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Light absorption in TiO_2 nanoparticles

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Abstract. Light absorption in TiO_2 nanoparticles is analyzed. The interface mechanism of light absorption, where the indirect interband electron transitions are caused by the possibility of the momentum nonconservation at the interface, is considered. This mechanism is found to be most important for crystallites, which are generally a few 10 nm or less in size.

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1 Introduction

It is well known that the interband electron transitions comprise the main mechanism of light absorption in pure semiconductors. These transitions are direct because the momentum that the electron obtains from the light wave is small in comparison with $\pi\hbar/a$, where a is the lattice constant. This absorption is especially small in direct-forbidden gap semiconductors, for which the direct electron transitions between the band centers are prohibited by the crystal symmetry. This is the case for TiO_2.

It is clear that the momentum is not conserved if the absorption takes place at the boundary of the crystal, e.g., at the surface or at the interface between two crystals. The possibility of indirect electron transitions there can result in the essential enhancement of light absorption. This means that considerable enhancement of the absorption can be observed in small nanocrystals, as well as in porous and microcrystalline semiconductors, where the share of the interface atoms is sufficiently large.

Enhancement of the effect has to be expected at a rough interface where not only the normal-to-interface component of the electron momentum, but also all of its components, become nonconservative.

This interface mechanism of light absorption should be most pronounced in TiO_2. The lowest conduction band in this material is narrow, and even becomes flat, in $\Gamma - M$ direction [1]. The possibility for the momentum nonconservation results in the interband electron transitions, not only to the bottom of the conduction band, but also to any arbitrary point of the Brillouin zone. This is why an essential enhancement of the interband absorption has to be expected in TiO_2 nanoparticles.

2 Light absorption at a plane interface

Let us consider the light absorption at the boundary of the semiconductor crystallite embedded in an insulator medium. Suppose that each size of the crystallite is large in comparison with the lattice constant. The band structure of the semiconductor is presented in Fig. 1. We suppose the effective mass approximation to be valid in each band and assume that the effective mass in the conduction band $m_{\rm c}$ essentially exceeds the effective mass in the valence band $m_{\rm h}$, ($m_{\rm h} \ll m_{\rm c}$). Such a situation occurs in the TiO_2 band structure in the Γ–M direction.

We introduce the Cartesian coordinates where the z axis is normal to the interface. The probability for the photon to be absorbed in the crystallite is

$$\eta = \frac{(2\pi\hbar)^2 e^2}{m_0^2 c\omega n S} \sum_{\mathbf{p},\,\mathbf{q}} \left| < f|\frac{\partial}{\partial z}|i > \right|^2 \delta(\varepsilon_{\rm c} - \varepsilon_{\rm v} - \hbar\omega), \qquad (1)$$

where $\hbar$, e, m_0, and c are the fundamental constants, ω is the photon frequency, n is the refraction index, S is the area of the crystallite side $z = 0$ where the absorption is considered, $\mathbf{p}$ and $\mathbf{q}$ are the electron momenta, p and q are their z components, $\varepsilon_{\rm c}(\mathbf{q})$, and $\varepsilon_{\rm v}(\mathbf{p})$ are the energies of the electron in the conduction and valence bands. The electric field of the light is directed along the z axis; $i >$ and $f >$ are the wave functions of the electron before the excitation (in the valence band) and after it (in the conduction band), respectively. We can write these wave functions as follows:

$$i >= \frac{1}{\sqrt{N}} \begin{cases} [v_p(\mathbf{r})e^{ipz} + R_{\rm v} v_p^*(\mathbf{r})e^{-ipz}]e^{i\boldsymbol{p}_{\|}\boldsymbol{\rho}}, & z < 0 \\ T_{\rm v} e^{-\gamma_{\rm v} z + i\boldsymbol{p}_{\|}\boldsymbol{\rho}}, & z > 0, \end{cases}$$

$$f >= \frac{1}{\sqrt{N}} \begin{cases} [u_q^*(\mathbf{r})e^{-iqz} + R_{\rm c} u_q(\mathbf{r})e^{iqz}]e^{i\boldsymbol{q}_{\|}\boldsymbol{\rho}}, & z < 0 \\ T_{\rm c} e^{-\gamma_{\rm c} z + i\boldsymbol{q}_{\|}\boldsymbol{\rho}}, & z > 0, \end{cases} \qquad (2)$$

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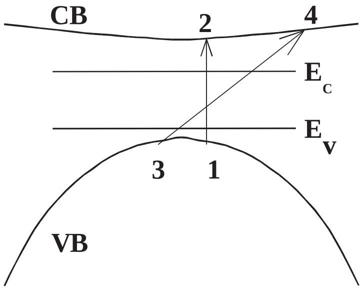

Fig. 1. Schematic band structure of the crystallite. Here $E_{\rm v}$ and $E_{\rm c}$ are the interface levels. Arrows indicate two ways that light absorption takes place: direct electron transition $1 \rightarrow 2$, and indirect $3 \rightarrow 4$ that occurs at the interface.

where N is the number of the unit cells in the crystallite; $\gamma_{\rm c,v}$ are decaying factors of the wave functions apart from the crystallite; $u_q(\mathbf{r})$ and $v_p(\mathbf{r})$ are the Bloch amplitudes, which are periodical functions of the coordinate $\mathbf{r}$; $\boldsymbol{p}_{||}$, $\boldsymbol{q}_{||}$, and $\boldsymbol{\rho}$ are the parallel-to-interface components of $\boldsymbol{p}$, $\boldsymbol{q}$ and $\boldsymbol{r}$; and $R_{\rm v}$, $R_{\rm c}$, $T_{\rm v}$, and $T_{\rm c}$ are the reflection and transmission coefficients.

In direct-forbidden gap semiconductors $u_0(\mathbf{r}) = 0$, we assume $u_q(\mathbf{r}) = 2i \sin(qa/2)\, w_q(\mathbf{r})$, where $w_q(\mathbf{r})$ is the periodic function of $\mathbf{r}$ that does not vanish at $q = 0$. Then we obtain

$$< f|\frac{\partial}{\partial z}|i >= i\frac{N_s}{N}\mathcal{P}_{\rm vc}, \tag{3}$$

where

$$\mathcal{P}_{\rm vc} = (1+R_{\rm v})(1+R_{\rm c}^*)U\,\delta_{\boldsymbol{p}_{||},\boldsymbol{q}_{||}}, \tag{4}$$
$$U = \int_{\Omega_0} w_0 \frac{\partial v_0}{\partial z}\,{\rm d}^3\mathbf{r},$$

and Ω_0 is the unit cell.

To consider the Coulomb interaction, which occurs between the exited electron and the hole in the valence band, within the framework of our model, it is necessary to input the weight factor $\Phi(\gamma) = \pi\gamma \exp \pi\gamma/(\sinh \pi\gamma)$ [where $\gamma = (qa_{\rm B}/\hbar)^{-1}$, and $a_{\rm B}$ is the effective Bohr radius] into the sum (1) [2].

It is possible to change summation in (1) by integration over the electron energy and parallel-to-interface components of the momentum $\mathbf{q}_{||}$. We obtain

$$\eta = \frac{e^2 m_{\rm c} m_{\rm h} a^2}{(2\pi)^2\hbar^4 m_0^2 \omega c n} \tag{5}$$
$$\times \int \frac{\Phi(\gamma)|\mathcal{P}_{\rm vc}|^2\,{\rm d}\varepsilon_{\rm c}\,{\rm d}^2 q_{||}}{\sqrt{2m_{\rm h}(\hbar\omega - \varepsilon_{\rm c}) - q_{||}^2}\,\sqrt{2m_{\rm c}(\varepsilon_{\rm c} - E_{\rm g}) - q_{||}^2}}.$$

Here $E_{\rm g}$ is the gap. The limits of integration are determined by the region in which the expressions under the square roots in the integrand are positive. Note that η value is independent of the crystallite length L.

To obtain the reflection coefficients $R_{\rm v}$ and $R_{\rm c}$, it is necessary to impose the boundary conditions on the wave functions (2). We use the envelope function approximation and write the boundary conditions for the envelopes Ψ of the wave functions (2) at the interface $z = 0$ as follows:

$$\begin{pmatrix}\Psi(+0)\\ \Psi'(+0)\end{pmatrix} = \hat{T}\begin{pmatrix}\Psi(-0)\\ \Psi'(-0)\end{pmatrix}, \tag{6}$$

where $\Psi' = \partial\Psi/\partial z$, $\hat{T}$ is the 2×2 matrix consisting of real components t_{ik}. They are independent of the electron energy and can be used as the phenomenological parameters.

It is difficult to obtain the values of t_{ik}. Nevertheless, we can relate them to the positions of the energy levels that are separated from the conduction and valence bands at the interface. In contrast to the parameters t_{ik}, the energy positions of these interface levels can be observed in optical experiments. We obtain

$$1 + R_{\rm v} = -\frac{2ip}{\kappa_{\rm v} - ip}, \quad 1 + R_{\rm c} = \frac{2iq}{\kappa_{\rm c} + iq}, \tag{7}$$

where $\kappa_{\rm v} = \sqrt{2m_{\rm h}E_{\rm v}}$, $\kappa_{\rm c} = \sqrt{2m_{\rm c}(E_{\rm g} - E_{\rm c})}$; $\kappa_{\rm v}^{-1}$ and $\kappa_{\rm c}^{-1}$ are the decay factors of the electron wave functions of the interface state; and $E_{\rm v}$ and $E_{\rm c}$ are the energies of the interface levels separated from the valence and conduction bands, respectively. We assume that energies are measured from the top of the valence band.

3 Frequency dependence of absorption

To determine the probability of the photon absorption, it is necessary to substitute (4) and (7) into (5). It follows from the integrand (5) that the frequency dependence of the absorption at the fundamental absorption edge is determined by the momentum dependence of $\Phi(\gamma)$ and $\mathcal{P}_{\rm vc}$. The latter is sensitive to the interface levels, whether or not they are close to the correspondent band extrema. The relations among $\kappa_{\rm v}$, $\kappa_{\rm c}$, and the characteristic momenta of the electron $p \sim \sqrt{2m_{\rm h}(\hbar\omega - E_{\rm g})}$, $q \sim \sqrt{2m_{\rm c}(\hbar\omega - E_{\rm g})}$, determine the value of this proximity.

If we assume the Coulomb factor $\Phi(\gamma)$ to be independent of q, then the result of integration (5) can be written as follows:

$$\eta \propto (\hbar\omega - E_{\rm g})^{\nu}, \text{ where} \tag{8}$$
$$\nu = \begin{cases} 3 \text{ if } \hbar\omega - E_{\rm g} \ll \min(E_{\rm v},\ E_{\rm g} - E_{\rm c}), \\ 2 \text{ if } \min(E_{\rm v}, E_{\rm g} - E_{\rm c}) \ll \hbar\omega - E_{\rm g} \ll \max(E_{\rm v}, E_{\rm c}), \\ 1 \text{ if } \hbar\omega - E_{\rm g} \gg \max(E_{\rm v},\ E_{\rm g} - E_{\rm c}). \end{cases}$$

In fact, $\Phi(\gamma)$ is independent of q if $qa_{\rm B} \gg \hbar$. Otherwise, if $qa_{\rm B} \ll \hbar$, it is proportional to q^{-1}; in this case, the exponent ν changes, so that $\nu \to \nu - 1/2$ when $\hbar\omega - E_{\rm g} \ll \mu e^4/(2\epsilon^2\hbar^2)$ (where $\mu^{-1} = m_{\rm c}^{-1} + m_{\rm h}^{-1}$, $\epsilon = n^2$).

Strictly speaking, (8) is valid only when $\hbar\omega - E_{\rm g} \ll W_{\rm c}$, where $W_{\rm c}$ is the conduction band width. This value is small in TiO$_2$. For that reason, it is interesting to consider the opposite limiting case $\hbar\omega - E_{\rm g} \gg W_{\rm c}$. In this case, $\varepsilon_{\rm c}$ can be considered as independent of q, so that it is possible to assume $\varepsilon_{\rm c} = E_{\rm g}$ in (1). Then, for the ν value, we find

$$\nu = \begin{cases} 3/2 \text{ if } \hbar\omega - E_{\rm g} \ll E_{\rm v}, \\ 1/2 \text{ if } \hbar\omega - E_{\rm g} \gg E_{\rm v}. \end{cases} \tag{9}$$

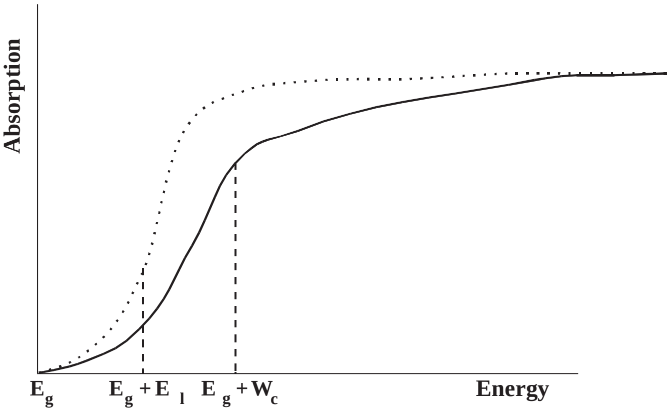

Fig. 2. Interband light absorption at the fundamental absorption edge in the TiO$_2$ crystallite. The dotted line indicates the influence of the interface roughness. Here $E_l = \hbar^2(2m_{\mathrm{c}\|}l^2)^{-1}$.

Frequency dependence of light absorption in the TiO$_2$ crystallite has the form presented in Fig. 2, where the slope of the curve is determined by the exponent ν from (8), if $E_{\mathrm{g}} < \hbar\omega < E_{\mathrm{g}} + W_{\mathrm{c}}$, and from (9), if $\hbar\omega > E_{\mathrm{g}} + W_{\mathrm{c}}$.

For the value of the absorption coefficient $\alpha = \eta/L$ of the microcrystalline solid, which has been composed from the crystallites under consideration, we obtain

$$\frac{\alpha}{\alpha_0} \sim \frac{a}{L}\left(\frac{W_{\mathrm{v}}}{W_{\mathrm{c}}}\right)^2, \tag{10}$$

where α_0 is the absorption coefficient of the bulk monocrystal, and W_{v} is the valence band width.

Thus, the interface mechanism of the absorption becomes comparable with the bulk one for the microcrystalline semiconductor, in which the mean size of the crystallite is $L \leq a(W_{\mathrm{v}}/W_{\mathrm{c}})^2$.

4 Light absorption at a rough interface

To investigate the light absorption at a rough interface, it is necessary to obtain the boundary conditions for envelope wave functions at this interface. We consider a special form of rough interface: the interface looks like an array of the plane areas of the same crystallographic orientation. The random function $z = \xi(\boldsymbol{r})$ of the coordinates in the XY plane determines the positions of these areas relative to the average plane $z = 0$.

We assume the average height of roughnesses σ to be small in comparison with the electron wavelength. Then it is possible to describe the rough interface by means of the correlation function $W(\mathbf{r}', \mathbf{r}'') = \overline{\xi(\mathbf{r}')\xi(\mathbf{r}'')}$. For the homogeneous rough interface, $W(\mathbf{r}', \mathbf{r}'') = W(\mathbf{r}' - \mathbf{r}'')$, i.e., the correlation function is the function of one variable: $\boldsymbol{\rho} = \mathbf{r}' - \mathbf{r}''$. There are two parameters that are most important when the statistical properties of a rough interface are considered: $\sigma^2 = W(0)$, and the correlation length l – the mean attenuation length of the correlation function. In our model, the correlation length l can be associated with the mean size of the plane area.

This special form of a rough interface allows us to apply the boundary conditions that are applicable for a plane interface at each plane $z = \xi$. Then the elements of the boundary conditions matrix $\hat{T}$ become dependent on $\boldsymbol{\rho}$. This results in the diffuse component of the electron wave function that must be taken into account in (2). For the diffuse component of the envelope in the conduction band $\varphi^c(\mathbf{r})$, we obtain

$$\varphi^c(\mathbf{r}) = -\frac{2iq}{(2\pi)^2}\int A^c(k_z)\tilde{\xi}(\mathbf{k} - \mathbf{q}_{\|})e^{i(\boldsymbol{k\rho} - k_z z)}\,\mathrm{d}^2\mathbf{k}, \tag{11}$$

where $\tilde{\xi}$ is the Fourier transform of ξ, $k_z = \sqrt{2m_{\mathrm{c}}\varepsilon_{\mathrm{c}} - k^2}$, and $A^c(k_z) \simeq 1$. A similar expression can be written for the envelope in the valence band.

In addition, the interface roughness leads to the effective shift of positions of the interface levels, so that

$$\tilde{\kappa}_{\mathrm{v,c}} = \kappa_{\mathrm{v,c}}\left[1 + \int(2m_{\mathrm{h,c}}\varepsilon_{\mathrm{v,c}} - \boldsymbol{k}^2)\tilde{W}(\mathbf{k} - \mathbf{p}_{\|})\,\mathrm{d}^2\boldsymbol{k}\right], \tag{12}$$

where $W(\boldsymbol{\rho}) = \overline{\xi(\boldsymbol{r} + \boldsymbol{\rho})\xi(\boldsymbol{r})}$ is the correlation function of the rough interface, and $\tilde{W}$ is its Fourier transform.

For the average squared module of the matrix element $\mathcal{P}_{\mathrm{vc}}$ in (3), we obtain

$$\begin{aligned}
&\overline{|\mathcal{P}_{\mathrm{vc}}|^2} = |\mathcal{P}^{(1)}_{\mathrm{vc}}|^2 + \overline{|\mathcal{P}^{(2)}_{\mathrm{vc}}|^2} + \mathcal{P}^{(1)}_{\mathrm{vc}}\overline{\mathcal{P}^{(3)^*}_{\mathrm{vc}}} + \mathcal{P}^{(1)^*}_{\mathrm{vc}}\overline{\mathcal{P}^{(3)}_{\mathrm{vc}}},\\
&\text{where}\ \ \mathcal{P}^{(1)}_{\mathrm{vc}} = (1 + R_{\mathrm{v}})(1 + R^*_{\mathrm{c}})U\,\delta_{\boldsymbol{p}_{\|},\boldsymbol{q}_{\|}}, \qquad (13)\\
&\overline{|\mathcal{P}^{(2)}_{\mathrm{vc}}|^2} = \frac{4U}{S}W(\mathbf{p}_{\|} - \mathbf{q}_{\|})\left|p(1 + R^*_{\mathrm{c}})A^c - q(1 + R_{\mathrm{v}})A^{v^*}\right|^2,\\
&\overline{\mathcal{P}^{(3)}_{\mathrm{vc}}} = 4ipqU\delta_{\boldsymbol{p}_{\|},\boldsymbol{q}_{\|}}\int A^c A^{v*}W(\mathbf{k}_{\|} - \mathbf{q}_{\|})\,\mathrm{d}^2\mathbf{k}.
\end{aligned}$$

The expressions (13) allow us to estimate the influence of the roughness on the value and the frequency dependence of light absorption. Note that the $\mathcal{P}^{(1)}_{\mathrm{vc}}$ value is of the same form as that for the plane interface (4). This value determines the influence of the shift of the interface levels caused by the interface roughness. Expressions for $\mathcal{P}^{(2)}_{\mathrm{vc}}$ and $\mathcal{P}^{(3)}_{\mathrm{vc}}$ in (13) determine the influence of the diffuse components of the scattered waves on the absorption; the values of these components are as small as σ/λ. In contrast, this small parameter is absent in the expression for $\mathcal{P}^{(1)}_{\mathrm{vc}}$. However, $\mathcal{P}^{(1)}_{\mathrm{vc}}$ is proportional to $(1 + R_{\mathrm{v}})(1 + R^*_{\mathrm{c}})$. This value is small if the interface electron levels are not close to any band. Then the values of $\mathcal{P}^{(2)}_{\mathrm{vc}}$ and $\mathcal{P}^{(3)}_{\mathrm{vc}}$ may be of the same order or even exceed $\mathcal{P}^{(1)}_{\mathrm{vc}}$.

The correlation length l of the rough interface is also important for the light absorption. If the correlation length is small, $l \ll \lambda$, then the roughness influence is determined by the terms $\mathcal{P}^{(1)}$ and $\mathcal{P}^{(3)}$. In this case, enhancement of the absorption arises because of an increase in the number of the interface atoms $N_s \to N_s\sigma/a$, in the vicinity of which the interband absorption with the momentum nonconservation occurs. The shift of the interface levels also affects the absorption.

In the opposite limit, $l \gg \lambda$, we can assume $\tilde{W}(\mathbf{k}) = \sigma^2\delta(\mathbf{k})$. It can be shown that $\overline{|\mathcal{P}_{\mathrm{vc}}^{(2)}|^2 + \mathcal{P}_{\mathrm{vc}}^{(1)}\mathcal{P}_{\mathrm{vc}}^{(3)^*} + \mathcal{P}_{\mathrm{vc}}^{(1)^*}\mathcal{P}_{\mathrm{vc}}^{(3)}} = 0$, i.e., $\overline{|\mathcal{P}_{\mathrm{vc}}|^2} = |\mathcal{P}_{\mathrm{vc}}^{(1)}|^2$ in this case. It is easy to understand the reason: Roughnesses, the mean lengths of which essentially exceed the electron wavelength, could not affect the electron properties of the interface.

The interesting situation arises when $l \sim \lambda$. In this case, the diffuse scattering that is described by the term $\overline{|\mathcal{P}_{\mathrm{vc}}^{(2)}|^2} \sim \kappa_{\mathrm{c}}^2\sigma^2 l^2[2m_{\mathrm{c}\|}(\hbar\omega - E_{\mathrm{g}})]|\mathcal{P}_{\mathrm{vc}}^{(1)}|^2$ leads to the change in the frequency dependence of the absorption, where $m_{c\|}$ is the mean parallel component of the effective mass. This means that absorption at the low frequencies, $2m_{\mathrm{c}\|}(\hbar\omega - E_{\mathrm{g}})l^2 \le \hbar^2$, increases more rapidly, so that the exponent ν changes its value $\nu \to \nu + 1$.

5 Discussion

We showed that the indirect electron transitions at an interface can lead to an essential enhancement of light absorption in TiO_2. The reason has to do with the indirect electron transitions $3 \to 4$ that are possible at an interface. There is a twofold advantage to such transitions. First, they are allowed, i.e., the dipole matrix element for the indirect transitions is not small. Second, there is a large density of states for the electron at point 4.

Thus the rapid increase of the absorption takes place at low ($\hbar\omega < E_{\mathrm{g}} + W_{\mathrm{c}}$) photon energies (Fig. 2). The electron transitions to any point of the conduction band become possible when $\hbar\omega = E_{\mathrm{g}} + W_{\mathrm{c}}$. Further enhancement of the absorption occurs due to an increase of the electron density of states in only the valence band. For this reason, the slope of the $\eta(\hbar\omega)$ curve decreases when $\hbar\omega > E_{\mathrm{g}} + W_{\mathrm{c}}$. Results of our analyses confirm these qualitative arguments.

The influence of the roughnesses on absorption is significant at the low frequencies, when $\hbar\omega \le E_{\mathrm{g}} + \hbar^2(2m_{\mathrm{c}}l^2)^{-1}$; enhancement of absorption in this case is due to an effective increase in the number of the interface atoms ($N_s \to N_s\sigma/a$), in the vicinity of which the interface light absorption occurs.

The absorption value and its frequency dependence at the fundamental absorption edge are sensitive to the conditions at the interface, namely, to the possible existence of the interface electron levels. Unfortunately, this question is not studied well for TiO_2. The energy position of these levels depends not only on the bordered materials, but also on the interface itself. The structure of the interface, as well as impurities and defects in it, affect the positions of these levels. Their positions can be measured in optical experiments as peaks in the absorption spectrum at the energies below the gap value.

It seems to us that the electron interface levels should be close to the valence band in the wide-gap semiconductors. The interface level becomes empty when it is shifted too far off the top of the valence band. This results in a large surface charge and a strong band bending that is not favorable from the energetic point of view. Nevertheless, the interface level can be shifted as the result of structure reconstruction of the interface. Such reconstruction does not essentially affect the interatomic spaces or angles, but it makes the interface level closer to the top of the valence band.

The roughness of the interface provides one of the possible ways of making such a reconstruction. It follows from our consideration (12) that significant shift of the interface level occurs if the correlation length of the rough interface is small ($\kappa_{\mathrm{v}}l \ll \hbar$). That causes the interface level to be closer to the band extremum. This is the particular case when the structure reconstruction of the interface decreases the interface energy; then the rough interface becomes more favorable than the plane one.

To estimate the relative value of the interface absorption, we can use (10) where W_{v} is the width of the upper valence band and W_{c} is the width of the lowest conduction band [1]. The value of W_{v} is about 1 eV. A considerable discrepancy exists for the values of W_{c} obtained by the different authors [1, 3]. Recent calculations [1] yield the value 10 meV for the energy difference between the Γ and M points in this band. Perhaps this value is beyond the accuracy of the calculations. Nevertheless, even if we assume this value to be of the order of 100 meV, then the estimation (10) shows that the interface absorption becomes the main mechanism of light absorption for the crystallites that are smaller than $100a \approx 20$ nm. Dependence of light absorption in the TiO_2 crystallite as a function of phonon energy is presented in Fig. 2; here, $\nu = 2$ if $\hbar\omega < E_{\mathrm{g}} + W_{\mathrm{c}}$, and $\nu = 1/2$ if $\hbar\omega > E_{\mathrm{g}} + W_{\mathrm{c}}$. Power dependence, where $\nu = 2$, of the absorption in microcrystalline TiO_2 has been observed in experiments [4].

In conclusion, we show that the possibility of momentum nonconservation at the interface leads to enhancement of light absorption in small TiO_2 crystallites. The effect increases at a rough interface, where the share of the interface atoms is larger.

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References

1. K. Glassford, J. Chelikowsky: Phys. Rev. B **46**, 1284 (1992); Shang-i Mo, W.Y. Ching: Phys. Rev. B **51**, 13 023 (1995)
2. R.J. Elliot: Phys. Rev. **108**, 1384 (1957)
3. K. Vos: J. Phys. C: Solid State Phys. **10**, 3917 (1977)
4. L. Kavan *et al.*: J. Phys. Chem. **97**, 9493 (1993)