Süleyman Demirel Üniversitesi
Fen Bilimleri Enstitüsü Dergisi
Cilt 21, Sayı 3, 738-742, 2017

Süleyman Demirel University
Journal of Natural and Applied Sciences
Volume 21, Issue 3, 738-742, 2017

DOI: 10.19113/sdufbed.19374

# Investigation of Photoluminescence Homogeneity Distribution of Nano-Porous Silicon by Imaging Spectroscopy

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(Alınış / Received: 27.02.2017, Kabul / Accepted: 08.07.2017, Online Yayınlanma / Published Online: 01.08.2017)

**Keywords**
Porous silicon,
Imaging spectroscopy,
Photoluminescence

**Abstract:** The observation of effective luminescence (PL) from the porous silicon (PS) at the visible region at room temperature is one of the prevalent topics in recent years. This is why there are many application areas in optoelectronics integration with the existing silicon technology. However, non-uniformity of PL is an important problem and should be solved before using its future applications as light emitting diodes (LEDs). In this study, spatial distribution properties of photoluminescence of porous silicon were investigated by imaging spectroscopy (IS) on macro (95 mm$^2$) and micro (10 μm$^2$) scale. It has been showed that the spatial distribution of PL is not homogeneous. The PS luminescence homogeneity is also affected by the production parameters and the post-anodization environmental conditions. It was showed that luminescence intensity and luminescence homogeneity increased with atmospheric aging.

# Nano-Gözenekli Silisyumun Mikro ve Makro Ölçekte Fotolüminesans Homojenliğinin Görüntü Spektroskopisi Yöntemi ile İncelenmesi

**Anahtar Kelimeler**
Gözenekli silisyum,
Görüntü spektroskopisi,
Fotolüminesans

**Özet:** Gözenekli Silisyumdan (PS) oda sıcaklığında görünür bölgede etkili lüminesans (PL) gözlenmesi son yılların oldukça popüler konularındandır. Bunun altında yatan temel neden mevcut silisyum teolojisi ile birleştirilerek opto-elektronikte pek çok uygulama alanın olmasıdır. Fakat özellikle ışık yayan diyot (LED) uygulamalarına geçilmeden önce lüminesans homojenliği probleminin çözülmesi gerekmektedir. Bu çalışmada Gözenekli Silisyumun fotolüminesans (PL) özelliği makro (95 mm$^2$) ve mikro (10 μm$^2$) ölçekte uzaysal dağılımı görüntü spektroskopisi (IS) yöntemi ile incelenmiştir. PL'nin uzaysal dağılımının incelenen ölçeklerde homojen olmadığı ve PS lüminesans homojenliğinin üretim parametrelerinden ve anodizasyon sonrası çevre koşullarından etkilendiği tespit edilmiştir. Lüminesans şiddetinin ve homojenliğinin atmosferik yaşlanmaya bağlı olarak arttığı görülmüştür.

## 1. Introduction

Porous silicon is obtained by electrochemically etching in hydrofluoric acid (HF) based solution from crystalline silicon (c-Si) [1-4]. It has an effective luminescence in the visible region at room temperature [1-4]. There are many possible applications using the available silicon technology in opto-electronic applications at near future. Although early studies are pointed at understanding the physical mechanism of the observed PL, the recent studies are focused at technological applications of PS such as sensors and LEDs [1,2]. However, there are important problems to solve for PS applications such as PL instability and PL efficiency. Another problem is PL homogeneity. Therefore, in this study the PL homogeneity was studied with aged and fresh PS samples. Recently, researchers have been also working on the PL stability and the PL efficiency problems of PS [3]. Among these solutions metallization coating of the PS surface can be given as example [4]. However, there were only few previous studies in literature about the spatial distribution of PL of PS. For example, Fujiwara et al. [5] and Ohmukai et al. [6] showed that, PL homogeneity, from different regions of PS surface were not identical by

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using PL spectrum. In other words, PL characteristic of edge regions and middle (center) regions are not the same. Hossain et al. (7) studied size distribution of Si crystallites on the PS surface together with the geometry of platinum (Pt) electrode and showed that the size of Si crystallites was influenced by electrode geometry. Nakagawa et al. [8] examined the PS surface with SEM and optical microscope and indicated that the PS surface consisted of particle-like structures whose sizes ranged from a few nanometers to several ten nanometers but they did not give any information about the spatial distribution of PL. The homogeneity of PL is very important for possible LED and display applications of PS.

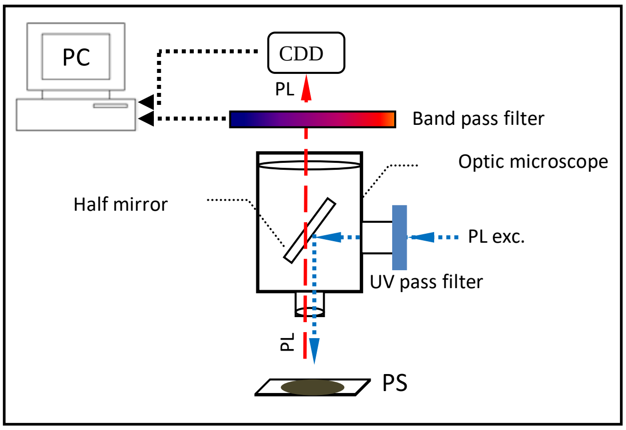


**Figure 1.** Schematic representation of imaging spectroscopy technique [9].

In this study, the effect of atmospheric aging and anodization illumination on spatial distribution of PL intensity using the imaging spectroscopy technique (spectral optical microscope) was investigated. The PL studies using the technique are also very important in terms of future PS applications and will bring a new vision to PL studies. The aging and anodization illumination effects on spatial distribution of PL using the imaging spectroscopy technique is discussed for the first time in this study.

## 2. Material and Method

### 2.1. Experiments

The porous silicon was formed on boron-doped silicon wafers (111) with resistivity of 10.5–19.5 Ω.cm using electrochemical anodization. The Si wafers were cleaned in a bath of ethyl alcohol and de-ionized water. The anodization then carried out in HF (48%): $H_2O$=1:4 (by volume). Etching process was subsequently applied for 30 min by using Pt as the counter electrode at a current density of 10 mA/cm$^2$. He-Ne laser of 632 nm (5mW) was used for illumination during the chemical etching. The PS samples which will be referred as "as-prepared" for the remainder of this paper were rinsed in ethanol and then dried in vacuum. Aging of PS was performed in atmospheric condition at room temperature in Lab for 7 months. PL studies were performed at room temperature. The details for the anodization procedure and production of PS were described elsewhere [10].

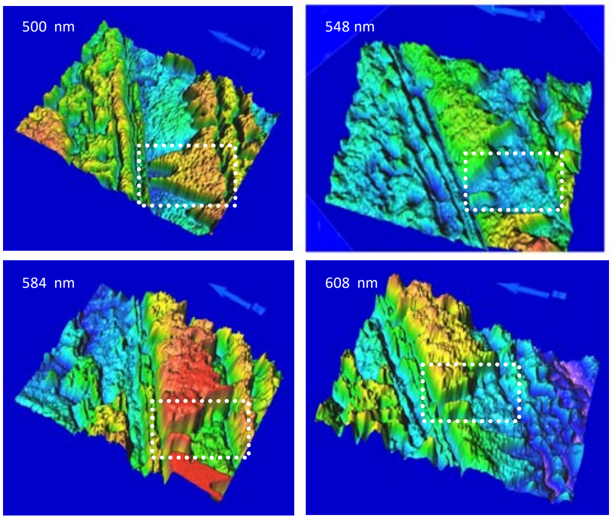


**Figure 2.** PL images at the micro-scale (10 μm$^2$) taken from the same region of PL. In order to be clarity, the area studied is shown in the circle.

Xenon and UV lamp (365 nm) were used for PL excitation. PL spectrum measurements were performed using computer-controlled MMS spectrometer have spectral range 310 to 1100 nm and spectral resolution is 3, 3 nm. The used band pass filter is linear variable dichroic filter from Edmund Optics. PS samples were aged in Lab condition in air for 7 months. The experimental setup shown in Fig. 1 is also used for spatial distribution of PL.

### 2.2. Imaging spectroscopy technique

Imaging spectroscopy technique is a quite new technology. The PL of PS in this technique is passed through a band-pass optical filter (linear variable dichroic filter) before coming to charge couple device (CCD), and a spectroscopic scanning of the image (PL) performed by computer-controlled mechanical motion of the filter. The band-pass filter is consisting collection of filters group operating between 400 nm and 1000 nm. Unlike the conventional optical microscopes, the modified optic microscope used in this way allows a spectroscopic examination of the image (PL) obtained due to the movement of the band-pass optical filter (wavelength scanning). The movement of the filter is controlled by a step motor. The clear image taken from the same point that obtained from movement of the band-pass filter shows us the maximum PL spectrum peak of the PS. The obtained PL images are then converted to 3D images using a computer.

## 3. Results

In the Figure 2, PL images of 7500 magnification of optical microscope are given. These images were obtained due to the motion of the band pass filter. The PL images were obtained by scanning a wavelength between 500 and 608 nm from the same spot. All images are shown in approximately the same direction and have a circular region on the image for simplicity. The Xenon lamp and UV pass filter are used together for PL excitation. The numbers given on the upper side of the figures correspond to the wavelength of the band-pass filter and give the PL wavelength of the examined region. In Figure 2, the presence of different color tones within a single image means that the PL intensity and wavelength are different for the region being examined. It can be also seen that same spatial region (showed with a circle) have different luminescence feature after the spectral scan. This difference can be understood by the nano-sized crystallites do not uniformly distribute on the PS surface. The size of nano-crystals formed on the PS surface after etching also affects PL energy [11,12]. When the size of nano-crystals decreases, the PL spectrum shifts towards high energy region (blue shift) [11-13].

Illuminations used during anodization affect the ability of PS to become macro-porous or micro-porous [14]. The illumination can be a distinction in the spatial distribution of the luminescence if a certain part of the PS surface is illuminated such as He-Ne laser used without a lens during the anodization. The spectral distributions of PL on macro scale at fresh and aged PS (7 months after the production in lab condition) anodized with He-Ne laser illumination are shown in Figure 3. PL spectra of the sample which getting a spectrometer are also shown in Figure 4. The area of the circular PS is 95 mm² (diameter is 11 mm) and the diameter of the He-Ne laser used during the anodization is 1.3 mm. During the anodization of PS, the He-Ne laser was sent directly (without any lens) to the center of porous silicon. The effect of He-Ne laser illumination on PL intensity and PL wavelength is clearly seen in Fig. 3-a and 3-b. Here, the PL peak observed at the center of the PS surface due to the laser illumination is lost in figure 3-b for the same sample. This PL peak shown at Figure 3-a was created by the influence of He-Ne laser. For the aged sample, it can be seen that the PL emission intensity at 700 nm is maximum and another PL peak is 520 nm. Two different PL distribution pictures of the same sample show us that the PL spectrum has two peaks. However, this difference cannot be observed in the PL spectrum obtained with the help of a spectrometer (see figure 4) due to small emission intensity at 620 nm. However, this small intensity only contributes to inhomogeneity of the PL spectrum. The spatial distribution of the PL obtained by this method has a significant advantage over the PL measurements obtained by the conventional methods using a spectrometer. It is also clearly obvious from PL distribution obtained by the imaging spectroscopy method that different regions have different luminescence properties.

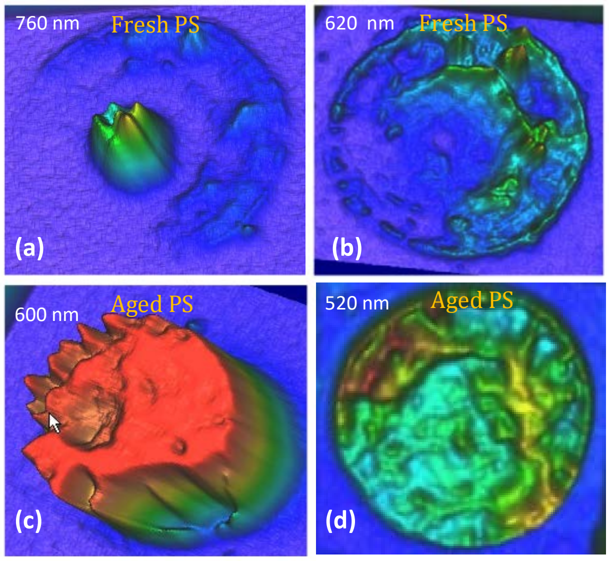


**Figure 3.** PL distribution of PS in macro scale (95 mm²). Where; a is PL picture of as-prepared (fresh) PS at 760 nm, b is PL picture of as-prepared PS at 620 nm, c is PL picture of aged PS at 600 nm and d is PL picture of aged PS at 520 nm.

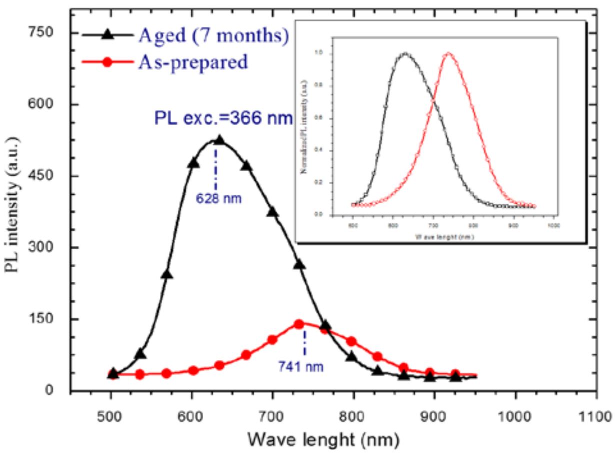


**Figure 4.** The PL spectra taken from the spectrometer of fresh and aged porous silicon.

The luminescence properties of PL spectra of the aged PS vary considerably. The regions that irradiated at 760 nm began to irradiate at 600 nm (means blue shift) and the showing peak caused by the He-Ne laser at fresh sample was lost and the PL homogeneity on the surface was increased. The PL properties of the PS shifted to high energy region and a new luminesce shown is different at 520 nm. The increase of PL homogeneity is a satisfactory result in terms of display applications of PS. The PL spectrum obtained from the spectrometer (see figure 4) shows that the magnitude of the PL intensity is about 10 times higher than the initial state and the peak energy is about 150 nm blue shift. The blue shift of the luminescence should be due to chemical changes on the PS surface such as oxidation, decreasing of un-paired dangling bonds and forming of siloxane like structures. It is well known that the un-paired dangling bonds behavior as non-radiative luminescence centers [10]. For this reason, it can be clearly understood that alone quantum confinement model which is used for PS luminescence mechanisms in literature is not sufficient. The quantum confinement (QC) model can be explained with spatial dimension of crystallite on PS surface forming after the anodization. Instead of QC model, a model that includes surface chemical structures such as siloxane like structures, carbonization and oxidations will be more effective for luminescence mechanisms.

The spatial distribution of PS luminescence is an important potential for future applications such as LEDs, screen displays where a homogeneous spatial PL distribution is desired. Since the PL spectra obtained by the spectrometer give us the integration of the total radiation obtained from the whole surface, we do not know about the surface homogeneity of PL. Moreover, the PL regions with different PL properties should not be shown in the same Gaussian curve due to integrated PL in the classical method. Whereas, in imaging spectroscopy this problem has been eliminated because the PL intensity is determined in different color tones.

Because of our IS studies, it has been found that there are regional differences of PL in macro and micro scale. This result indicates that the nano-crystals on the PS surface forming after the anodization of crystalline silicon are not uniformly distributed. At the same time, the nano-crystals are affected by He-Ne laser illumination during anodization. The PL images obtained from the IS technique and the PL spectra obtained from the spectrometer are supports each other.

## 4. Discussion and Conclusion

In this study, the spatial distribution of PS luminescence in micro (10 $\mu m^2$) and macro (95 $mm^2$) scale was investigated by imaging spectroscopy technique. The results obtained are listed below:

- PL homogeneity and wavelength difference of PS are important problems that need to be solved in terms of future micro and macro dimensional PS applications. Furthermore, imaging spectroscopy studies are needed to determine the PL homogeneity in the technological applications of PS.
- The illuminations used during anodization affects the microstructure of porous silicon. Luminescence patterns can be also created in macro and micro scale on the PS surface. In order to obtain a homogeneous luminescence, the illuminations used must be homogeneous at the whole c-Si surface during anodization.
- PS luminescence is affected by environmental conditions. PL intensity increases and PL spectrum shifts towards the high-energy region with atmospheric aging. PL homogeneity also increases with the aging.
- PS surface chemical structure plays an effective role in PL. Therefore, the quantum confinement model which determined with size of PS crystals used alone in PL statements is insufficient. The quantum confinement effect supported by surface states can be understood for luminescence of PS.
- New production technologies of PS are needed to increase the PL homogeneity.

## Acknowledgment

The author is grateful to Prof. Dr. F. Hacizade (TUBITAK-UEKAE at Turkey) and Prof. Dr. A.Y. ORAL (Gebze Technical University at Turkey) for their helpful discussions.

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