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Luminescence of porous silicon and porous silicon encapsulated structures

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Spectroscopic properties of encapsulated porous silicon (PS) have been studied in detail. In order to investigate different heterostructures of porous silicon a complex of analysis methods such as photoluminescence (PL), electroluminescence (EL), cathodoluminescence (CL) and thermostimulated depolarisation (TSD) were applied. The process of light emission shows a tendency to decrease. This decrease varies for different kinds of luminescence. The EL intensity dynamics depends on polarization effects in porous silicon.

1. Introduction

For the first time CANHAM [1] reported on the exotic visible room-temperature photoluminescence of porous silicon. But even now the nature of the PS red luminescence has not been exactly established despite intensive investigations. This may also be related to the fact that investigations were performed on specimens obtained in different technological conditions. It should be noted that up to now photo-, electro- and cathodoluminescence using the same PS specimens has not been studied systematically.

In this work, the luminescence properties of PS and encapsulated PS structures created in the same technological conditions have been studied. Additionally, the purpose of encapsulation was to decrease the PS instability properties in air.

2. Experimental methods

Layers of porous silicon were grown by electrochemical etching of *n*-, *p*-types of monocrystalline silicon in HF ethanolic solution [1], [2]. The substrates of (111) Si of about 400 μm in thickness were used. The HF-ethanolic solution with 25% HF concentration was used as electrolyte. The samples of *n*-type conductivity were irradiated by white light during electrochemical etching. Some samples were etched in concentrated HF after anodisation for 2.5 hours to improve the porosity. The thickness of porous silicon layers varied within the range from 0.1 to 100 micrometers.

The PL and EL in visible (400–800 nm) spectrum range was studied with automatic equipment. The luminescence excitation was stimulated by nitrogen or argon lasers with 337 and 488 nm wavelength, respectively.

We registered PS EL in electrochemical cell with 0.5M H_2SO_4+0.1M $K_2S_2O_8$ electrolyte in current injection regime. Initial PS layers were created on *n*-Si (100) substrates with resistivity 4.5 Ω cm at anode etching in HF ethanol solution with current density 10 mA/cm^2 and under white light irradiation during 30 s. Direct or pulsed current of varying duration and polarity in the current stabilization regime were passed between silicon substrate and platinum electrode [3].

We have studied the cathodoluminescence of PS in the spectrum range of 300 – 700 nm. The parameters of exciting electron beam were the following: $U = 9$ kV, $\tau = 2.5$ μs, $I = 100-200$ μA, $S = 0.1$ mm^2, $f = 30-50$ Hz. The investigation was carried out at room and liquid nitrogen temperatures.

The investigation of thermostimulated depolarisation current (TSDC) was performed on formed electret state in the PS sample with 1 cm^2 area in vacuum cryostat. Polarisation was formed in the electric field of the capacitor cell at a temperature between 450 – 480 K. The electric field was about $1-2\cdot10^4$ V/m. After switching off the polarising electric field the TSD current was measured under linear heating.

3. Results and discussion

The intensive PL has been observed in *p*- and *n*-types of PS under the conditions of excitation mentioned above. The PL properties of PS films were changed according to the electrochemical etching conditions, to the type and rate of silicon substrates doping. The PL spectra have also been changed after deposition of different thin solid films on PS surface. The films of polymetacrylic acid (PMA), SiO_2, Al_2O_3 and ZnS were investigated experimentally. We have studied the processes of PMA polymer film precipitation from water solution on PS surface according to the fact that chemical reactions continue under the air conditions [4]. Precipitation was carried out by placing down the PS samples into PMA water solution for 5 – 24 hours. The PMA water solutions of different molecular masses (10000 – 70000) and different ionisation degrees (0 – 1.0) were used. It follows from the results of the experiments that precipitation rate decreases with decreasing molecular mass of the polymer, and increasing ionisation degree for –COOH clusters containing PMA leads to ionisation of –COO$^-$ while alkaline solution is being added. The actual average rate of precipitation is 0.8 – 1 μm/h for 5 – 10 μm PMA film thickness. The decrease in precipitation rate leads to an increase in the number of clusters with the same polarity, which causes their repulsion, in other words, it diminishes the possibility of adsorption and precipitation. The PMA adsorption model may be presented as creating ionised bonds –COO$^-$ with Si-dangling bonds (Fig. 1, insertion).

Figure 1 shows photoluminescence properties of the created PMA–PS heterostructures. Photoluminescence spectrum of the PS has been transformed owing to the interaction between PMA and PS surfaces. Photoluminescence curves are Gaussian in shape with one wide maximum at the room temperature, which has been moved on 70 – 80 nm towards short wave band of the spectrum compared with PS spectrum without polymer film. The maximum of luminescence is located at about 600 – 625 nm because of the ionisation degree. Luminescence intensity in the maximum is

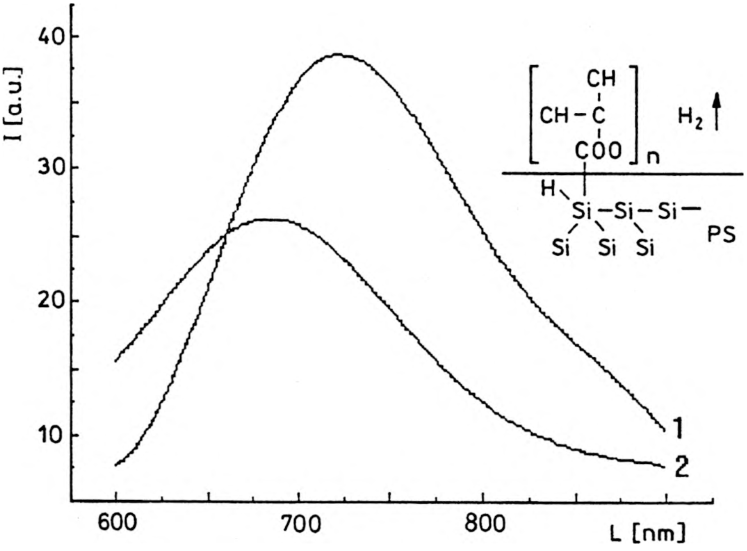

Fig. 1. Photoluminescence spectra of PS without thin film coating (1) and with polymer film coating (2). Insertion: the model of polymer (PMA) adsorption on PS surface.

decreased twice compared with uncoated PS (Fig. 1). The character of PS photoluminescence with polymer PMA film coating can be explained by the model of PMA modification of dielectric penetrability of the medium in quantum threads, in other words, by the influence of PMA molecular adsorption on light-emitting PS-centres.

The SiO_2–PS, Al_2O_3–PS and ZnS–PS structures with SiO_2, Al_2O_3 and ZnS solid films as a coating (thickness $d < 0.5$ μm) were also used in our investigation. They had been obtained by HF-sputtering of SiO_2, Al_2O_3 and ZnS on PS substrate at temperature of 100 – 120 °C in Ar atmosphere during 30 – 40 min. Intensive band in the range 725 – 760 nm has been observed under nitrogen laser excitation conditions in SiO_2–PS. The investigation of Al_2O_3–PS structure shows the 725 – 760 nm band intensity to decrease five times and a band of small intensity appears in the range 800 – 820 nm. The absence of light emission for ZnS–PS structure has been observed only in the infrared range. Figure 2 illustrates a weak light emission in the range of 820 nm.

A wide band EL of PS was observed within the wavelength interval of 500 – 900 nm for various regimes under direct PS shift (Fig. 3). The EL intensity approaches zero under incesre PS shift. Integrated PS EL, which was registered by PEM-62 photoelectronic amplifier, decreases after switching on the injection direct current. It is particularly characteristic of *p*-type PS samples that the integrated intensity decreases twice during 1 min. We have investigated the effect of pulsed excitation irradiation on EL intensity and degradation.

The EL intensity is higher by an order for *n*-type samples of PS than for those of *p*-type, and it is rather stable during the time of measurements (30 min). The EL has been excited by periodic direct and inverse pulse of 1 and 0.2 second duration,

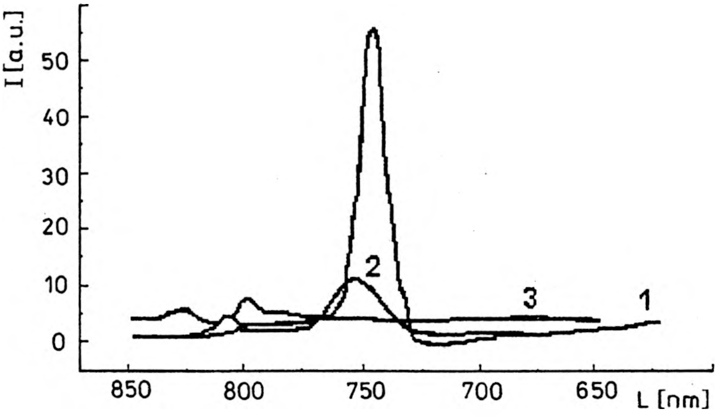

Fig. 2. Photoluminescence spectra of SiO_2–PS (1), Al_2O_3–PS (2), ZnS–PS (3) heterostructures.

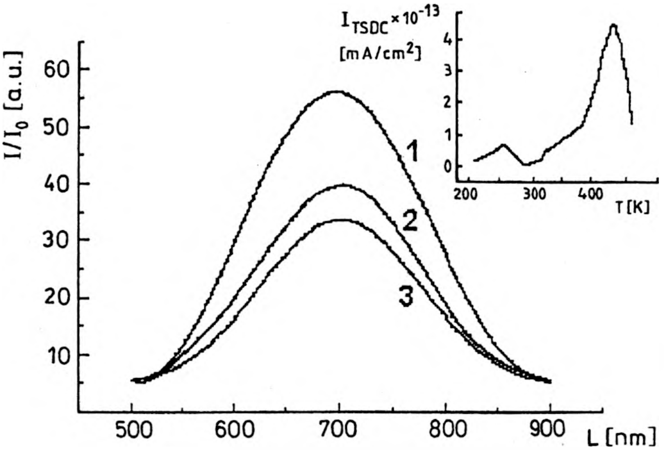

Fig. 3. The EL spectrum of PS in electrolyte: 1 — initial time moment, 2 — after 5 min, 3 — after 10 min Insertion: the TSDC spectra of PS–Si heterostructure.

respectively, and amplitudes of −10 and +5 mA. There is a peculiar feature of a full EL spectra reproduction after the fifth measurement. It means that no irreversible changes have been observed in this excitation regime. The width of EL band does not vary when EL is excited by pulses of short duration (direct pulse duration is 0.2 s and inverse 0.05 s) with the previous values of current. Nevertheless, the EL maximum intensity increases by 25% and does not change for 30 min. during five consecutive measurements, but decreases exponentially by 3–5 times as compared with the initial one. The EL degradation is irreversible. The EL restoration becomes possible only after electrochemical etching of the sample in HF (30 min.), that is, it likely results in dissolution of the oxide film on PS surface. It should, however, be mentioned that the intensity of renewed EL is 5–10 times less than the initial one, which can be explained by reduction of PS layer thickness. Spectral dependence of PS EL decreasing has been investigated in the regime of inverse changes, that is, the regime of long duration pulses (direct pulse 1 s, inverse pulse 0.2 s). The EL decreasing varies with the inverse pulse wavelengths. Moreover, a decrease in intensity over the same testing time is greater for the EL short wavelength region of the spectrum. There are some groups of EL centres in PS which are characterized by sharp decay of short wavelength groups with faster kinetics and long wavelength groups with slower kinetics.

Thus, we assume that fast luminescence decay during the direct current passing over junction PS–electrolyte may be due to PS electrostatic charging. The process of thermostimulated depolarisation of PS has been examined to verify this suggestion. Temperature relations of depolarisation currents have been measured (Fig. 3, insertion). One can observe two stripes at 300–425 K and 450–525 K. So, high polarisation effects in PS have been found within this temperature range.

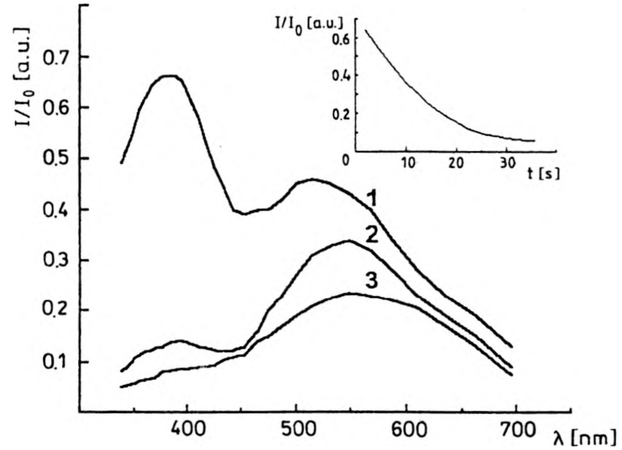

Fig. 4. CL PS spectrum at 77 K (1, 2) and 300 K (3) at initial time moment (1, 3) and after 20 min. (2). Insertion: CL intensity decreasing at λ_{max}

Cathodoluminescence of PS has also been investigated. Two dominant CL bands with maxima in visible (550–570 nm) and ultraviolet (360–380 nm) regions have been observed (Fig. 4). The intensity of short-wave band is greater by several times, but CL luminescence decreasing is significantly higher compared with the intensity in long -wave band.

The CL blue band confirms the existence of dielectric coating on surfaces with quantum wires ($\varepsilon_g \approx 3.1$ eV). Long wave CL peak shifts into short-wave region compared with the same PL and EL bands ($\varepsilon_g \approx 2.4$ eV). This is, probably, related to different depths of PL, EL, CL excitation and radiation absorption by porous silicon.

4. Conclusions

Encapsulated structures PMA–PS, SiO_2–PS, Al_2O_3–PS and ZnS–PS have been created by deposition of thin solid films on PS surface. It has been shown that these films can be used not only as capsulation coatings against atmospheric effects, but also as PS light transmitting media.

We have used the same specimens of PS for investigating photo-, electro- and cathodoluminescence. The kinetics of these kinds of luminescence has been shown to decrease. It has also been shown that EL decreasing may be explained by polarisation effects in PS. In order to decrease the PS luminescence instability in air, we have created and investigated encapsulating processes of PS by thin solid polymer or oxide films on the surface of PS. Change in photoluminescence spectra of encapsulated samples of PS have been investigated. Some materials for encapsulating of PS have been proposed.

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