^{-4} \exp\left(-\frac{4}{2-u}\right) \tag{26}$$

where $u = R/R_C$.

The normalizing constant C can be obtained from equation (25).

Apparently, the above given nucleus size distribution function does not cover all possible mechanisms of particle coarsening. To account for other mechanisms, e.g. diffusion toward the particle, one would have to make assumptions that do not follow directly from the physical model described in section 2.

5. Conclusion

We have demonstrated a unified approach to nucleus formation and later stages of condensation, i.e. Ostwald ripening, as applied to photoinduced phase transition on the surface of a semiconductor with a renormalized bandgap for a strongly nonequilibrium system. When considering the kinetics of the nonequilibrium phase transition only those assumptions have been made that follow directly from the physical model representing the system in question.

The proposed approach is also applicable to a broad range of nonequilibrium systems. The latest achievements in the theory of self-organizing systems are known to be due to the fact that thermodynamically nonequilibrium systems which are stationary and exhibit local equilibria are formally indistinguishable from the equilibrium systems [8] for which well developed mathematical apparatus is available [9]. Such a thermodynamical system, which is far from equilibrium, is dependent upon its characteristic function, i.e. the generalized thermodynamic potential [16–18].

However, in most physically meaningful situations encountered in nonequilibrium kinetics (e.g. the model described by equation (6)) the above method is not applicable because of the difficulties associated with the construction of the generalized thermodynamical potential. The approach proposed here enables one to describe the evolution of a strongly nonequilibrium system using a formal analogy with decomposition of a supersaturated solid solution without invoking the generalized thermodynamical potential.

The bistable behaviour of a semiconductor with self-induced dramatic increase of the absorption coefficient has been studied extensively [1, 2, 7, 18] with a view to produce an optically bistable system. The similarity of this absorption increase to the first-order phase transition has been pointed out repeatedly. However, for zero-dimensional and one-dimensional models no in-depth similarity can be observed, as no adequate concept of a nucleus of a new phase can be introduced. For the cylindrical symmetry case under consideration, such similarity arises in a natural way, and allows us to formally, in a unified manner, describe

the growth of both spontaneously emerging nuclei of the strongly absorbing phase and their Ostwald ripening, i.e. the final stage of transition.

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