

EFFECT OF HUMIDITY ON OPTICAL AND ELECTRICAL PROPERTIES OF FREE STANDING POROUS SILICON FILMS

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The PS films were prepared on n-type Si substrates by anodic etching under the white light illumination. Free standing PS films of thickness 5-10 μm and porosity (30-90) % were obtained by electropolishing. The main results of this investigation are the following, (a) The rising of film porosity (from 30% to 90%) results in both the increase of band gap of PS (from 1.4 to 1.9 eV) and resistivity (from $2 \cdot 10^4$ to $4 \cdot 10^4 \Omega \text{ cm}$), (b) The resistivity of films along pores approximately 2-4 times as large as than that in across direction, (c) The band gap of films in humid ambient in the range of 40-95 %RH increases from 1.6 to 1.9 eV. The observed porosity-stimulated and humidity-stimulated changes optical and electrical characteristics were discussed on the base of model including the quantum confinement of charge carries in the PS microcrystallites and chemical activity of PS surfaces.

Keywords: Porous silicon; Optical band gap; Resistivity; Humidity.

1. Introduction

The discovery of visible photoluminescence from porous silicon (PS) has attracted considerable interest due to its potential application in the development of silicon-based optoelectronic devices. However, the origin of photoluminescence in PS is still controversial. A few models are suggested for explanation mechanism of photoluminescence. According model proposed by Canham [1,2] radiative recombination of electron-hole pairs occurs within nanometer silicon wires and their energy gaps become larger than that of bulk Si (quantum confinement effect). This model modified by Koch et al. [3] suggests that electron-hole pairs are photo-excited in nanometer silicon particles and radiatively recombined via Si intrinsic surface states. Another model [4, 5, 6] suggests that luminescence from PS was caused by some special luminescence materials, such as SiH_x complexes, polysilanes, or SiO_2 rather than an intrinsic property of nanometer Si. A third model believes that excitation of charge carriers occurs in nanometer silicon particles and the photoexcited carriers transfer into the luminescence centers (defects and impurities) in the surrounding SiO_2 layers [7].

In general, main models proposed for explaining the origin and mechanism of visible photoluminescence in PS can be divided on three groups. The first group comprises intrinsic effects in nanometer Si, whereas the second group of model is related with processes proceeding an external surfaces of nanocrystals, i.e. on surfaces of PS. These processes are determined with composition and structure of materials on PS surfaces. The third group combines models of the first and second group. The structure of PS is characterised by an extremely large surface area to volume ratio (up to $10^3 \text{ m}^2 \text{ cm}^{-3}$). It is known that surface bonds, in particular Si-H and Si-O bonds play an important role in regulating optical, electrical and gas sensing properties of PS. These properties of PS are very sensitive to humidity of ambient. Investigations of optical properties of the free standing PS films can promote understanding mechanism of photoluminescence. The optical and electrical characteristics of free standing films depending on porosity are rarely considered [8]. Xu et al. [9] have measured evolution of the optical absorption of free standing PS films during thermal oxidation in air and decreasing of the gap have explained due to the Si-O bonds formation. Sagnes et al. [10] have

measured the absorption spectra of the free standing PS films with porosity in a range of 45-79 % and observed a blue-shift of curves with an increase of the porosity. As far as our knowledge goes, data on effect of humidity on optical absorption spectra of free standing PS films are absent in literature.

In this work optical transmission spectra of the free standing PS films with porosity in a range of 30-85 % were measured and the increase of energy band gap of PS films with rising in the porosity have observed. Further, humidity-stimulated changes of optical absorption spectra and band gap of PS films have discovered.

2. Experimental Procedure

PS films were formed by anodization of (111)-oriented n-type silicon wafers ($0.01 \Omega \text{ cm}$) in HF-ethanol solution at constant current density under the white light illumination [11]. The PS films were then detached from the Si substrates by electropolishing at a current density of about 0.8 A/cm^2 . The free standing PS films were characterized by porosity, thickness, resistivity and optical measurements. Average porosity of films was determined by gravimetry. Free standing PS films of thickness 5-10 μm and porosity of $P=30-90$ % were analysed in this work.

The transmission spectra of free standing PS films were measured from 300 to 1000nm at room temperature by using 'UV/VIS Lambda 2S' (Perkin Elmer) spectrometer. Resistivity measurements were performed along and across of pores. Optical and electrical measurements of PS films were examined at the normal room conditions ($T=300\text{K}$, 40%RH) and in the measuring cell at different ambient humidity (water vapour) in the range of 40-95%RH. The relative humidity in cell was measured by using 'Extech-444701' Hygro-Thermometer.

This investigation focuses on the analysis of the transmission spectra and resistivity in dependency on both porosity of PS films (for normal room conditions) and relative humidity of ambient (for PS films with given porosity). Time-dependence transmission spectra and time-dependence resistivity measurements under humidity exposition in cell were carried out after 5-or 10-min intervals of humidity exposition.

The absorption coefficient (α) was determined from the measurements of transmission spectra of two porous silicon films of same porosity with different thickness by using the relation [12]

$$\alpha = (d_1 - d_2)^{-1} \ln(T_1/T_2) \quad (1)$$

Here T_1 and T_2 are the transmission of films with thickness d_1 and d_2 respectively.

3. Results and Discussion

Measuring of transmission spectra at room conditions ($T=300$ K, 40%RH) were carried out for free standing PS films with porosity of 46%. fig.1 shows the absorption coefficient spectrum for PS film. Analysis of measured curves of absorption coefficient (α) versus photon energy ($h\nu$) for PS films with porosity in range of 30-90% showed that spectra discovered behaviour expected for direct semiconductors

$$\alpha^2(h\nu)^2 = A(h\nu - E_g) \quad (2)$$

Here E_g is energy gap and A is constant. Absorption coefficient curves for PS films discovered a continuous blue-shift with porosity increase in range of 30-90 %.

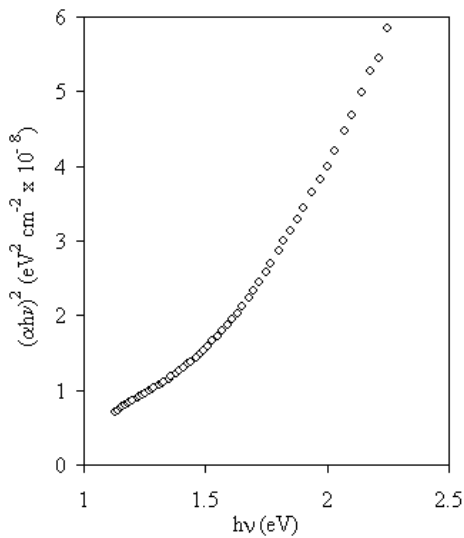


Fig. 1. Optical absorption spectrum of PS film of P= 46 % porosity (40 %RH).

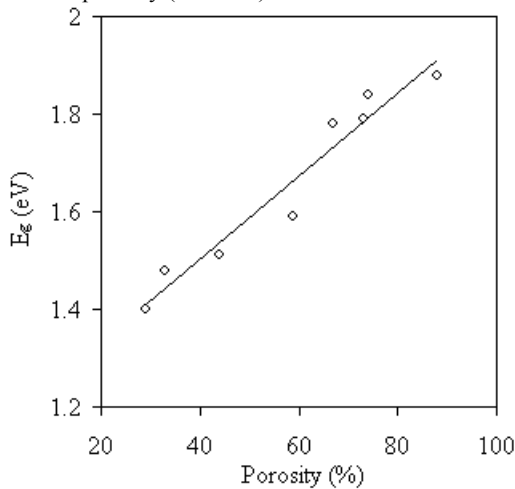


Fig. 2. Energy gap of PS films in dependency on porosity (40%RH).

Fig. 2 shows energy gap in dependency on porosity of the free standing PS films, calculated from extrapolation of the high energy part of $(\alpha^2 - h\nu)$ spectra. Near linear increase of band gap from 1.4 to 1.9eV with rising of porosity of PS films in the range of 30-90 % is observed.

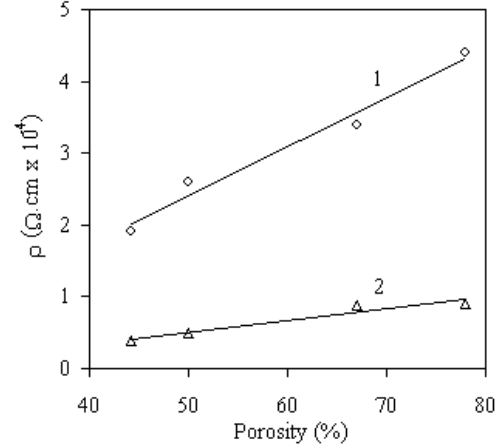


Fig. 3. Resistivity of PS films (1) along and (2) across of pores (40 %RH).

Fig. 3 presents resistivity along and across of pores for free standing PS films with porosity in a range of 45-78%. Increase of resistivity with increase of porosity is observed for both directions. These data on resistivity - porosity dependence (fig.3) correlate with increase of energy band gap of PS films with rising in porosity (fig.2). Lower values of resistivity across of pores can be related with presence of lower-porosity layer along PS film-Si substrate interface.

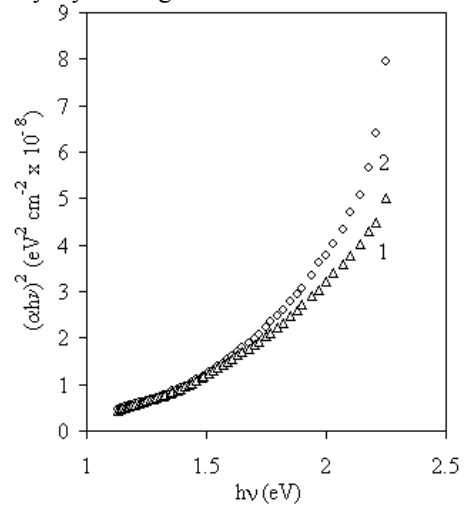


Fig. 4. Optical absorption spectra of PS film at (1) 40 %RH and (2) 90 %RH (P=68 %).

Data on absorption spectrum of PS films with different porosity at normal room ambient above have been presented. Data on the absorption spectra of PS films in dependency on humidity will be below considered. The absorption spectra of PS film with a porosity $P= 68$ % for normal room conditions ($T=300$ K, 40%RH) and under exposition in humid ambient (90 %RH) are shown in fig.4. The blue-shift of the absorption curves with increasing the relative humidity is observed. Energy gap of PS films in humid atmosphere ($E_g=1.9$ eV for 90%RH), calculated from the absorption spectra is considerable larger than that for normal room conditions ($E_g=1.6$ eV for 40 %RH).

It will be noted that optical absorption spectra of PS films at once after placing in humid ambient are changes and then after exposition in humid during approximately 20-25 min these changes are ended. Fig. 5 shows evolution of the energy band gap of PS film with porosity of 68% at once after placing the sample in humid atmosphere of 90 %RH ($t=0-20$ min) and after removal from humid ambient to normal room conditions with 40%RH ($t=20-45$ min). It will be noted that evolution of resistivity of PS films (with porosity 64%) on placing in humid ambient with 90%RH and the further removal from humid ambient showed behaviour which is similar to (E_g-t) curve presented in Fig. 5. Increase of energy gap of PS film from 1.6 to 1.9eV under humid exposition at first 20min can be tentatively explained by diffusion hydrogen or oxygen from humid atmosphere (water vapour) and formation Si-H and Si-O bonds on PS surfaces. Further decrease of energy gap as result of removal PS film from humid ambient in normal room conditions, can be caused by rediffusion of hydrogen or oxygen atoms or molecules from PS surfaces out of sample. We believed that increase of energy gap in humid atmosphere is mainly caused by hydrogen diffusion into PS films, rather than oxygen diffusion [13]. The indirect confirmation of this suggestion can be data of Xu et al. [9] on decrease of energy gap of PS films with an increase in oxygen termination atoms. Further, hydrogen diffusion coefficient in PS is larger than oxygen diffusion coefficient [13] and therefore formation of Si-H bonds under humid exposition is more preferably. On accepting hydrogen-stimulated model of increasing of energy gap of PS films, rate of increase in energy gap is determined by diffusion coefficient of hydrogen in PS films. Then estimation of diffusion coefficient of hydrogen in PS films at room temperature for 90 %RH results in $D \sim 2 \cdot 10^{-10} \text{ cm}^2/\text{s}$ [14].

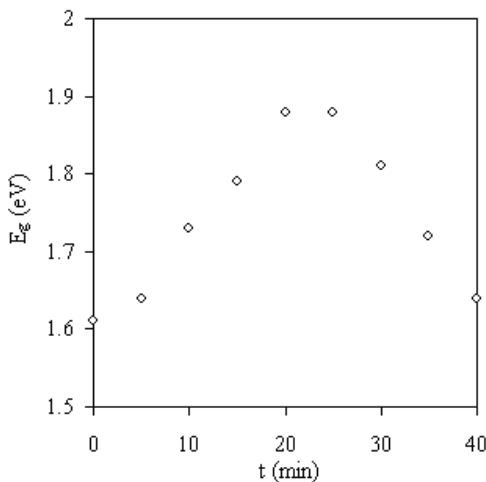


Fig.5. Change of energy gap of PS film ($P=68\%$) during exposition in humid (90%RH, $t=0-20$ min) and subsequent removal of PS film from humid atmosphere ($t=20-40$ min).

Fig. 6 presents the energy band gap of PS films (with porosity of 68%) in dependency on the relative humidity. These data were received from optical transmission measuring carried out after exposition of PS film in humid ambient for 30 min. As it is seen from fig. 6, $E_g - RH$ dependence as a energy gap versus porosity (E_g-P) curve (fig.2), shows nearly linear increasing of energy gap.

Data on fig. 2 and Fig. 6 concerning a increase of the energy gap in dependency on porosity of PS films and ambient humidity respectively, can be explained by a model including the quantum confinement of carriers in the PS microcrystallites and the formation of the Si-H bonds on pore surfaces in humid atmosphere.

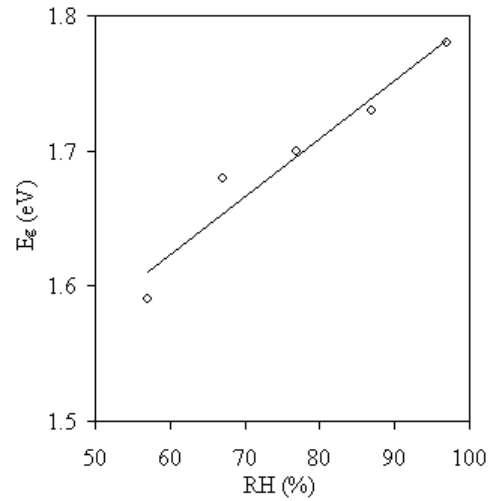


Fig. 6. Energy gap of PS film in dependency on relative humidity ($P=68\%$).

Visible light emission photoluminescence in PS, as it is known is closely related with the band gap of PS. Therefore data on the band gap-porosity and the band gap-humidity dependencies (fig.2 and fig.6) can be further for understanding of mechanism of photoluminescence in PS films. As it is mentioned above, two main groups of models were suggested for explanation of photoluminescence in PS. The first group of models [1,2,3] suggest that the luminescence in PS is related with quantum confinement of charges in nanostructures, causing the widening of the Si band gap. The second group of models believes [4,5,6,7] that the visible luminescence was caused by some special luminescence materials (such as SiH_x complexes, polysilanes etc) forming on PS surfaces. Data of present investigation on increase of the band gap with the rising of porosity of PS films (fig. 2) can be support of the quantum confinement model of luminescence, since the rising of porosity is accompanied by decrease of nanocrystals sizes. At the same time, data on increase of band gap of PS films with increase of humidity can be evidence of realization of luminescence in SiH_x -type complexes on PS surfaces, since the surface concentration of these complexes must increase in humid ambient. This, in turn, can cause the chance of composition of complexes on PS surfaces.

In conclusion, data on increase of the band gap of PS in dependency on porosity and humidity, received in this work, can be support for both quantum confinement based and the surface complexes based models of luminescence in PS respectively.

Acknowledgement

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NƏMİŞLİYİN NAZİK TƏBƏQƏLİ MƏSAMƏLİ SİLİSIUMUN OPTİK VƏ ELEKTRİK XASSƏLƏRİNƏ TƏSİRİ

Məsaməli Si nasik təbəqələrin (5-10) μm optik və elektrik xassələrinin nəmişlik və nümunələrin məsaməlilikdən asılılığı araşdırılmışdır. Göstərilmişdir ki, məsaməli Si təbəqələrin məsaməliliyi 30%-dən 90%-ə qədər artdıqda, onların qadağan olunmuş zolağı 1.4 eV-dan 1.9 eV qədər yüksəlir və xüsusu müqaviməti 2×10^4 -dən 4×10^4 Ohm sm qədər artır. 40-95% nəmişlik ortamında məsaməli Si təbəqələrin qadağan olunmuş zolağı 1.6eV-dan 1.9 eV qədər artır. Müşahidə edilən nəticələr yükdaşıyıcılarının kvant sınılanma modeli ilə və məsaməli səthin kimyəvi aktivliyi ilə izah edilmişdir.

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ВЛИЯНИЕ ВЛАЖНОСТИ НА ОПТИЧЕСКИЕ И ЭЛЕКТРИЧЕСКИЕ СВОЙСТВА ТОНКИХ ПЛЕНОК ПОРИСТОГО КРЕМНИЯ

На пленках пористого кремния (5-10 мкм) с различной пористостью выполнены измерения оптического пропускания и электропроводности. Показано, что увеличение пористости пленок от 30% до 90% приводит к возрастанию ширины запрещенной зоны от 1.4 эВ до 1.9 эВ, а также сопровождается увеличением удельного сопротивления от 2×10^4 до 4×10^4 Ohm cm. Под действием влажности в интервале 40 - 95% RH ширина запрещенной зоны возрастает от 1.6 эВ до 1.9 эВ. Наблюдаемые изменения оптических и электрических свойств пористого кремния, стимулированные пористостью или влажностью, объяснены на основе модели квантово-размерного эффекта ограничения носителей заряда и модели химической активности поверхности пор.

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