Investigation of vibrational and electronic properties of oxide nanopowders by spectroscopic methods

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Abstract. Raman spectroscopy technique has been successfully used to study the microscopic nature of structural and/or morphological properties of investigated nanopowders. The phonon confinement model has been applied for the estimation of nanocrystals dimensions (TiO₂ and CeO₂), as well as the correlation length (ZnO), from the frequency shift and asymmetrical broadening of Raman optical phonon modes. The particle size distribution in nanopowders has been estimated from the low frequency Raman spectra, using the fact that the acoustic phonon modes in nanosized TiO₂ and CeO₂ can be well described by the elastic continuum model. In addition, the appearance of surface optical phonon modes has been predicted theoretically by the dielectric functions approach and detected experimentally in the Raman spectra of ZnO nanopowders, whereas the resonant behaviour of the first and second order ZnO Raman modes has been used for estimation of the electron-phonon interaction in this kind of nanomaterial. The optical properties of oxide nanopowders have been investigated by spectroscopic ellipsometry and photoluminescence spectroscopy. It has been shown that bandgap energy, as well as the energies of the other interband electronic transitions in investigated nanopowders can be determined by spectroscopic ellipsometry. On the other side, the existence of the broad bands in visible region of the photoluminescence spectra of TiO₂ and ZnO nanopowders points out to the various electronic transitions mediated by defect levels within the bandgap.

1. Introduction

The dependence of structural and optical properties of oxide nanopowders on particle size, stoichiometry, microstrain, as well as on the impurities and defect concentration, opens possibilities for such materials to be widely used in optoelectronics, energy conversion, photocatalyses and many other applications. The investigation of several wide band-gap semiconductors (TiO₂, CeO₂ and ZnO nanopowders) has been demonstrated that the quantum size and confinement effects become important, and that the optical and electronic properties of nanomaterials differ significantly from their bulk counterparts, depending on length dimensions in comparison with the excitation wavelength and Bohr exciton radius [1-15]. Moreover, it has been shown that the structural, optical and electronic properties of oxide nanoparticles depend not only on crystal structure, bulk composition, and morphology of the oxide particles, but also on their defect structure [16]. Thus, controlling of defects, especially nonstoichiometry related ones, becomes one of the most important goals of contemporary technology of oxide nanomaterials. Therefore, main purpose of this study is to correlate the results of experimental investigation of vibrational and optoelectronic properties of nanopowders with the variation of the crystallite size, microstrain, nonstoichiometry, as well as the presence of intrinsic defects and impurities.
2. Vibrational properties of nanocrystalline powders

Raman scattering can give important information about the nature of the solid on a scale of a few lattice constants. Therefore, Raman spectroscopy technique can be used to study the correlation between the change in vibrational properties and structural and/or morphological changes in nanostructured material. At different length dimensions \( L \) of nanostructure, compared to the excitation wavelength \( \lambda \) and Bohr exciton radius \( a_0 \), new Raman features may occur \([17]\). In case of \( a_0 \ll L \ll \lambda \) the confinement effects become important for optical and acoustic phonons, and Raman spectra of nanostructure differ significantly from the spectra of its bulk counterpart. On the contrary, when \( a_0 \ll L \ll \lambda \) the confinement effect is not so relevant, but additional surface phonon modes may appear between the TO and LO modes in the Raman spectra of polar semiconductors.

2.1. Phonon confinement model and elastic sphere model

It is well known that using optical techniques such as Raman spectroscopy, only zone-center optical phonons can be observed in ideal single crystals. However, this \( q \approx 0 \) selection rule is relaxed due to the interruption of the lattice periodicity in a nanocrystalline material. Hence, the behaviour of Raman modes in nanocrystalline materials due to crystallite size decrease can be simulated by phenomenological phonon confinement model (PCM) in an isolated nanoparticle. According to this model, the phonons in nanocrystal are confined in space and all the phonons over the entire Brillouin zone will contribute to the first-order Raman spectra. The weight of the off-center phonons increases as the crystal size decreases and the phonon dispersion causes an asymmetrical broadening and the shift of the Raman mode. According to Richter et al. \([18]\) and Campbell and Fauchet \([19]\), for crystallite size \( L \) and Gaussian confinement function, the resulting Raman intensity \( I(\omega) \) is presented as a superposition of weighted Lorentzian contributions over the whole Brillouin zone by the equation:

\[
I(\omega) = \sum_{i=1}^{\infty} \rho(L) dL \int_{0}^{\infty} \exp\left(-q^2 L^2 / 8 \beta \right) d^3 q \frac{\exp\left(-q^2 L^2 / 8 \beta \right)}{(\omega - \omega(q) + \Delta \omega)^2 + (\Gamma / 2)^2},
\]

with \( \rho(L) \) as distribution of crystallite size, \( q \) - wave vector, \( \beta \) - confinement strength and \( \Gamma \) - the intrinsic mode linewidth. The sum is carried over \( n \) dispersion curves \( \omega(q) \), depending on mode degeneration. The slope of dispersion curves away from the center of BZ determines the Raman line shift and asymmetrical broadening, as the crystalline size reduces: a negative slope, towards lower frequency, produces a redshifted (\( \text{ZnO, CeO}_2 \)), while a positive slope results in blueshifted Raman peak (\( \text{TiO}_2 \)). The peak centered at \( \omega(q) \) is shifted by the value of \( \Delta \omega \) due to the strain \([1, 2, 12]\).

Similar to the optical phonons, the acoustic phonons also get confined within the particles. In the elastic continuum limit, the confinement of long-wavelength acoustic phonons (sound waves) is followed by the appearance of discrete modes of particle. These modes depend on the elastic properties through the longitudinal and transverse sound velocities \([20]\). The frequencies of the spheroidal and torsional modes of the particle depend on the angular momentum associated with the vibration. Raman scattering from confined acoustic vibrations in nanoparticles has been observed in the low frequency part of spectra of various materials. The elastic sphere model (ESM) has been generally used to analyze the acoustic phonon confinement. This model describes the oscillations of homogeneous elastic sphere using Navier’s equation and imposing spherical symmetry \([13, 14]\). Rigid boundary and stress-free surface condition can be applied as boundary conditions in solving that equation. The frequency of an acoustic Raman mode is related to the particle diameter \( D \) as:

\[
\omega_l^2 = \frac{\omega}{2 \pi c} \beta_l \frac{l}{D},
\]

where \( \omega_l \) characterize the solutions of the Navier’s equation, while \( l \) is the angular momentum quantum number. According to the group theory analysis the spheroidal \( l=0 \) and \( l=2 \) modes are Raman active \([21]\). Thereby, the intensity of Raman scattering by nanoparticles can be expressed as \([22]\):

\[
I(\omega) = A \frac{n(\omega)}{\omega} C(\omega) g(\omega),
\]

where \( n(\omega) \) is Bose-Einstein factor, \( C(\omega) \) is the mode-radiation coupling factor, \( g(\omega) \) is the phonon density of states and \( A \) is the scaling constant. It had been shown that the mode-radiation coupling
factor scales inversely with the vibrational frequency: \( C(\omega) \sim 1/\omega \) for small spherical particles [22]. According to ESM, Raman spectrum would consist of discrete peaks if all the particles were of same dimensions. It can be assumed that the density of states reflects the particle size distribution, \( N(D) \), through the relation: \( g(\omega) = N(D) \) [23]. The most often size distributions encountered in different nanomaterials can be well approximated with Gaussian or log-normal distribution functions.

2.1.1. Determination of particle size distribution in pure and La-doped TiO\(_2\) nanopowders synthesized by sol-gel method. Decreasing of nanocrystals size to a few tens of nanometers leads to the appearance of low frequency Raman modes and blueshift and asymmetrical broadening of dominant \( E_g \) mode in the Raman spectra of anatase TiO\(_2\) nanopowders, as shown in figure 1.

\[
\text{Figure 1. The effects of crystallite size decrease on Raman spectra of anatase TiO}_2\text{ nanopowder.}
\]

The particle size distribution in pure and La-doped TiO\(_2\) nanopowders synthesized by sol-gel method has been estimated from the low-frequency Raman spectra, using the fact that the phonon modes in nanosized TiO\(_2\) observed in the low frequency region can be well described by the ESM, assuming that nanoparticles are of perfect spherical shape and isotropic [10]. The procedure proposed by Ivanda et al. [23] has been performed. Values of longitudinal and transversal sound velocities of rutile titania were used in calculations due to the lack of this data for anatase and value of \( \beta_{in} \) was calculated. Inhomogeneous broadening of the spectrum as a consequence of the non-uniform particle size distribution of the sample was incorporated. The evaluated particle size distributions in pure and La-doped TiO\(_2\) are shown in figure 2a together with the best fits of these distributions obtained by Gaussian or asymmetric Gaussian functions. The particle size distributions obtained by ESM were
used as initial distributions for the best-fit calculations of the $E_{g(1)}$ mode by PCM (figure 2b) [1, 6, 10]. The dependence of the most frequent particle size $L_C$ on La content in TiO$_2$ nanopowders is shown in figure 2c. The values of $L_C$ in the distributions finally used in PCM are very close to the corresponding values of $L_C$ in the distributions obtained by ESM. Note that the effects of compressive strain in the calculations of $E_{g(1)}$ mode intensity in nanopowders with higher La content had to be included in PCM [10]. Obtained results have shown that the particle size in TiO$_2$ nanopowders doped with La up to 4 wt.%, is close to or smaller than in the pure TiO$_2$, whereas nanoparticles with higher La content are larger and strained. This study confirms that the combined use of ESM and PCM in the analysis of Raman spectra of TiO$_2$ nanopowders gives the information not only about particle size distribution but also about influence of dopants on microstrain in anatase nanostructures.

2.1.2. Use of ESM and PCM in determination of particle size distribution in CeO$_2$ nanopowders synthesized by self-propagating room temperature method. Decreasing of nanocrystals size has the similar effects on vibrational properties of CeO$_2$ nanopowders as in the case of TiO$_2$. The appearance of low frequency Raman modes together with large redshift and asymmetrical broadening of $F_{2g}$ mode in the Raman spectra of CeO$_2$ nanopowders, are evident from figure 3 [13].

Raman intensity in the low-frequency range was calculated as the sum of three ESM modes intensities: $(l=2, n=0)$, $(l=0, n=0)$ and $(l=0, n=1)$, taking into account the correspondence between Raman intensity and particle size distribution [14]. The best agreement between experimental and calculated spectrum was obtained for the rigid boundary case but not for stress-free boundary condition (figure 3, left). The reason can be found in high agglomeration of the nanoparticles or in microstrain effects that influence strongly the optical Raman mode in ceria nanopowders [14]. If the results from the fits (figure 3) are compared to the value of the mean particle size diameter $D_0=8$ nm, acquired from PCM (figure 3, right), it can be concluded that Gaussian size distribution with values of $D_0$ from the interval 7–8 nm describes best the particle size distribution of the investigated sample.

2.2. Surface optical phonons

Surface modes of small particles have been observed for particle sizes smaller than the wavelength of the exciting laser light inside the particle in many polar crystals [17]. Although for powders or nanocrystals embedded in homogeneous media 3D effective-medium models are successfully applied, it appears that 2D models are more appropriate to describe the morphology of polar porous semiconductors [24]. The effective dielectric function of the nanopowder thus is given by [25, 26]:

$$
\varepsilon_{||} = (1-f)\varepsilon_{\text{air}} + c\varepsilon_{\text{osc}}^c,
$$

(exactly) and

$$
\varepsilon_{\perp} = \frac{(1+f)\varepsilon_{\text{osc}}^c + (1-f)\varepsilon_{\text{air}}}{(1-f)\varepsilon_{\perp} + (1+f)\varepsilon_{\text{air}}} e_{\text{air}},
$$

(in a two-dimensional Maxwell-Garnett approximation), where $\varepsilon_{\text{osc}}^c$ and $\varepsilon_{\text{osc}}^e$ are the dielectric functions in normal and parallel polarization, whereas $f$ is the volume fraction of porous
semiconductor (psc) and $\varepsilon_{\infty}=1$. Taking into consideration the plasmon contribution, the dielectric functions of semiconducting nanopowders with wurtzite structure can be written as \cite{25}:

$$
E_{\parallel(\perp)} = E_{A(E_i)} = E_{\infty} \left( \frac{\omega^2_{A(LO,E_i,TO)} - \omega^2 - i \omega \gamma}{\omega^2_{A(LO,E_i,TO)} - \omega^2 - i \omega \gamma} - \frac{\omega_p^2}{\omega^2 + i \omega \Gamma} \right),
$$

(5)

where $\omega_{A(E_i)}$ is the uncoupled phonon frequency of the $A(E_i)$-type mode in bulk semiconductor and $\gamma$ is phonon damping rate. The plasmon frequency is given by $\omega_p = (Ne^2/\varepsilon_{\infty}m^*)^{1/2}$, whereas $\Gamma = e/\mu m^*$ is plasmon damping rate. $N$ is free carrier concentration, while $m^*$ is the effective mass of electron, $\mu$ - electron mobility, and $\varepsilon_{\infty}$ - static dielectric constant.

The Raman line shape of surface optical phonon modes is derived according to the assumption that the excitation of extraordinary phonons is dominant, and that the Raman intensities can be written as:

$$
I_{\text{eo}} \sim \text{Im} \left[ -1/(\varepsilon_0 \cos^2 \theta + \varepsilon_{\perp} \sin^2 \theta) \right],
$$

(6)

where $\theta$ is the angle between the exciting light wave vector and the direction parallel to the $c$-axis. It is necessary to take into account multiple scattering by averaging $I_{\text{eo}}$ over $\theta$ with a weight $\exp(-\theta^2/\sigma^2)$, as well as inhomogeneity of the sample by averaging over $f$ with a weight $\exp(-(f-f_0)^2/\sigma_f^2)$ \cite{25}.

2.2.1. Surface optical phonon modes in the Raman spectra of mechanically activated ZnO powders. As a result of mechanical activation, the frequency and shape of Raman modes characteristic for wurtzite ZnO structure are changed due to the structural and stoichiometric variation, depending on the milling time and the choice of equipment \cite{3, 12}. Observed redshift and asymmetrical broadening of the first order $E_{2}^{\text{high}}$ and $E_1(\text{LO})$ Raman modes (figure 4) are ascribed to decrease of correlation length, due to increase in intrinsic defect concentration induced by mechanical activation. Such behaviour is simulated by PCM, which includes Brillouin zone anisotropy and high sensitivity of $E_2^{\text{high}}$ mode to lattice strain \cite{12}. The modes, which appear at about 510 and 550 cm$^{-1}$ in the Raman spectra of mechanically activated ZnO powders, are ascribed to the surface optical phonon (SOP) vibrations, which occur at grain boundaries between ultrafine nanocrystals and disordered regions in nanosize ZnO crystallites. With increasing disorder in activated ZnO powders, the SOP modes in experimental Raman spectra are significantly increased in intensity, whereas no measurable shift of these modes can be observed. The Raman line shape of SOP modes is efficiently simulated by dielectric function approach described in previous section. The great difference in the intensity and line shape of simulated SOP modes is mainly the result of variation in mean volume fraction $f_0$ of ZnO and phonon damping rates, as a consequence of vacancies induced porosity and high disorder in damaged surface layers. The higher relative SOP intensity and vacancies induced porosity is correlated to higher
surface defects concentration, probably the oxygen vacancies.

2.3. Electron phonon interaction

2.3.1. Dependence of electron phonon coupling on correlation length in highly disordered ZnO nanopowders. The electron-phonon coupling (EPC) is very important in understanding the optoelectronic properties of the crystalline semiconductors. The coupling strength between electrons and LO phonons in polar semiconductors is determined by the ratio of the second- to the first-order Raman scattering cross sections [27].

The intensity ratio of $E_{1}(2LO)$ to $E_{1}(LO)$ Raman modes, as an indicator of EPC strength, is shown in figure 5a for starting and several mechanically activated ZnO powders. From the dependence of the $E_{1}(2LO)/E_{1}(LO)$ ratio on incident photon energy it is obvious that the EPC strength has the highest value in the starting powder and decreases with activation. A great enhancement of the oscillator strength for the second-order resonance can only be understood if the relevant resonant intermediate state is a localized exciton, interacting strongly with the LO-phonon, forming a localized exciton-phonon complex [28]. The origin of great EPC strength, observed here in nonstoichiometric ZnO-0, may lie in the increasing concentration of oxygen vacancies ($V_O$) and interstitial atoms (Zn) followed by the presence of their electronic levels within the bandgap.

![Figure 5. Dependence of the $E_{1}(2LO)/E_{1}(LO)$ ratio on (a) incident photon energy and (b) correlation length in starting and mechanically activated ZnO powders. Crystallite sizes determined by XRD analyses are denoted in (b) for all powders.](image)

Weakening of the electron-LO-phonon coupling in the activated ZnO powders is a consequence of great sensitivity of second-order structures to atomic scale disorder [29] induced my mechanical activation. So, it can be concluded that low level of disorder, induced by nonstoichiometry of starting powder, strongly enhances EPC strength, whereas this strength become weaker in highly disordered activated powders. Note that the $E_{1}(2LO)/E_{1}(LO)$ ratio gradually decreases with activation time in the powders activated in vibro-mill. However, in the powders activated in planetary mill, the $E_{1}(2LO)/E_{1}(LO)$ ratio has minimal value after 30 min of activation, and slightly higher value after 300 min, though crystallite size continuously decreases with activation. These results have shown that electron phonon coupling strength in crystalline ZnO powders has the same trend as the correlation length, but not as crystallite size. Such conclusion is explicitly confirmed by figure 5b, where dependence of the $E_{1}(2LO)/E_{1}(LO)$ ratio on correlation length in starting and activated ZnO powders has been shown together with the crystallite size determined by XRD analysis.

2.3.2. The influence of Fe$^{2+}$/Fe$^{3+}$ doping on vibrational properties of cerium dioxide nanopowders. It can be seen from the Raman spectra of Fe-doped CeO$_2$, shown in figure 6, that changing of Fe valence state causes evident redshift and broadening of $F_{2g}$ Raman mode, followed by increased intensity of intrinsic oxygen vacancy mode at 600 cm$^{-1}$. This unexpected redshift and broadening of the $F_{2g}$ mode can be only a consequence of the coupling between charge located at Ce$^{3+}$(Fe$^{3+}$)-O$^2-$ complex and $F_{2g}$ vibration arising from electron molecular vibration coupling [30]. The change in
vibrational properties of Fe-doped CeO$_2$ nanopowders is followed by drastic variation of their magnetic properties as well [28].

Figure 6. Raman spectra of undoped and Fe-doped CeO$_2$ samples. Inset: Dependence of full width at half maximum (FWHM) and frequency ($\omega$) of $F_{2g}$ Raman mode varying the valence state of dopant.

3. Optoelectronic properties of nanocrystalline powders

Optical and electronic properties of nanocrystalline materials strongly depend on their composition, structural and morphological characteristics, but also on the presence of defects. For crystallite size comparable to Bohr exciton radius of particular materials the quantum size effects become important, the bandgap grows, and the optical and electronic properties of nanomaterial differ significantly from its bulk counterpart. On the other hand, presence of intrinsic defects and impurities may introduce different electronic levels within the band-gap, which can cause the various electronic transitions mediated by these levels and variation of the optical bandgap energy as well.

3.1. Interband electronic transitions

The dielectric function $\varepsilon(\omega)$ of TiO$_2$ nanopowders synthesized by laser-induced pyrolysis has been determined by spectroscopic ellipsometry in the energy range from 1.5 to 6 eV at room temperature. The features observed in $\varepsilon(\omega)$ have been fitted to analytical line shapes by using the second derivatives of experimental spectra (figure 7). In such a way, the energies corresponding to different interband electronic transitions have been determined. Obtained results point out that the energy of $E_1$ transition, which can be related to the energy bandgap transition, is higher in nanopowder with smaller crystallite size, $d_c$. Namely, this energy reaches 3.384 eV in the powder with $d_c \approx 12$ nm (TiS57), whereas in the powder with $d_c \approx 17$ nm (TiS12) its value is 3.285 eV. Such increase ($\sim 0.1$ eV with crystallite size decrease by $\sim 5$ nm) coincides with the behavior predicted for the energy bandgap in anatase nanostructures [11, 31, 32]. However, the energies related to the other interband electron transitions between valence and conduction band have similar values in both nanopowders - $E_1 + \Delta E_1 \approx 3.8$ eV.

Figure 7. 2nd derivatives of $\varepsilon_1(\omega)$ (real) and $\varepsilon_2(\omega)$, (imaginary) components of dielectric functions obtained by SE measurements of anatase nanopowders, together with the fitting curves determined by using critical point (CP) analysis.
$B \approx 4.2 \text{ eV}$ and $E_2 \approx 4.9 \text{ eV}$. Possible explanation of such behaviour of the interband electron transitions may be the following: the last three transitions are considered to be direct, whereas the first one is can be assumed to be a kind of transition between direct and indirect.

3.2. Determination of band gap energy

The values of the bandgap energy ($E_g$) in direct bandgap semiconductors can be obtained by extrapolating the straight-line portion of the $(\alpha E)^2$ vs. $E$ plots to the photon energy $E$ axis. Figure 8 shows those plots for nonactivated and mechanically activated ZnO powders, where the absorption coefficient have been obtained from measured SE data by using $\alpha = 4\pi k/\lambda$ ($\lambda$ is the incident light wavelength) [15]. It is obvious that $E_g$ for all samples is narrower than the bandgap of bulk ZnO (3.37 eV), with the lowest value in the most disordered powder ZnO-p-30. This is most likely a consequence of a drastic structural change in ZnO crystal, as some of the surface states, defects and dangling bonds induce formation of band tail and can cause the bandgap narrowing [33]. The shift of optical bandgap of ZnO to values smaller than the bulk $E_g$ can be also induced by electrons generated from $V_0$ and Zn$_i$ [34]. On the other side, the origin of the bandgap widening in the ZnO-p-300 powder is not related only to the lower concentration of defects but also to the raising zirconia content, due to prolonged milling in zirconia vessels. Namely, the presence of zirconia in these samples causes shifting the energy gap to the high energy, as the energy-gap values of ZrO$_2$ ranges 5.0–5.85 eV [35].

3.3. Sub-bandgap electronic transitions in ZnO and TiO$_2$ nanopowders

From the photoluminescence spectra of ZnO samples excited by 325 nm (3.81 eV) line of He-Cd laser shown in figure 9 it is obvious that a significant impact of defects on the electronic properties of the ZnO reflects not only on the bandgap energy variation (figure 8), but also on the changes in the PL spectra. The excitation with the photon energy greater than $E_g$ causes the appearance of the luminescence at different emission wavelengths in the visible range, due to different intrinsic or extrinsic defects in ZnO. Highly intensive violet emission (at ~3 eV) and green luminescence (at ~2.4 eV), whose origin were related to oxygen deficiency, dominate the PL spectrum of non-stoichiometric starting ZnO powder, where the most abundant bulk point defects are supposed to be Zn$_i$ and $V_0$ [15]. On the contrary, the PL in mechanically activated ZnO powders is readily quenched due to high defect concentration. Decrease in the PL intensity in mechanically activated ZnO powders can be also a consequence of an unlimited access of oxygen to the nanoparticles surface during activation in air and the fact that oxygen is efficient in electron collecting [15]. Moreover, increasing concentration of interstitial oxygen defects on the surface layers of ZnO nanoparticles is probably the
main reason for the shift of the PL maximum to yellow and orange range in activated ZnO powders.

Under the laser irradiation with subband photon energy of 2.41 and 2.71 eV anatase TiO₂ nanocrystals also displayed strong visible light emission, even at excitation power as low as 0.05 W/cm² [11]. The line shape and position of this broad luminescence band vary with excitation energy and temperature, as can be seen from figure 10. The analysis of those variations suggests that the PL spectra of nanopowder TiS₁₂, with larger crystallite size, are dominated by a radiative recombination of electrons via intrinsic surface states for all applied excitation energies and temperatures. The energy of these optical electron transitions is about 2.2 eV [11, 36]. However, excitation of the sample with smaller nanocrystallites, TiS₅₇, by higher photon energies (close enough to the energy bandgap) activates self-trapped exciton luminescence with the energy of ~2.41 eV [37 and the references therein]. PL blueshift with sample heating also points out to the recombination of self-trapped excitons as dominant PL mechanism in TiS₅₇ nanopowder.

![Figure 10. PL spectra of anatase nanopowders with variation of laser excitation energy (a) and temperature (b).](image_url)

4. Conclusion
This study gives an overview of theoretical interpretation and experimental evidences of the strong correlation of vibrational and optoelectronic properties with composition, structure, morphology and presence of defects and impurities in nanocrystalline semiconductors. Raman scattering measurements have proven as a valuable tool for determining particle size distribution as well as surface and defect structure in nanosized materials, whereas spectroscopic ellipsometry and photoluminescence spectroscopy have shown their efficiency in estimation of the energies of optical bandgap, different interband electronic transition as well as electronic levels within the bandgap.

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