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LIGHT EMITTING STRUCTURES POROUS SILICON-SILICON SUBSTRATE

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The research of spectroscopic properties of porous silicon has been done. Complex of photoluminescence , electroluminescence , cathodoluminescence , thermostimulated depolarisation current analyth methods have been applyed to study of geterostructures and free layers of porous silicon. Lightemitting processes had tendency to decrease. The character of decay for all kinds of luminescence were different.

Introduction

For the first time Canham [1] in Appl. Phys. Letters (1990) reported about exotic visible room-temperature photoluminescence of porous silicon. So it become the possibylyty to create light-emitting dicodes (LED) and lasers on the same substrate of Si. Porous silicon may be a new material for intergrated micro- and optoelectronics.

Experimental methods

Layers of porous silicon (PS) were obtained by electrochemical etching of n,p-types monocrystalline silicon in HF ethanolic solution. We used (111) Si substrates with thickness of about 400 μm. HF-ethanolic solution with 25% HF concentration was used as electrolyte. Specimens of n-type conductivity were irradiated by white light during electrochemical etching. Some specimens after anodization were etched in concentrated HF about 2.5 h for increasing the porosity [1].

Studies of surface and near surface region of por-Si were done by ellipsometry on wave length of He-Ne laser (633 nm). In the result of experiment we have obtained polarization angles ψ and Δ for different angles of incident light. Using measured values the inverse problem of ellipsometry - determination of refractive index **n**, absorbtion coefficient **k**, layers thickness **d** has been solved. It was nessesary to use two- or three-layers model and create computer programme for obtaining **n**, **k**, **d** values of por-Si layers. We also investigated the influence of technological conditions on optical constants of por-Si and porosity **p** of the material. The porosity was calculated on the base of **n** and **k** using Lorentz-Lorenc equation [2]. Error of calculations was about 10%.

The Thermo Stimulated Depolarisation Current (TSDC) investigation was made by formed thermoelectret state in the sample PS with area 1 cm^2 in vacuum cryostat. Polarisation was carried out in the electric field of the capacitor cell at the temperature betwien 450 and 480 K. The electric field was about $1\text{-}2*10^4$ V/m. After switcing off the polarising electric field the TSD current has been measured with linear heating [3].

For identification of the nature of the defects wich are responsible for the electret state we have carried out the analysis of the energy distribution g(E) of the involved in polarization defect. According phenomenological theory of TSD current for disordered dielectric by way of numerical solving of the Fredgolm integral equation wich is based on the Tikhonov's regularisation method we have calculated g(E) [3].

The photoluminescence (PL) and electroluminescence (EL) in visible (400÷800 nm) spectrum range was studied by automatic equipment. Exciting of luminescence was obtained by nitrogen or argon lasers with wave length 337 and 488 nm, respectively.

PS EL was registered by us in electrochemical cell with 0.5M H_2SO_4 + 0.1M $K_2S_2O_8$ electrolyte in current ingection regime. Initial PS layers were created on n-Si (100) substrates with resistivity 4.5 Ω·cm by anode

etching in HF ethanol solution with current density 10 mA /cm^2 and white light irradiation during 30 seconds. Direct or pulsed current of various duration and polarity in the current stabilization regime was applied between ohmic contact to the silicon substrate and platinum electrode [4,5].

Cathodoluminescence (CL) of PS we was studied in 300-700 nm spectrum range. The electron beam exiting had such parametres: U=9 KV, τ=2.5 μs, I=100-200 μA, S=0.1 mm^2, f=30-50 Gz. The investigation were made at room and temperature of liquid nitrogen.

Results and discussion

PS optical properties were studied on the basis of ellipsometrical research. In the Fig.1 is shown the relation of refractive indexes of PS pre-surface areas to the degree of porosity which is in its turn determined by the parameters and duration of electrochemical etching of silicon.

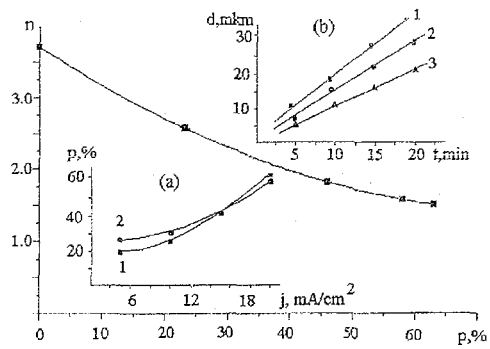

Fig.1. Refractive index dependence via porosity degree of PS:
Insert (a): PS porosity changes wiht increasing of electrochemical etching current density determined by gravimetric (1) and ellisometric (2) metods.
Insert (b): Time electrochemical etching dependence of porous layer thickness for different etching current density: 1-30 mA/cm^2, 2-20 mA/cm^2, 3-10 mA/cm^2.

Refrective index decreases 2 times with the increase in porosity from 0 to 80%.The porosity was calculated from Lorentz-Lorenc equation [2]:

$$\frac{\tilde{n}^2_{por}-1}{\tilde{n}^2_{por}+2}=\frac{\tilde{n}^2_{Si}-1}{\tilde{n}^2_{Si}+2}(1-p')+\frac{n^2_0-1}{n^2_0+2}p',$$

were n_{Si}, n_{por} - refractive indexes of silicium and porous silicon, n_0 - refractive index of porous syrround, p'-porosity.

Thickness of porous silicon layer changed from 0.1 to 100 micrometers. Such a profound change of pre-surface areas can be atributted due to the change of the composition of porous silicon surface films with different porosity in the process of electrochemical etching.

The typical TSDC spectra of the porous Si-Si substrate structures in the temperature range between 200-450 K are presented on the Fig.3. Structures show guite clear maxima at the temperatures near 350-375 and 425-450 K. The TSDC spectra are not enough informative in indentification of the nature the defects wich are responsible for the electret state. That is why we have carried out the analysis of the energy distribution function g(E) of the involved in polarization defects. The phenomenological theory TSD currents for disordered dielectrics with quasicontinous energy distribution of the electrically active defects was used with this purpose. According to [3] the thermally stimulated discharge current j(T) can be writtenes:

$$J(T)=\int g(E)\xi(E,T)dE,$$

where

$$\xi(E,T)=\omega\exp\left(-\frac{E}{kT}\right)-\frac{\omega}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{kT'}\right)dT',$$

ω - is the frequency factor, E - is the activation energy, β - the rate of increase of temperature to the initial temperature. For our experimental results j(T) is expressed by the Fredgolm's integral equation, wich has been solved for g(E) by numerical integration wich is based on the Tikhonov regularisation method.

For solving this equation we have used the method of the regularisation by Tikhonov.The left part of the equation numerical file.

So, ater numerical calculation we must be introduce by have oltained energy activation distribution function for chared defects (ions) in porous silicon (Fig.2). There were distribution function of fill electron states in energy gap by energy and frequency factor. From this curves

we have seen exiting of thermoelectret condition in PS wich have made by redistribution of ions wich are defect in PS. Obtained spectra were characterised not one date of activation energy but certain distribution.

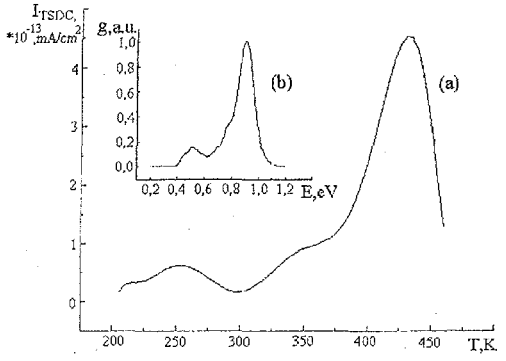

Fig.2. (a).The TSDC spectra of PS-Si heterostructure. Insert (b): The activation energy distribution functions of the defects in por-Si-Si heterostructure.

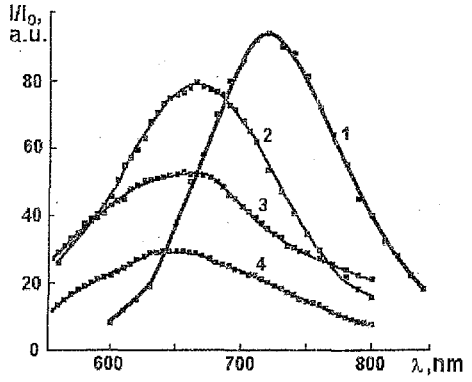

Fig.3. a) The photoluminescence spectra of por-Si under nitrogen (2, 3, 4) and argon (1) laser exciting at T=293 K: 1- p=40%, 2- p=40%, 3- p=60%, 4- p=44% (1, 2- p-type Si, 3, 4- n-type Si).

The intensive photoluminescence (PL) (which was visible at daylight) in p- and n-types of por-Si took place under such conditions of exciting. PL properties of por-Si films were changed with electrochemical etching conditions, type and level of silicon substrates doping. It has been obtained after mathematical approximation of PL spectrum by Gauss curves that luminescence maximum of n-type porous Si specimens was at wavelenght about 660 nm and intensity of peak depended on porosity values. In contrast the maximum of luminiscence band of p-type was near λ equal to 667 nm. The intensity of light also depends on electrochemical etching conditions (Fig.3). Absolute value of PL intensity of p-type por-Si was higher than PL in n-type por-Si. PL intensity of n-type porous Si increased after additional chemical etching in pure HF, with the material porosity raise.

There have been studied the processes of polymetacrylic acid (PMA) polymer film precipitation from water solution on PS surface swing to the fact that chemical reactions on PS surface continue under atmospheric condition. Precipitation was conducted by placing PS samples into PMA water solution for 5-24 hours. There have been used PMA water solution with different molecular masses (10000-70000) and different ionization degrees (0-1.0). Real medium speed of precipitation was 0.8-1 μm/hour for 5-10 μm PMA film thickness.

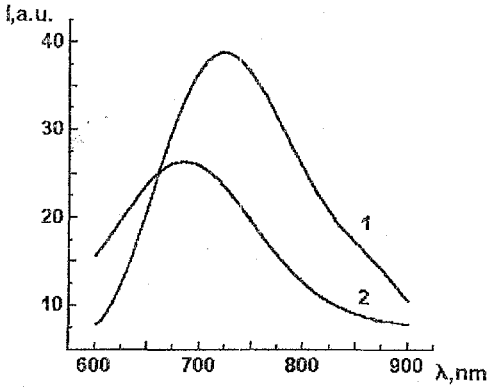

Fig.4. The photoluminescence spectra of PS with nature thin film coating (1) and with polymer film coating (2).

The obtained heterostructures of PS-PMA had photoluminescence properties. Photoluminescence spectrum of the PS was transformed owing to interaction beween PMA and the PS surface. Photoluminescence curves had gaussian shape with one wide maximum at room temperature which was moved by 70-80 nm toward short wave band of the spectrum in connection with PS spectrum without polymer film. The maximum of luminescence was located at about 600-625 nm owing to the ionization degree. Luminescence in the maximum

decreased 2-2.5 times with the increase in intensity (Fig.4).

EL with wide band in the interval of wave lengths of 500-900 nm was observed for various regimes under direct PS shift (Fig.5). Under inverse PS shift EL intensity approached zero. Integrated PS EL, wich was registered by PEM-62 photoelectronic multiplier, decreased after switching on the injection direct current. That was especially characteristic for p-type PS samples, when the integrated intensity decreased twice during 1 minute.We have investigated the effect of the character of pulsed excitation regime on EL intensity and degradation (Fig.6).

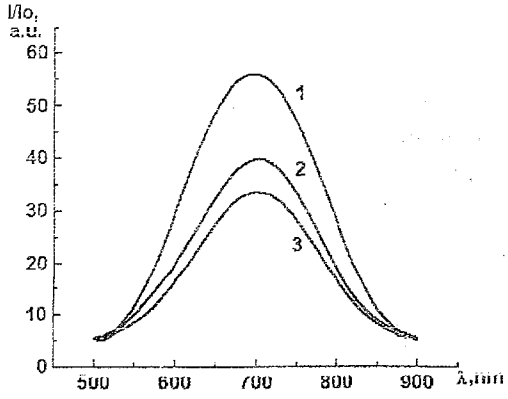

Fig.5. EL spectrum of PS in electrolyte contact: (1) - initial time moment, (2) - after 5 min, (3) - after 10 min.

For n-type samples EL PS intensity was by an order higher than for those of p-type, and it was stable during the time of measurements (30 minutes). EL was excited by periodic direct and inverse pulses of 1 and 0,2 seconds duration, respectively, and with -10 and +5 mA amplitude. A peculiar feature here is full reproduction of EL spectra after the fifth measurement.That is, in this exitation regime no irreversible changes were observed.

EL bandwidth did not change when EL was excited by short duration pulses (direct pulse of duration- 0,2 sec. and inverse - 0,05 sec.)with the previous values of current. Nevertheless, EL intensity in maximum increased by 25 % and it did not changed for 30 minutes during 5 consecutive measurements, but decreased exponentially by 3÷5 times as compared with the initial one. EL degradation was irreversible. EL restoration was possible only after electrochemical etching of the sample in HF (30 minutes),what is likely to have resulted in dissolution of the oxide film on PS surface. It should however be mentioned that the intensity of renewed EL was 5÷10 times less than the initial one,what may be explained by reduction of PS layer thickness. Spectral dependence of PS EL velosity decay was investigated by us in the inverse changes regime, that is, in the regime of long duration pulses (direct pulse 1 sec., inverse pulse 0,2 sec.). EL decay velocity was different when the inverse pulse was sent with different wavelengths. Moreover, intensity decay within the same testing time was greater for EL short wavelength part of the spectrum. That is, in PS there are the groups of EL centres which are characterized by sharp decay kinetics short - wave length groups by faster kinetics and long wave length by slower kinetics.

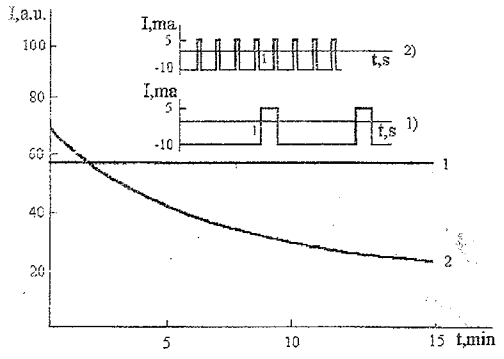

Fig.6.Time dependence of maximum EL intensity decay: 1-a)-type ingection current; 2-b)-type ingection current.

We also have investigated cathodoluminescence (CL) from PS. Two dominant CL bands with maximum in visible (at 550-570 nm) and ultraviolet (360-380 nm) regions were observed (Fig.7). The intensity of short wave band was in some times more, but decreasing velocity was strongly high comparatively with long wave one.

CL blue band confirm existing of dielectric coating on quantum wires surface ($\varepsilon_g \approx 3.1$eV). Long wave CL peak shift into short wave region comparatively with the same bands of PL and EL ($\varepsilon_g \approx 2.4$ eV). This may be connected with

different depth of exciting PL,EL,CL and absorption of radiation by porous silicon.

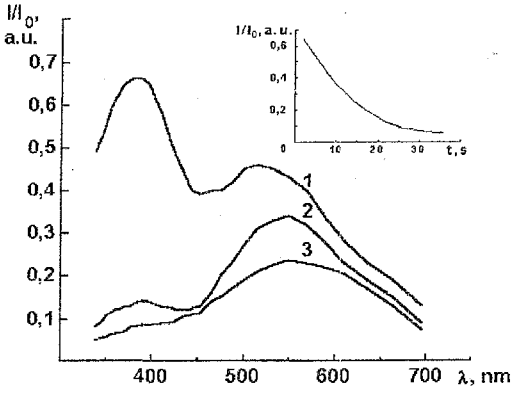

Fig.7.CL PS spectrum at 77 K (1,2) and 300 K (3) at initial time moment (1,3) and after 20 min.(2). Insert - CL time intensity decay at λ_{max}.

Decreasing kinetics of this kinds of luminescence were different: PL was stable for investigation time (~1 h). Decreasing times for CL and EL were 15-20 min and 10-15 min. So the photo-, electro- and cathodoluminescence in porous silicon have strong the different nature.

CONCLUSIONS

All specimens have wide band of PL with maximum in range from 650 nm to 760 nm. Intensity of n-type por-Si specimens PL is by 5÷6 times lower than from p-type por-Si ones.

Thus, PS EL intensity has a tendency to decrease when passing though direct and pulsed injection current. These changes may be reversible or irreversible depending on the excitation conditions. The character of luminescence fatigue in both cases is different. PS EL spectral decay in the inverse changes regime is faster for the spectrum of short range part as compared with the long range part, what testifies to the existence in PS of different types of kinetic radiation centres.

The possibility of precipitation of PMA film on PS surface have been applied to isolate PS from external and athmospheric influences.So from our investigations we have said that the surface of porous silicon is not gomogenous with presence on it fragments Si or SiH_y and also thin dielectric coating of SiO_xC_y.

Besides SiOC clusters on the surface and SiH_y coatings play the significant roles in the light emission of porous silicon. The intensive PL, EL and CL of PS were observed all speciments have wide bond of PL with maximum in the range from 650 nm to 750 nm. PS LE intesity has a tendency to decrease when passing direct and pulsed injection current throught the electrochemical cell. This spectral decay is connect with depolarisation process in PS.

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