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THE EFFECT OF THICKNESS OF SILVER THIN FILM ON STRUCTURAL AND OPTICAL PROPERTIES OF POROUS SILICON

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In this study, porous silicon (PS) samples were prepared on n-type silicon (100) wafers by electrochemical etching method, varying the current density from 20 to $100\,\text{mA/cm}^2$ and keeping constant HF concentration (10%) and etching time of 15 min. Then, Ag thin films, which have 10, 50 and 100 nm film thicknesses, were deposited on PS layers by using thermal evaporation to investigate the influence of Ag film thickness on structural and optical properties of PS. The structural and optical properties of PS and Ag deposited PS layers have been investigated by XRD, FE-SEM, Raman and photoluminescence (PL) spectroscopy. FE-SEM XRD and Raman analyzes indicate that average pore size and porosity of PS layers increase with the increasing current density. Further, Ag nanoparticles have embedded in pore channel. PL measurement reveals that higher porosity of PS would be better to form the Ag–PS nano-composite material leading to stronger PL band. The PL spectra of PS and Ag–PS samples indicate that PL bands show blue shift with increasing current density and film thickness. Consequently, it has been found that the structural and optical properties of PS depend on current density and Ag film thickness individually.

Keywords: Semiconductors; thin films; Raman spectroscopy; crystal structure; luminescence.

PACS Number(s): 81.05.Ea, 68.55.−a, 78.30.−j, 81.07.Bc, 78.55.Mb

1. Introduction

Porous silicon (PS) was discovered by Uhlir while performing electropolishing process on Si wafers in 1956. However, there was little interest in PS until 1990 when Canham published his results on the discovery of its room temperature visible photoluminescence (PL) from PS, and explained it as a result of quantum confinement effect (QCE).[1] Since the discovery of its visible light emission from PS, the material has attracted many scientists. Light emitting PS layer has been produced by using different techniques, such as electrochemical anodization etching technique,[2] stain etching process,[3] and hydrothermal etching technique.[4] Among these methods, anodization has been recognized as the most technologically feasible and economically superior technique for production of PS layer. Compared to other methods, the advantages of

anodization technique are easy to control, versatility and low cost. It has long been known that by varying the anodization parameters, such as concentration of HF, current density, time, doping type of substrate, etc., various PS samples with different structural, morphological and optical properties can be obtained.[5] These controllable properties enable PS to be used in different areas, such as optoelectronics, microelectronics, chemical and biological sensors.

It has been reported that the pore size, porosity and grain size in PS layer, which are believed to be the reasons for strong visible PL from PS at room temperature, strongly depend on the applied current density of the anodization.[6,7] But the effect of current density on the structural and optical properties of PS layers grown on n-types of Si wafer is not understood well. For this reason, in this work, we have tried to focus our attention on the structural and optical properties of PS by controlling the applied current density in the range from 20 to 100 mA/cm^2. On the other side, electrochemically prepared PS has been reported to show unstable PL. This behavior has been attributed to the unstable character of its surface in the air.[6] To improve the PL stability of PS and to meet device requirements, it is necessary to change the PS surface structure.[7] Many surface modification methods have been employed to improve PL properties of PS such as passivation of PS using various methods such as electrodeposition,[8] sputtering[9] and thermal evaporation.[10] Thermal evaporation is an economical and simple method to produce high quality thin film. The main aim of this study is to investigate the influence of Ag film thickness on optical properties and structural properties of PS samples. Ag has been deposited on PS samples using thermal evaporation method to passivation of PS surface with three different thicknesses, 10, 50 and 100 nm, respectively. We have used Ag to modify surface of PS samples due to unique characteristics, such as chemical stability, excellent adhesion to substrates and high conductance.[10] It has been also reported that Ag passivation is the most effective in enhancing the PL of PS among other metals.[9] We have expected the potential use of Ag–PS as an optical material in material science and new silicon-based optoelectronic devices with optimization of the film thickness and current density. According to our best knowledge, there are no reported results where Ag–PS nano-composite material is investigated depending on a wide current density

(20–100 mA/cm^2) and Ag film thickness (10, 50 and 100 nm) range.

2. Material and Methods

The PS samples were prepared by electrochemical etching of lightly P-doped double-polished n-type Si (100) wafers with a resistivity of 1–10 Ω-cm. Before etching, the Si wafers were cut into a constant area of 1 cm ×1 cm, and immersed in acetone and distilled water, respectively. After that, the native SiO$_2$ layer was removed by immersing the samples in 4% aqueous hydrofluoric acid (HF) for 5 min. The electrolytes used for the etching process were based on a mixture of 40% aqueous HF and ethanol (C$_2$H$_6$O, absolute) solution in the volume ratio of 1:3 by using two electrodes configuration in a Teflon tank. A platinum wire was used as a cathode and Si wafer as anode. The samples were obtained by applying five different current densities 20, 40, 60, 80 and 100 mA/cm^2 (sample 1, 2, 3, 4 and 5, respectively) and constant etching time of 15 min. All samples were illuminated from the back side of Si substrate with halogen lamp (150 W) during the etching process. It is widely known that illumination during anodization is essential to generate luminescent porous Si in lightly doped n-type substrates. At room temperature, the number of thermal generated holes is little, so the silicon wafer must be illuminated or the applied bias reached the breakdown field strength for dissolution of n-type silicon wafer.[11]

After etching, the samples were dried in the air and were kept under vacuum at room temperature for several minutes in desiccator.

Ag thin films, with thickness ranging from 10 to 100 nm, were deposited on PS samples (Ag–PS) at 295 K by thermal evaporation of Ag wire of purity 99.99% with a diameter of 1.0 mm, using an Edward high vacuum coater system with the base pressure of about 1×10^{-6} Torr. The thickness of the Ag film was determined by a quartz crystal oscillator with an accuracy of ±0.1 nm during the deposition.

The structural analysis of all the samples was performed by using Micro-Raman measurements (S&I Trivista Raman Spectroscopy system) at room temperature with Argon ion (488 nm) laser excitation source and field-emission scanning electron microscope (FESEM, FEI QUANTA250 FEG). XRD measurements were also carried out using the Philips X'Pert Pro X-ray diffractometer with Cu K$_\beta$ line for the

identification of crystallographic phases of Ag–PS samples. The optical analyses of all samples were investigated by employing PL measurements at room temperature, and the excitation wavelength was 488 nm.

3. Results and Discussion

3.1. *SEM and XRD results*

In order to investigate the influence of current density on the surface morphology of PS sample, five different current densities (20, 40, 60, 80 and 100 mA/cm^2) were applied by keeping constant HF concentration (10%) and etching time (15 min) under illumination.

Figure 1 shows SEM and X-SEM images of PS samples for current densities of 20, 40 60, 80 and 100 mA/cm^2 (from up to down, respectively). As clearly seen from Fig. 1, the pores seem to be distributed uniformly (dark regions) in the Si matrix (bright regions). Furthermore, the pore sizes are approximately uniform for each sample. As can be seen in Figs. 1((a)–(e)), the porosity of PS layers increases with the increasing current density, as does the average pore size, which is in agreement with Cetinel *et al.* report.[12] Porosity of the samples was also calculated by the gravimetric method[2] and the results have been summarized in Table 1. In the gravimetric method, the porosity (P) was calculated by Eq. (1),

$$P(\%) = \frac{(m_1 - m_2)}{(m_1 - m_3)} \times 100, \qquad (1)$$

where m_1 is the weight of sample before etching, m_2 is the weight of sample after etching; m_3 is the weight of sample after dissolution of the PSi layer in a molar NaOH aqueous solution, respectively.

As can be seen in Table 1, as the current density increases from 20 to 100 mA/cm^2, average pore size increases from 700 to 1150 nm, respectively. The X-SEM images shown in Figs. 1(a*–e*) reveal that the pores are approximately columnar in shape with thickness of 40 μm.

Figure 2 shows the SEM and X-SEM images of Ag–PS surface (10, 50 and 100 nm, respectively). Our SEM measurements show that as the Ag film thickness increase, Ag grains start to agglomerate and comparatively cover the pores on the PS surface. For this reason, pore diameter decreases. As can be seen from Fig. 2, the relatively white regions show the Ag nanoparticles on the PS surfaces and also the Ag
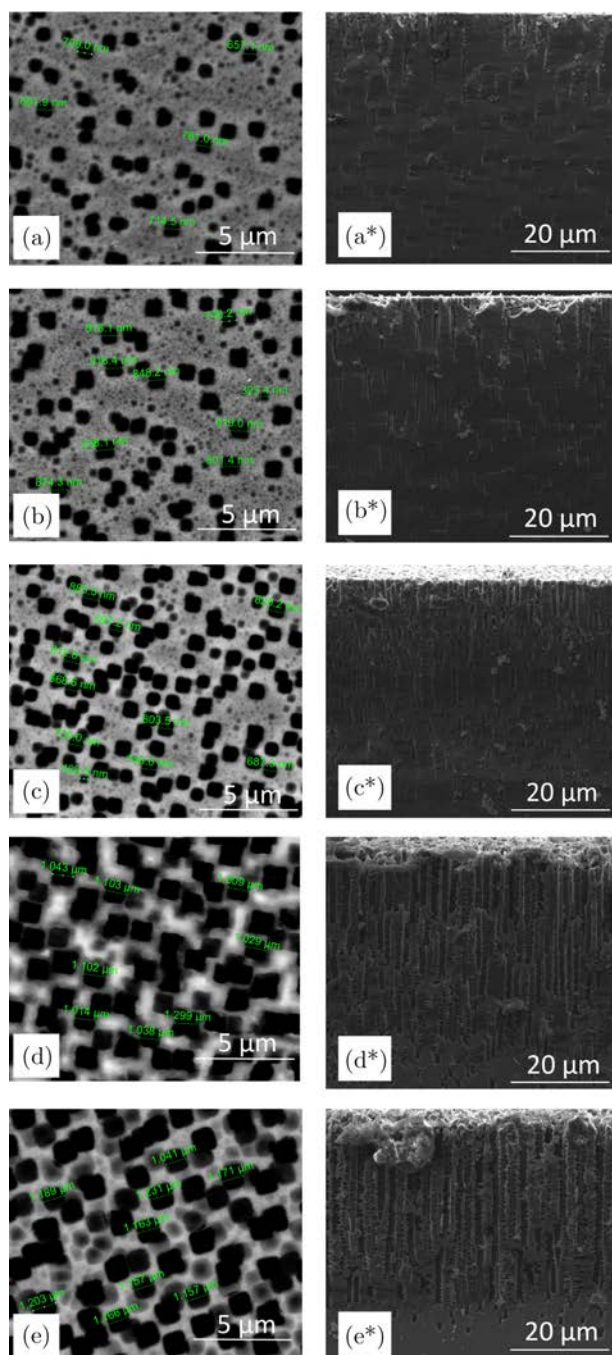

Fig. 1. The SEM and X-SEM images of PS samples prepared at (a) and (a*) 20, (b) and (b*) 40, (c) and (c*) 60, (d) and (d*) 80, (e) and (e*) 100 mA/cm^2, respectively.

nanoparticle distribution is uniform. In Fig. 2, insets show the X-SEM images of related PS samples. The X-SEM images reveal that at higher porosity (>60%), Ag nanoparticles penetrate into pore channels especially for 50 and 100 nm Ag deposition. This penetration

Table 1. The porosity, average pore size and layer thickness of PS samples.

Sample	Current density (mA/cm^2)	Porosity (%)	Average pore size (nm)	Layer thickness (X-SEM) (μm)
1	20	44.2	700	24
2	40	60.6	800	37
3	60	63.8	850	42
4	80	77.0	1100	42
5	100	79.4	1150	36

can be clearly seen in Figs. 2(m), 2(i), 2(n), 2(j) and 2(o) inset images.

The XRD spectra of the Ag–PS samples, with thicknesses of 10, 50 and 100 nm Ag film, are given in Figs. 3(a), 3(b) and 3(c), respectively. As seen from Fig. 3, the Si (400) peak observed at $2\theta = 69.15°$ is the main peak of Si (100) substrate. The diffraction peak at $2\theta = 33°$ correspond to the (200) plane of Si. Apart from this the peak observed at $2\theta = 61.7°$ belongs to the Cu K$_\beta$ radiation diffracted from Si (400) planes. The Ag thin films exhibited a dominant diffraction peak at $2\theta = 38°$ corresponding to the Ag (111) plane in all samples. The other Ag related peaks can also be seen at 44°, 65° and 77° for Ag (200), (220) and (311) planes, respectively. It is clearly seen from Fig. 3 that Ag (111) peak has high intensities compared with those of the other Ag related peaks. The strong Ag (111) peak is more important for VLSI and ULSI technologies in terms of electro-migration. If the Ag (111) peak has high intensity, it enhances electro-migration lifetime that is important for device applications.[10] From our SEM, X-SEM and XRD investigations, we can conclude that the pore size and morphology of PS are very sensitive to the current density and the higher porosity and pore size of PS favors to better morphology of Ag–PS.

3.2. Raman and PL results

3.2.1. The effects of current density and Ag deposition on Raman spectra of PS samples

Figure 4(a) shows the Raman spectra of the PS samples prepared at different current density ranging from 20 to 100 mA/cm^2, under constant HF concentration (10%) and etching time of 15 min. The first-order transverse optical (TO) phonon centered at 520 cm^{-1}

with a full width at half maxima (FWHM) of 2.4 cm^{-1} for our n-type (100) c-Si reference sample is also shown as for comparison in Fig. 4(a). In addition, we could not detect the existence of amorphous-silicon (a-Si) because of the absence of a bump around 480 cm^{-1}. Apart from this, we cannot attribute any Raman peak to the defects resulting in a significant effect on the Raman spectra of our PS samples in Fig. 4(a). Moreover, we also found a broad peak at $\sim$302 cm^{-1} in all PS spectra. According to our best knowledge, we may conclude that the peak at 302 cm^{-1} in Raman spectra does not come from the PS layer but comes from the c-Si.[12,13]

It is clearly seen from Fig. 4(a) that Raman spectra of PS samples shifted to lower wavelength with increasing the current density from 20 to 100 mA/cm^2. For the sample prepared at 100 mA/cm^2, we have observed the biggest shift from 520 to 518.0, around 2 cm^{-1} and FWHM 7.0 cm^{-1}. It is well known that when the crystallite size of the PS decreases, the Raman shift and peak width increase and the lineshape becomes asymmetric due to phonon confinement effects.[12,14] Therefore, in order to explain our experimental results in Fig. 4(a), we have calculated average crystallite sizes of PS samples using the equation reported by Zhong $et~al.$[13] and the results summarized in Table 2. It should be noted that nano-crystallite size of PS samples calculated from Raman spectroscopy has a good agreement with previous studies.[12,15,16]

To investigate the nanostructures of Ag–PS samples, Raman spectroscopy was used due to its good sensitivity for the bonding nature of nano-composite materials.[17] Figure 5 shows the Raman spectra of Ag–PS samples (10, 50 and 100 nm, respectively). It was found that the only Raman spectra of Ag-PS (for 10 nm in Fig. 5(a)) slightly shift to lower frequency (518 cm^{-1}) compared to that of bulk Si (520 cm^{-1}). This observed shift appeared due to the phonon confinement effect and the strain effect caused by nanoparticles in PS samples.[17,18] It is seen in Raman spectra of all Ag–PS samples that a wide Raman band is observed at the low frequency position about 230 cm^{-1}, which is caused by Ag nanoparticles.[18] Besides the Raman peaks at 230 cm^{-1} due to Ag deposition, the new peaks were observed at wavenumber about 300 and 450 cm^{-1} for 50 nm and 100 nm Ag–PS samples. The weak Raman band at 300 cm^{-1} is associated with the two transverse acoustic (2TA) phonons. The sharp peak at about 450 cm^{-1} is suggested to be Si–H$_x$ bond vibrations.[18]
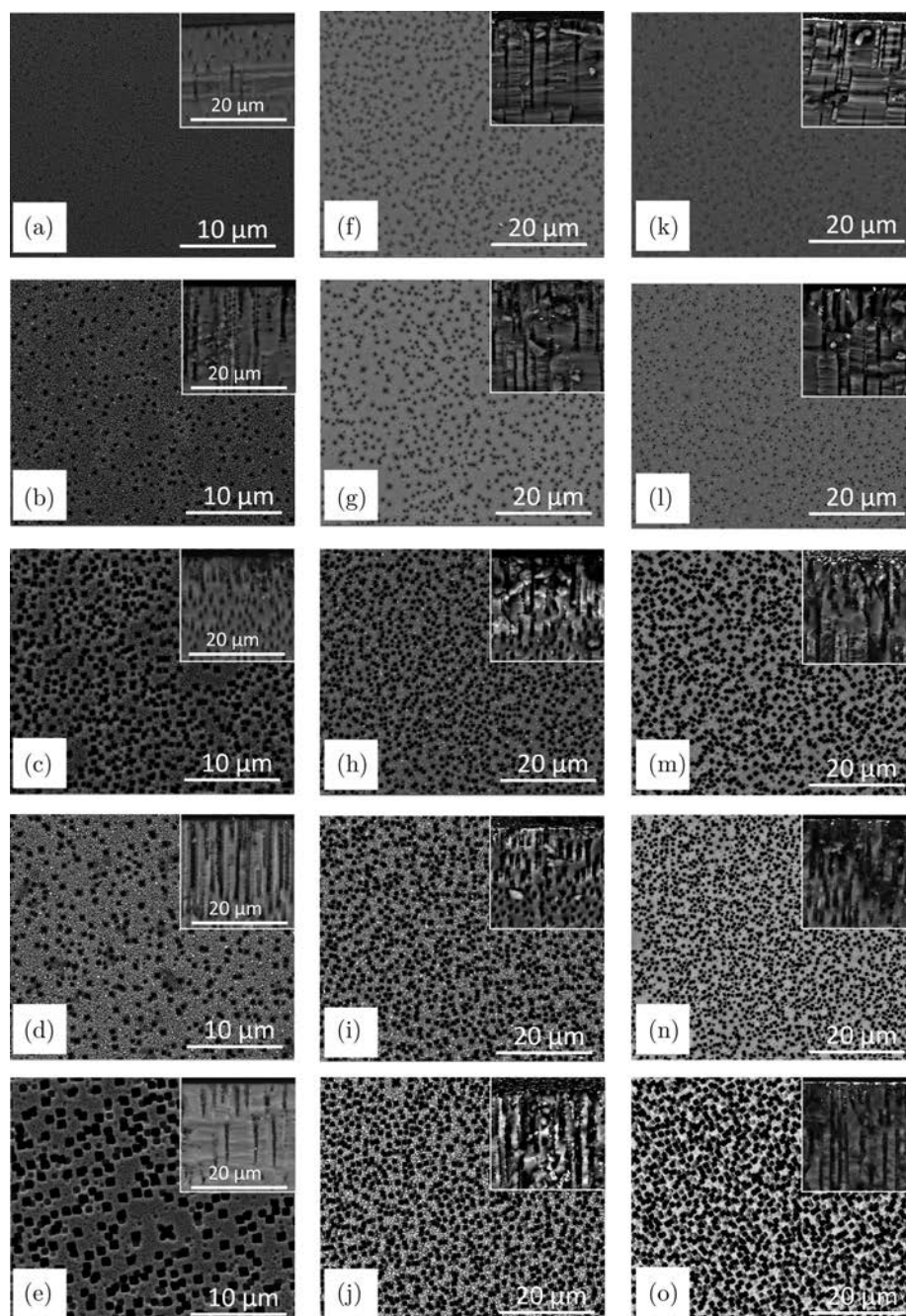
Fig. 2. The SEM images of Ag–PS samples: ((a)–(e)) 20, 40, 60, 80 and 100 mA/cm^2, up to down respectively for 10 nm Ag thickness, ((f)–(j)) 20, 40, 60, 80 and 100 mA/cm^2, up to down respectively for 50 nm Ag thickness, ((k)–(o)) 20, 40, 60, 80 and 100 mA/cm^2, up to down respectively for 100 nm Ag thickness. In each SEM images, insets show the related X-SEM images of Ag–PS samples.

It can be also seen from Fig. 5 that as the current density increases, the peak intensity of Raman bands at 300 and 450 cm^{-1} increases and the Raman peaks at 230 cm^{-1} decrease slightly. These observed results can be explained by considering porosity of PS samples. It is well known that as the current density increases, the porosity of PS samples increases, hence the Si density decreases since pore diameter increases gradually.[19] The latter result is confirmed by our FE-SEM investigations in this study. Considering the
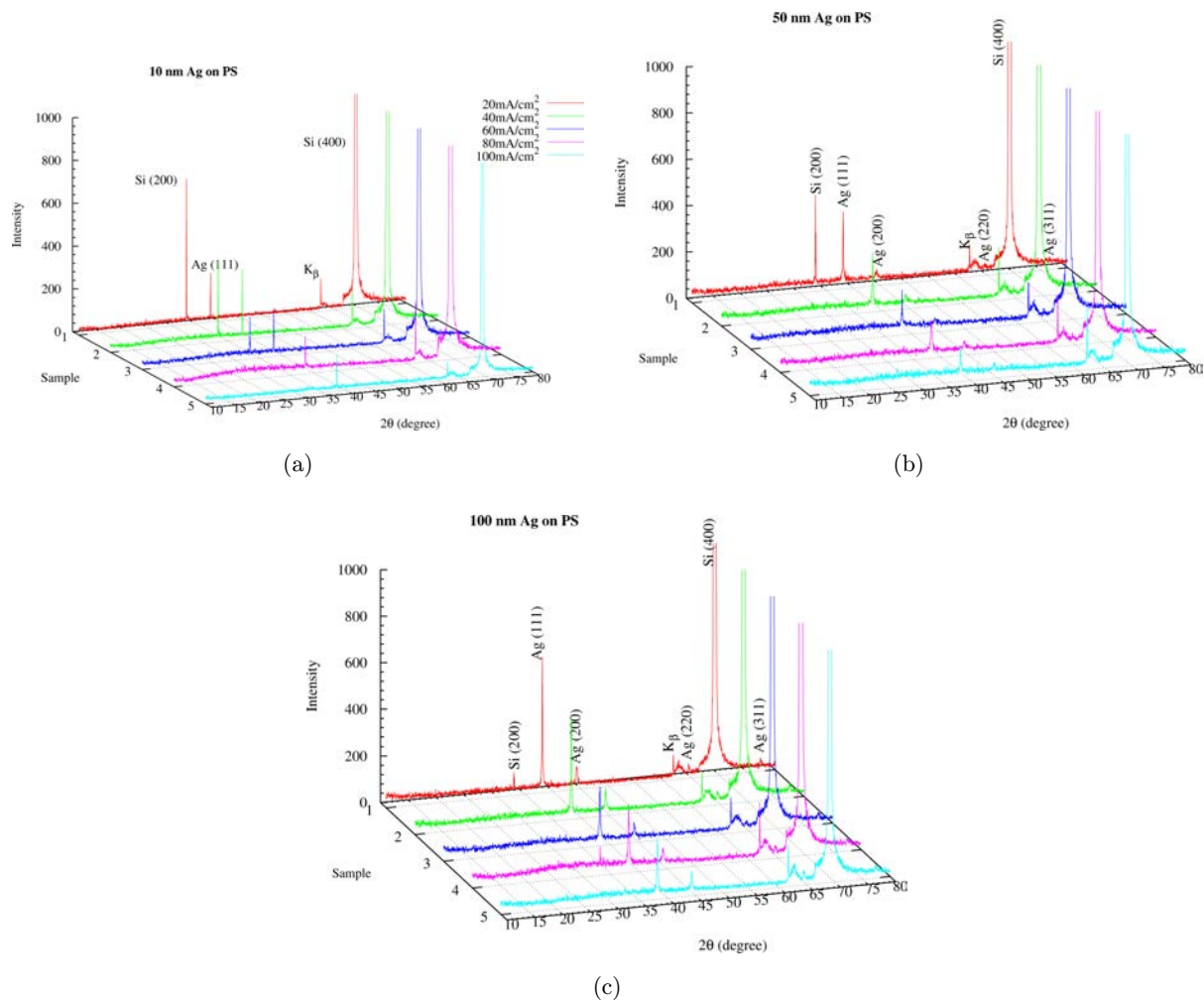
Fig. 3.   (Color online) The XRD spectra of Ag–PS samples: (a) 10 nm, (b) 50 nm and (c) 100 nm Ag thickness on PS layers.

calculated porosity values of PS samples, at low porosity rate, for instance, PS sample prepared at 20 mA/cm2 (porosity~45%), we have observed from FE-SEM and X-SEM images in Fig. 2 that most of the Ag particles stay on the surface of PS layer. On the other hand, owing to high porosity rate in PS sample prepared at 100 mA/cm^2 (porosity~79%), the continuity of the Ag film on the surface of PS sample has broken down and Ag nanoparticles have been embedded in pore channel (Fig. 2). This result is consistent with FE-SEM and XRD analyzes. For the sample prepared at 80 and 100 mA/cm^2, the relatively weak Raman scattering of PS and the background noise levels indicate that a large amount of the Ag particles embed in the PS layer with increasing porosity of PS. In addition to FE-SEM and XRD investigations, the Raman results also reveal that the

higher porosity of the PS layers (prepared at 80 and 100 mA/cm^2, ~77 and 79%, respectively) are suitable to form Ag–PS nano-composite material.

3.2.2.   *The effects of current density and Ag deposition on PL spectra of PS samples*

The effects of current density on the electronic structure of PS, thereby the changes in the nano-crystallite size, porosity and pore size of PS samples induced by varying current density were investigated by PL measurements. The PL spectra of PS samples were measured at room temperature and recorded in the range of 540–760 nm, presented in Fig. 4(b) and summarized in Table 3. It has been already known that bulk silicon has an indirect band gap and does not show any PL peak, while PS structures have
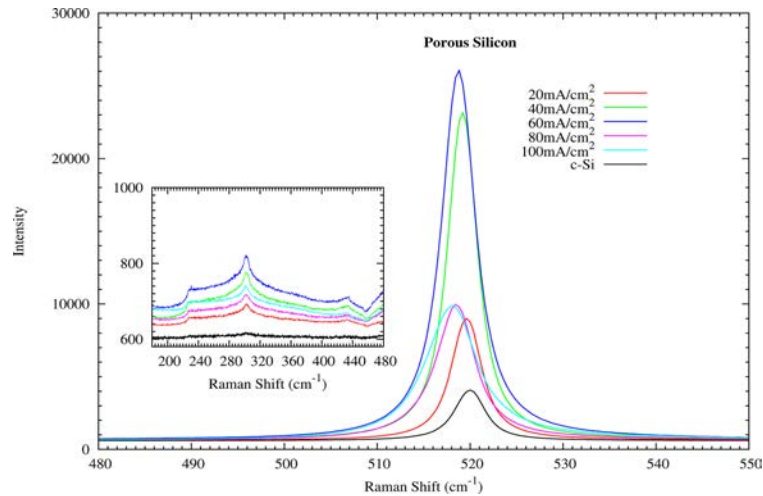
(a)
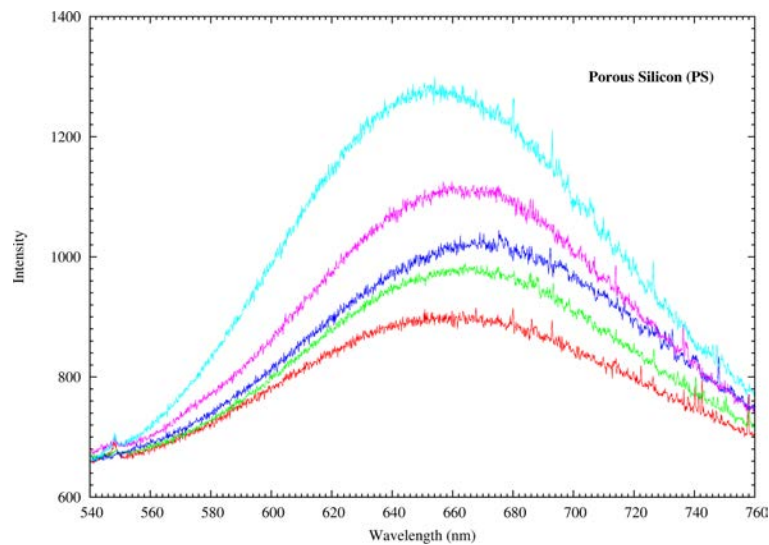
(b)

Fig. 4. (Color online) (a) The Raman spectra of PS samples prepared at 20, 40, 60, 80 and 100 mA/cm^2, and also c-Si is shown for comparison. (b) The PL spectra of PS samples for the same current densities.

direct band gap and show efficient luminescence in a range extending from the near infrared to the blue region of the visible spectrum.[12,19] It is clearly seen in Fig. 4(b) that the current density is increased from 20 to 100 mA/cm^2, the PL band of PS samples shows a blue shift from 665 to 645 nm. Based on the origin of the luminescence, the blue shift in PL spectra should result from the quantum-sized silicon crystallites among the pore walls,[1,12,20] or from the defects and the species formed during the etching process in Si complexes.[21] According to our Raman scattering analysis, we have not observed a broad peak at

480 cm^{-1}, indicating that there is no substantial contribution to the Raman intensity from possible amorphous silicon on the PS surface. Furthermore, we have not detected any defects in the PS layer, which is presented in Raman spectra. In our study, a blue shift is observed with increasing current density and porosity, but decreasing nano-crystallite size, as confirmed by our Raman, FE-SEM and PL results. These observed results can be explained satisfactorily in terms of QCE. According to the QCE, the average size of nanoparticles in PS is expected to get smaller both with the increasing current density and porosity,

Table 2. The Raman peak positions, maximum Raman intensities, full-with half maximum values and calculated average crystallite sizes of PS samples.

Samples	Current density (mA/cm^2)	Raman peak position (cm^{-1})	Peak intensity (a.u.)	FWHM (cm^{-1})	D (nm)
c-Si	—	520.0	6482	2.4	—
1	20	519.6	9010	4.2	14.8
2	40	519.2	23142	3.9	10.5
3	60	518.8	26058	4.5	8.5
4	80	518.4	9952	5.5	7.4
5	100	518.0	9901	7.0	6.6

Table 3. The PL peak positions, maximum PL intensities, calculated average crystallite sizes and pore diameter of PS samples.

Samples	Current density (mA/cm^2)	Peak position (nm)	Peak intensity (a.u.)	Crystallite size (nm)	Pore diameter (nm)
1	20	665	890	14.8	700
2	40	665	980	10.5	800
3	60	670	1020	8.5	850
4	80	655	1120	7.4	1100
5	100	645	1275	6.6	1150

of excitation wavelengths. It is clearly seen in Fig. 6 that the PL intensity of Ag–PS samples decreases when the Ag film thickness increases. It should be noted that the PL spectra have a blue shift from 618 to 570 nm by increasing current density and Ag film thickness from 20 to 100 mA/cm^2 and from 10 to 100 nm, respectively. Our PL analyses indicated that in all of the Ag thickness, the PS samples prepared at 100 mA/cm^2 have shown higher PL band than other
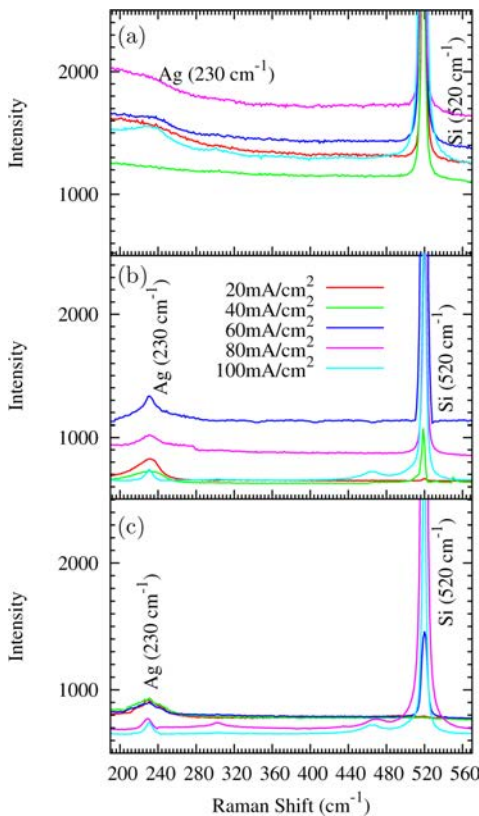

Fig. 5. (Color online) The Raman spectra of Ag–PS samples: (a) 10 nm, (b) 50 nm and (c) 100 nm Ag thickness on PS layers.

which make a blue shift in PL peaks.[12,22] Our PL analysis suggests that current density has a significant effect on the luminescence properties of PS samples.

Figure 6 shows the effect of Ag thin film thickness (10, 50 and 100 nm, respectively) on the PL spectra of Ag–PS samples in company with current density. PL spectra have been measured at room temperature and the emission spectra have been collected with 480 nm
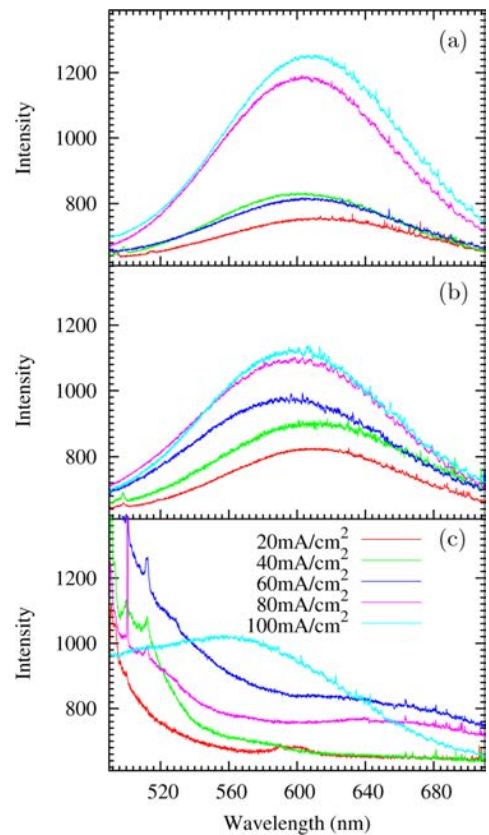

Fig. 6. (Color online) The PL spectra of Ag–PS samples: (a) 10 nm, (b) 50 nm and (c) 100 nm Ag thickness on PS layers.

current densities. This sample also has the highest porosity 79%. As mentioned in Raman and FE-SEM analyses, the high porosity of PS would be better to form the nano-composite material leading to stronger PL band. In this study, the highest PL band intensity was obtained for the Ag–PS sample at $100\,\text{mA/cm}^2$ with thickness of 10 nm. The PL band of this sample shows a blue shift from 645 to 610 nm compared to that of the uncoated PS prepared at same conditions. The observed result can be explained by the fact that stable Si–Ag bonds can suppress the formation of Si dangling bonds and result in more intensive visible luminescence than that of PS.[6,23,24] Moreover, this result also indicates that we must use the optimum Ag film thickness to enhance PL intensity.[25] On the other hand, there are two opposing factors as follows: First, as the thickness of the Ag layer increases, carrier concentration increases, therefore the probability of the recombination of electrons and holes increases and consequently, PL intensity increases. Second, as the thickness of the Ag film increases, the final PL intensity of the Ag–PS decreases since the light emitted from the PS must pass through the metal layer. The high PL enhancing effect of Ag passivation must be attributed to the high electrical conductivity or carrier concentration of Ag.[9] Consequently, our PL analysis reveals that Ag deposition has a certain influence on the PL intensity of PS, while the excessive Ag deposition could cause the phenomenon of fluorescence quenching.

4. Conclusion

In this study, we have systematically analyzed the structural and optical properties of PS and silver deposited PS layers by XRD, FE-SEM, Raman and PL spectroscopy. Our SEM analysis has revealed that as the current density increases from 20 to $100\,\text{mA/cm}^2$, porosity and average pore sizes of the PS samples increase from 44.2 to 79.4% and 700 to 1150 nm, respectively. In addition to SEM analysis, Raman scattering spectra have been used to investigate microstructure of the PS and Ag–PS. Our results reveal that Raman spectra of our PS samples shifted to lower wavenumber with increasing current density. Here, we also discuss the intensity of Raman spectra of Ag–PS. The suppression of Raman band by Ag deposition seems to be due to the fact that the scattering of the incident beam occurs before reaching the silicon bulk

or the scattered light is blocked by the deposited Ag. Besides SEM and Raman analyses, the optical analyses of all samples were investigated by employing PL measurements at room temperature, and the excitation wavelength was 488 nm. The PL band of PS samples showed a blue shift from 665 to 645 nm. Based on the origin of the luminescence, blue shift in PL spectra should be resulted from the quantum-sized silicon crystallites among the pore walls. These results can be explained satisfactorily in terms of the QCE.

According to our experimental analyses, in order to obtain nano-composite material having stronger PL band, the high porosity of PS would be better. In this study, the highest PL band intensity has been obtained for the Ag–PS samples at $100\,\text{mA/cm}^2$ current density with Ag thickness of 10 nm. Depending on the material under investigate; the PL spectra of Ag–PS samples have a blue shift from 620 to 570 nm by increasing current density from 20 to $100\,\text{mA/cm}^2$ and Ag film thickness from 10 to 100 nm, respectively.

Furthermore, FE-SEM, XRD and Raman analyses show that as the pore diameter and porosity increased, the continuity of the Ag thin film on the surface of PS has broken down and Ag nanoparticles have embedded in pore channel. For this reason, in order to enhance PL intensity, we must use the optimum Ag film thickness. Our PL analysis reveals that Ag deposition has a certain influence on the PL intensity of PS, while the excessive Ag deposition could cause the phenomenon of fluorescence quenching.

In conclusion, our experimental analysis reveals that current density and the Ag film thickness have a significant effect on the structural and luminescence properties of PS samples. By changing applied current density and Ag film thickness, the light emitting and structural properties of PS samples can be controlled. These results suggest that the PS sample with finely controlling of atomic-scale structure is a good candidate for potential applications in optoelectronic and sensor devices.

Acknowledgments

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