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Quantum-sized effects in oxidized silicon structures with surface II-VI nanocrystals

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Abstract. The Si-SiO₂ interface in oxidized macroporous silicon structures with surface CdS and ZnO nanocrystals was investigated using the methods of electroreflectance and photoconductivity. The Franz-Keldysh effect, built-in electric field and surface quantization of charge carriers in the Si-SiO₂ region were revealed. The splitting of photoconductivity peaks was detected in the area of indirect band-to-band transition due to quantization of charge carriers in the surface silicon region, too. The latter data correlate with the results of the electroreflectance spectra measurements in the area of direct interband transition of oxidized macroporous silicon structures with surface CdS and ZnO nanocrystals.

Keywords: macroporous silicon, Si-SiO₂ interface, CdS and ZnO nanocrystals, Franz-Keldysh effect, surface quantization.

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1. Introduction

Nanotechnologies of II-VI nanocrystals in oxidized macroporous silicon structures are perspective for manufacturing light emitting elements. There were proposed the oxidized macroporous silicon structures with surface CdS and ZnO nanocrystals [1] to produce efficient light emitting elements by reducing the flow of electrons and its recombination outside the nanoparticle layer. Macroporous silicon is promising material for the development of 2D photonic structures with the required geometry and large effective surface [2, 3]. It determines optical and electro-optical characteristics of macroporous silicon structures [4, 5]. In [6, 7], we investigated the near-IR light absorption oscillations in 2D macroporous silicon structures with surface II-VI nanocrystals and SiO₂ nanocoatings, taking into account the electro-optical Wannier-Stark effect within the strong electric field approximation.

In this paper, the Si-SiO₂ interface in oxidized silicon structures with surface CdS and ZnO nanocrystals was investigated using the methods of electroreflectance and photoconductivity. The direct interband transition energy, broadening parameter and relaxation time of charge carriers were identified from the electroreflectance spectra of silicon structures with silicon oxide layer of 7, 15 and 30-nm thickness and surface CdS, ZnO nanocrystals. Photoconductivity spectra of silicon nanocoating “silica – nanocrystals CdS, ZnO” and the structure of macroporous silicon with oxide layer with the thickness 30 nm were measured, too.

2. Procedure

The SiO₂ nanocoatings with the thickness 7, 15 and 30 nm were formed on silicon samples in the diffusion oven after treatment in nitrogen atmosphere and in dry oxygen for 40 to 60 min at the temperature 1050 °C. The oxide thickness was measured using ellipsometry.

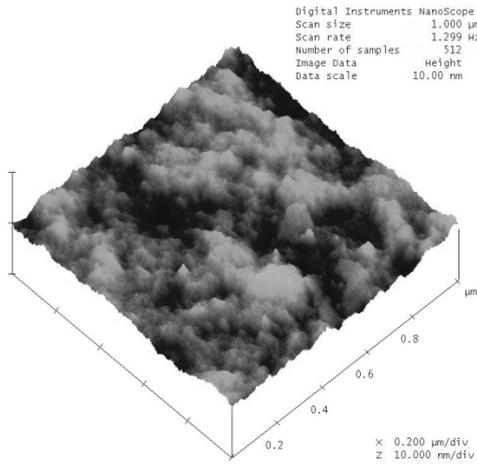


Fig. 1. Morphology of CdS nanocrystals in polyethylenimine according to AFM data.

CdS nanocrystals (1.8...2 nm) were deposited onto silicon substrate from colloidal solution in polyethylenimine. The nanocrystal size values were obtained with AFM (Fig. 1). ZnO nanocrystals (5-6 nm) were synthesized in colloidal solution of $Zn(CH_3COO)_2$ in ethanol [8]. Colloidal solution of ZnO nanocrystals was deposited onto silicon, and the sample was kept until complete evaporation of the solvent. The obtained sample was washed with distilled water to remove residual salts.

For the purpose of studying, the macroporous silicon samples were made using photoelectrochemical etching [2, 3] the *n*-silicon wafers of [100] orientation (the electron concentration $n_0 = 10^{15} \text{ cm}^{-3}$). Macroporous silicon structures with the macropore depth $h_p = 70...80 \mu\text{m}$, diameter $D_p = 2...4 \mu\text{m}$ and concentration $N_p = (1.2-1.9) \times 10^6 \text{ cm}^{-2}$ were formed.

3. Experimental results and discussion

3.1. Electroreflectance spectra

Electroreflectance spectra of Si-SiO₂ with nanocoatings of nanocrystals CdS, ZnO and the original surface of the silicon substrate are shown in Figs 2 and 3. The

electroreflectance spectra were measured by the standard electrolytic technique at room temperature. It is evident from the figures that all the electroreflectance spectra correspond to silicon of *n*-type conductivity, while the electroreflectance spectra of macroporous silicon structures correspond to the surface of *p*-type conductivity silicon [5] due to its passivation by hydrogen atoms.

High-energy Franz-Keldysh oscillations [5] with the photon energy higher 3.6 eV indicate the presence of the built-in electric field for CdS and ZnO nanocrystals on silicon oxide with the thickness 15 and 30 nm (Fig. 2, curves 3, 4 and Fig. 3, curves 3, 4). It is possible to determine the dependence of the slope $(4/3\pi) \cdot (E_m - E_g)^{3/2}$ on the number of oscillations, electro-optical energy and value of the built-in electric field for the thickness 15 nm and 30 nm of the oxide layer (Table 1). The energy transition E_g , spectrum broadening parameter Γ (that characterized the structural perfection of the Si-SiO₂ interface) and relaxation time of the charge carrier energy $\tau = \hbar/2\Gamma$ were identified from electroreflectance spectra, too (Figs 2 and 3, Table 1).

The direct optical transition energy for the investigated samples varies from 3.29 to 3.38 eV (Table 1) and is low in comparison with the direct optical transition energy for monocrystalline silicon (3.38 eV). The energy shift may indicate the internal mechanical stresses in Si-SiO₂ heterosystem. The main cause of stress is a significant difference in temperature expansion coefficients of Si ($3.1 \cdot 10^{-6} \text{ K}^{-1}$) and SiO₂ (10^{-7} K^{-1}) and, consequently, a larger volume of phases SiO₂ and SiO_x as compared to monocrystalline silicon. The direct optical transition energy of the unstrained silicon surface is 3.38 eV [5]. Thus, the maximum deviation from that of the unstrained silicon surface is 90 meV for samples with the CdS nanocoating and the oxide thickness 30 nm as well as for samples with the ZnO nanocoating with the oxide thickness 15 nm. The reduction of the direct optical transition energy of the samples corresponds to the mechanical stress stretching of monocrystalline silicon. The shift of the direct optical transition energy can also be the result of formation of local electric field at the Si-SiO₂ interface:

Table 1. Energy transition E_g , spectrum broadening parameter Γ , value of the built-in electric field F_s .

c-Si		d_{SiO_2} , nm	CdS			ZnO		
E_g , eV	Γ , meV		E_g , eV	Γ , meV	F_s , 10^5 V/cm	E_g , eV	Γ , meV	F_s , 10^5 V/cm
3.38	92	7	3.34	183	–	3.35	147	–
		15	3.38	211	6.65	3.30	164	7.74
		30	3.29	228	3.11	3.33	203	4.35

$$\Delta F_g = -(\hbar^2 \sigma^2 F^2) / [24(kT)^3 \mu], \quad (1)$$

where σ is the conductivity of the surface layers of crystalline silicon. On the other hand, the shift of the main peak of photoconductivity to the high photon energy side by 170...200 meV was explained with account of the interband transition of electrons to the Fermi level in the conduction band.

As shown in Table 1, the broadening parameter for oxidized silicon with CdS and ZnO nanocoatings is much higher than the value of Γ for monocrystalline silicon, indicating the influence of defects on the interface of Si-SiO₂. The broadening parameter increases with the thickness of silicon oxide within 7 to 30 nm from 183 up to 228 meV for the structures with CdS nanocoating and from 147 up to 203 meV for ZnO nanocoating. Small values of the broadening parameter for the structures with ZnO nanocoating show lower defectiveness of Si-SiO₂ boundary or higher electron localization and, consequently, higher electron relaxation time.

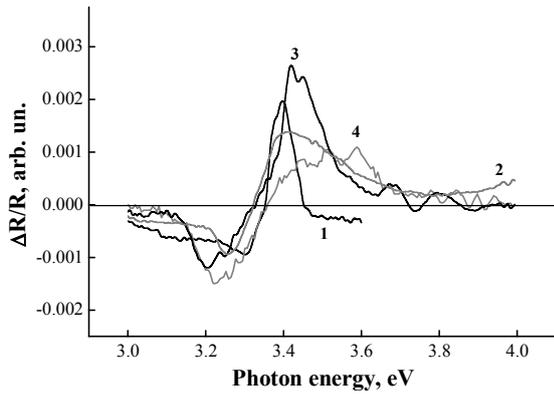


Fig. 2. Electroreflectance spectra of silicon substrate (1) and silicon structures with CdS nanocrystals on silicon oxide layer of the thickness: 7 (2), 15 (3), and 30 nm (4).

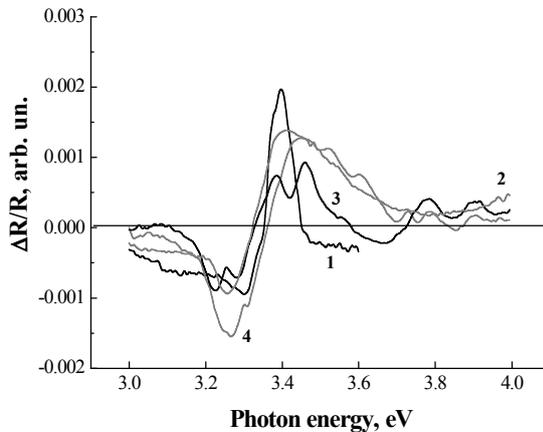


Fig. 3. Electroreflectance spectra of silicon substrate (1) and silicon structures with ZnO nanocrystals on silicon oxide layer of the thickness: 7 (2), 15 (3), and 30 nm (4).

The main electroreflectance peak (Figs 2 and 3) revealed the quantization of charge carriers in the near-surface region of silicon and splitting of peaks corresponding to one quantized energy level near 40 meV (oxide thickness 15 nm) and two quantum levels with the energies 70 and 140 meV (oxide thickness 30 nm). The electric field F_S (Table 2) was determined on the basis of the model of the triangular potential well [9]:

$$E_n = \left[\frac{3\pi\hbar e F_S}{(8m^*)^{1/2}} \left(n + \frac{3}{4} \right) \right]^{2/3}. \quad (2)$$

For the first and second quantum levels

$$E_{0,1} = E_1 - E_0 = \left[\frac{3\pi\hbar e F_S}{(8m^*)^{1/2}} \right]^{2/3} \cdot K_{0,1},$$

where $K_{0,1} = 0.626$.

$$E_{1,2} = E_2 - E_1 = \left[\frac{3\pi\hbar e F_S}{(8m^*)^{1/2}} \right]^{2/3} \cdot K_{1,2},$$

where $K_{1,2} = 0.511$.

The electric field intensity F_S :

$$F_S^{0,1} = \left[\frac{(8m^*)^{1/2}}{3\pi\hbar e} \right] \cdot \left[\frac{E_{0,1}}{K_{0,1}} \right],$$

$$F_S^{1,2} = \left[\frac{(8m^*)^{1/2}}{3\pi\hbar e} \right] \cdot \left[\frac{E_{1,2}}{K_{1,2}} \right].$$

Table 2. The electron Fermi level, first quantum energy level $E_{0,1}$ and electric field $F_S^{0,1}$, second quantum energy level $E_{1,2}$ and electric field $F_S^{1,2}$ obtained from the electroreflectance spectra.

Sample	d_{SiO_2} , nm	E_F , eV	$\Delta E_{0,1}$, 10^{-3} eV	$F_S^{0,1}$, 10^5 V/cm	$\Delta E_{1,2}$, 10^{-3} eV	$F_S^{1,2}$, 10^5 V/cm
CdS	15	3.41	36	0.762		
CdS	30	3.42	67	1.93	74	3.05
ZnO	15	3.41	75	2.29		
ZnO	30	3.39	69	2.02	74	3.05
macPS	–	3.38	–	–	–	–

3.2. Photoconductivity spectra

Photoconductivity spectra of oxidized silicon structures with CdS and ZnO nanocrystals were measured at room temperature using a spectrometer within the spectral range 0.5...2 μm . The sample parameters and measurement conditions are given in Table 3. The resistance of samples (R_{samp}) was 0.2 to 10.5 k Ω , additional resistance (R_{add}) – 6.8 k Ω , external voltage – 2.6 V, voltage on the sample – 0.3 to 1 V.

The photoconductivity spectra of the macroporous silicon structure with the oxide layer thickness 30 nm; silicon structures with CdS and ZnO nanocrystals on silicon oxide layer are presented in Figs 4 and 5. There is the high photon energy shift 0.17...0.20 eV in the main photoconductivity peak. The main peak in the photoconductivity spectra was measured for ZnO nanostructuring on oxide of 7-nm thickness. The splitting of the main peak into two peaks with the distance between them, respectively, 65 and 70 meV was measured for CdS and ZnO nanocoatings on oxide with the thickness 15 nm. The splitting of the main peak by three ones with the distance between them, respectively, 65 and 70 meV was measured for CdS nanocoating on oxide with the thickness 30 nm. Spectra of the macroporous silicon structure with the oxide thickness 30 nm (Figs 4 and 5, curve 1) also hold the main peak splitting by three ones with a separation 70 and 80 meV.

The shift of the photoconductivity maxima of the investigated structures (Figs 4 and 5) to the higher photon energy side can be attributed to the quantum-sized effect. This shift was explained in [10, 11] by the quantum-sized effect in the transition from silicon matrix to Si nanoclusters in dielectric (SiO_x). The value of the shift is consistent both with theoretical estimates for the energy gap and experimental photoluminescence peak for Si nanoclusters of the size ≤ 5 nm in the oxide environment. On the other hand, quantization of charge carriers in the near-surface region of silicon indicates strong enrichment of silicon surface by electrons and quantum well formation. Therefore, the shift of the main peak of photoconductivity to the higher photon energy can be explained by the band filling effect [9] and interband transitions of electrons to the Fermi level in the conduction band. Thus, the quantum energy levels are, respectively, $E_{0,1} = E_1 + E_F - E_g$ and $E_{1,2} = E_2 + E_F - E_g$.

Table 3. Parameters of silicon structures with nanocoatings and conditions of the photoconductivity spectra measurements.

	Nano-particles	d_{SiO_2} , nm	R_{samp} , k Ω	R_{add} , k Ω	$\lambda_{\text{spectr.}}$, μm	ν , Hz
1	CdS	15	0.2	6.8	0.5–2	317
2	CdS	30	0.19	6.8	0.5–2	310
3	ZnO	7	0.33 0.34	6.8	0.5–2	313
4	ZnO	15	0.33	6.8	0.5–2	317
5	macPS	30	2.6 10.5	6.8	0.5–2	317

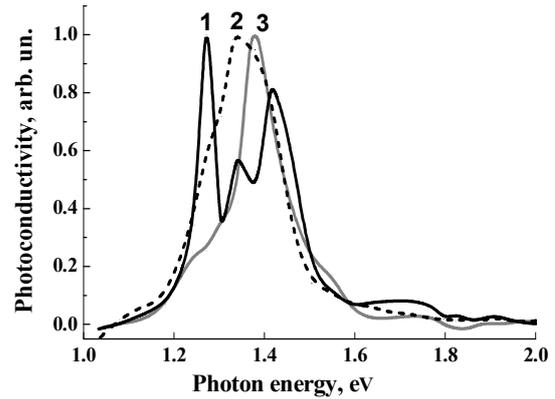


Fig. 4. Spectra of photoconductivity of the macroporous silicon structure with the oxide thickness 30 nm (1); silicon structures with CdS nanocrystals on silicon oxide layer of 15-nm (2) and 30-nm (3) thickness.

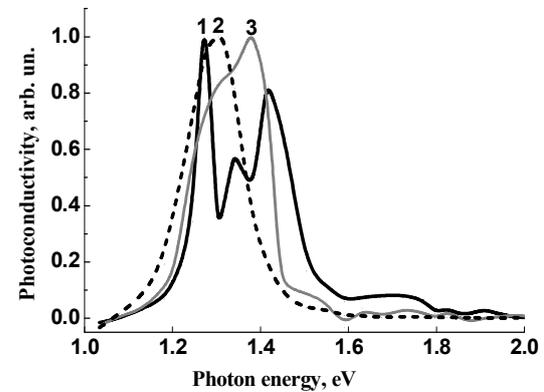


Fig. 5. Spectra of photoconductivity of the macroporous silicon structure with the oxide thickness 30 nm (1); silicon structures with ZnO nanocrystals on silicon oxide layer of 7-nm (2) and 15-nm (3) thickness.

The electric field intensity F_S was determined on the basis of the model of the triangular potential well (Eq. (1)). And the electric field in the near-surface region of silicon with CdS nanocrystals is equal to $(0.8...2) \cdot 10^5$ V/cm for the first quantum level and $3 \cdot 10^5$ V/cm for the second one. In the near-surface region of silicon with ZnO nanocrystals, F_S is equal to $(2...2.3) \cdot 10^5$ V/cm for the first quantum level and $3 \cdot 10^5$ V/cm for the second one. These data are lower than the F_S values obtained via the Franz-Keldysh oscillations (Table 4).

The electric fields obtained from the electroreflectance (Franz-Keldysh effect and main peak splitting) and photoconductivity spectra (main photoconductivity peak splitting) are summarized in Table 5. The data obtained for the nanocoating of CdS nanocrystals on oxide with the thickness 30 nm are most correlated: $F_S = 3.11 \cdot 10^5$ V/cm (Franz-Keldysh effect); $F_S^{1,2} = 3.05 \cdot 10^5$ V/cm (quantization in the electroreflectance spectra); $F_S^{1,2} = 3.12 \cdot 10^5$ V/cm (quantization in the photoconductivity spectra). For this

Table 4. Fermi level in the conduction band E_F , first quantum energy level $E_{0,1}$ and electric field $F_S^{0,1}$, second quantum energy level $E_{1,2}$ and electric field $F_S^{1,2}$ obtained from the photoconductivity spectra.

Sample	d_{SiO_2} , nm	Photoconductivity				
		E_F , eV	$E_{0,1}$, 10^{-3} eV	$F_S^{0,1}$, 10^5 V/cm	$E_{1,2}$, 10^{-3} eV	$F_S^{1,2}$, 10^5 V/cm
macPS	30	1.27	70	2.07	80	3.43
CdS	15	1.27	70	2.07	–	–
CdS	30	1.24	65	1.85	75	3.12
ZnO	7	1.31	–	–	–	–
ZnO	15	1.31	65	1.85	–	–

Table 5. The electric fields in Si-SiO₂ boundary obtained from the electroreflectance and photoconductivity spectra.

d_{SiO_2} , nm	Franz-Keldysh effect	Quantization (electroreflectance)		Quantization (photoconductivity)	
	F_S , 10^5 V/cm	$F_S^{0,1}$, 10^5 V/cm	$F_S^{1,2}$, 10^5 V/cm	$F_S^{0,1}$, 10^5 V/cm	$F_S^{1,2}$, 10^5 V/cm
CdS_15	6.65	0.762	–	2.07	–
CdS_30	3.11	1.93	3.05	1.85	3.12
ZnO_15	7.74	2.29	–	–	–
ZnO_30	4.35	2.02	3.05	1.85	–

sample, the high photon energy shift 140 meV is equal to the sum $E_{0,1}+E_{1,2}$ in the electroreflectance and photoconductivity spectra due to the interband transitions (direct and indirect) of electrons to the Fermi level in the conduction band.

4. Conclusions

The Si-SiO₂ interface in oxidized silicon structures with surface CdS and ZnO nanocrystals was investigated using the methods of electroreflectance and photoconductivity. The direct interband transition energy, broadening parameter and relaxation time of charge carriers were identified from the electroreflectance spectra of silicon structures with silicon oxide layer of 7, 15 and 30-nm thickness as well as CdS, ZnO nanocrystals. There were revealed the Franz-Keldysh effect, built-in electric field and surface quantization of charge carriers in the Si-SiO₂ region. The broadening parameter for oxidized silicon with CdS and ZnO nanocoatings increases with the thickness of silicon oxide and is much higher than the value of Γ for monocrystalline silicon, indicating the influence of defects on the interface of Si-SiO₂. The main electroreflectance peak indicates quantization of charge carriers in the near-surface region of silicon and splitting

of peaks corresponding to one quantized energy level with the oxide thickness 15 nm and two quantum levels with the oxide thickness 30 nm.

It was detected the splitting of photoconductivity peaks in the area of indirect band-to-band transition due to quantization of charge carriers in the surface silicon region, too. The splitting of the main peak by two peaks was measured for the nanocoating on oxide with the thickness 15 nm. And the splitting of the main maximum by three peaks was measured for the nanocoating on oxide with the thickness 30 nm. Quantization of charge carriers in the near-surface region of silicon indicates strong enrichment of silicon surface by electrons and quantum well formation. Therefore, the shift of the main peak of photoconductivity to the higher photon energy can be explained by the band filling effect and interband transitions of electrons to the Fermi level in the conduction band.

The electric fields obtained using the electroreflectance and photoconductivity spectra are most correlated for the nanocoating of CdS nanocrystals with the oxide thickness 30 nm. For this structure, the high photon energy shift is equal to the sum $E_{0,1}+E_{1,2}$ in the electroreflectance and photoconductivity spectra due to the interband transitions (direct and indirect) of electrons to the Fermi level in the conduction band.

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