

Effects of a H₂SO₄ treatment on the optical properties in porous Si layers and electrical properties of diode devices fabricated with a H₂SO₄ treated porous Si layer

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The effects of a H₂SO₄ treatment on the optical properties in porous silicon (PS) layers were investigated by using photoluminescence (PL) measurements, and electrical properties of diode devices fabricated with a PS were investigated by current density-applied voltage (J-V) measurements. Scanning electron microscopy images showed that the PS layers were formed by electrochemical anodization. While the PL intensity of the PS layer immersed into H₂SO₄ solution was significantly increased in comparison with that of the as-formed PS layer, the PL peak position did not change regardless of variations in the H₂SO₄ treatment time due to the invariance of the crystal structure of the PS layer. The J-V curve for the indium-tin-oxide/H₂SO₄ treated PS layer/n-Si/Al structure showed diode characteristics with a small turn-on voltage.

Key words: porous Si layers, H₂SO₄ treatment, optical property, electrical property.

Introduction

Potential applications of porous silicon (PS) layers in next-generation optoelectronic devices have driven extensive and successful efforts to form various kinds of PS layers and investigate optical properties [1-7]. Visible light emission from the PS layer has been particularly attractive because of the interest in promising applications in complete Si-based-optoelectronic technologies [8]. Even though the PS layers have emerged as promising candidates for potential applications in the fabrication of Si-based optoelectronic devices, there are still many inherent problems because the optical properties of the PS layer is not stable in ambient air, which should be solved for this material before it can be used in industry. An appropriate post-treatment on the PS layer is necessary to enhance the optical properties of the PS layer and for passivating the internal surface of the PS layer [9, 10]. Even though some studies on the enhancement of the optical properties in the PS layer by post treatment have been performed [11-16], systematic studies concerning the enhancements of the optical properties for the PS layer are still very important to achieve high performance of the optoelectronic devices fabricated utilizing a PS layer. Furthermore, the PS layers are currently receiving considerable attention because of their possible applications in electronic and electroluminescence devices [17-20].

This paper reports the effects of a H₂SO₄ treatment on optical properties of the PS layers and electrical properties of the indium-tin-oxide (ITO)/H₂SO₄ treated PS layers/n-Si/Al diodes. The PS layers were formed by anodizing p-Si and n-Si wafers. Photoluminescence (PL) measurements were carried out to investigate the optical properties of the as-formed and H₂SO₄ treated PS layers, and current density-applied bias voltage (J-V) measurements were performed to investigate electrical properties of the ITO/H₂SO₄ treated PS layer/n-Si/Al diode.

Experimental Details

The resistivities of the p-type and n-type Si (100) substrates used in this study were 10 and 0.001 Ωcm, respectively. The PS layers were prepared by anodization. Prior to anodization, the Si substrates were degreased in a solution of acetone and methanol for 20 minutes, rinsed in de-ionized water, and etched in a mixture of HF and de-ionized water (1:10) at 27°C for 2 minutes to remove a native oxide layer. The electrolyte for the anodization of the p-Si substrate consisted of a solution of hydro-fluoride (HF) and ethanol (1:9), that of the n-Si substrate consisted of a solution of HF and ethanol (1:2). The anodization was carried out at a constant current density of 10 mA/cm² under illumination of a 100 W tungsten lamp in order to form the PS layers. The etching times were 10, 30, and 120 minutes. The as-prepared PS layers were rinsed with methanol for 2 minutes, and dried in a N₂ gas flow. As soon as the anodization process was finished, the sample surface was passivated by immersing in a 1 mol H₂SO₄

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solution. The electrochemical oxidation of the PS layers was achieved by anodizing (3 mA/cm^2) PS layers in an aqueous solution containing $1 \text{ mol H}_2\text{SO}_4$ to fabricate the diode. After, the samples were rinsed with methanol for 2 minutes and dried, the samples were transferred into a vacuum chamber, and a thin and semi-transparent ITO film with a thickness of 100 nm was sputtered onto the PS layers. An Al metal film with a 200 nm thickness was evaporated onto the back side of the wafer, and rapid thermal annealing for 3 minutes at 450°C was performed for ohmic contact in a N_2 atmosphere.

Scanning electron microscopy (SEM) images were produced in a Hitachi S-4100 operating at 20 keV . Top and cross sectional views were observed to investigate the structural properties of the PS layers. The PL measurements were carried out using a 75 cm monochromator equipped with a GaAs photomultiplier tube. The excitation source was the $3250 \text{ \AA}$ line of a He-Cd laser, and the sample temperature was kept at 27°C . J-V measurements were performed using a Hewlett Packard pA meter/dc voltage source (Model 4140B).

Results and Discussion

Figure 1 shows top view and cross-sectional SEM images of samples anodized in p-type and n-type (100) Si substrates. While the top view SEM image on the p-type Si layer exhibits a periodic rectangular-shaped domain structure, as shown in Fig. 1-(a), the corresponding image of the n-type Si layer depicts an irregular pore structure with a diameter of $1 \mu\text{m}$, as shown in Fig. 1-(b). The cross-sectional SEM image of the p-type Si layer exhibits a microscale cubic structure, as shown in Fig. 1-(c), and the corresponding image of the n-type PS layer depicts an irregular porous structure, as shown in Fig. 1-(d). The shape, the size, and the depth of the pores in the PS layers are also significantly affected by the current density and the time during anodization. The depth of the pores in

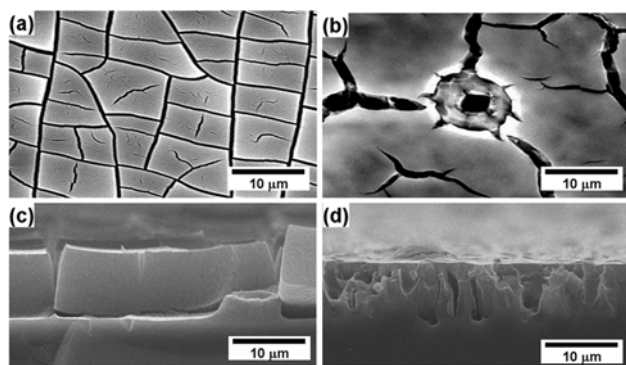


Fig. 1. Top view scanning electron microscopy images for the porous Si layers formed on (a) p-type and (b) n-type Si substrates and cross-sectional scanning electron microscopy images for the porous Si layers formed on (c) p-type and (d) n-type Si substrates.

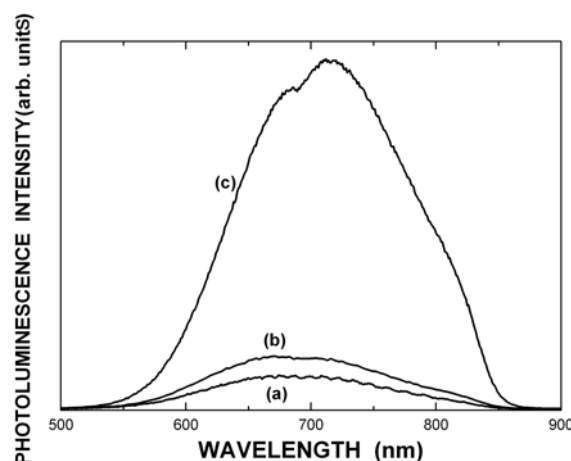


Fig. 2. Photoluminescence spectra for the porous Si layers formed from the p-type Si substrates anodized for (a) 10, (b) 30, and (c) 120 minutes.

the PS layer increases with increasing anodization time, resulting in an increase of surface volume.

Figure 2 shows PL spectra for the PS layers formed from the p-type Si substrate anodized for (a) 10, (b) 30, and (c) 120 minutes. Since the PL intensity for the PS layer formed from the p-type Si substrate is higher than that for the PS layer formed from the n-type Si substrate, only the PL results for the PS layers formed from the p-type Si substrate are described in this study. A dominant PL peak around 700 nm is observed. The PL peak around 700 nm is attributed to the surface-related states [7]. While the PL intensity at 700 nm for the PS layer increases with increasing anodization time, the PL peak position at 700 nm does not significantly change. A significant enhancement of the PL intensity with increasing anodization time is attributed to an increase in the surface volume.

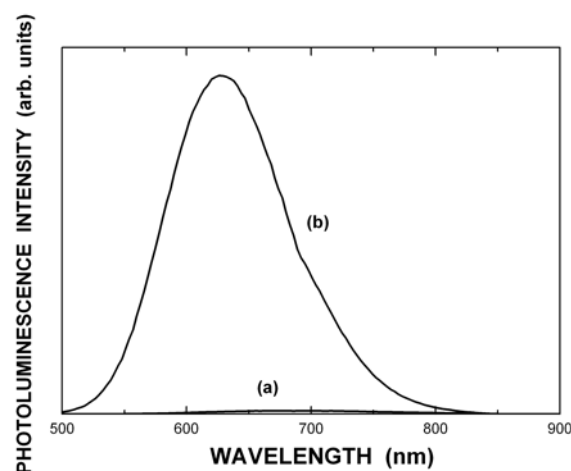


Fig. 3. Photoluminescence spectra for the (a) as-formed porous Si layers formed from the p-type Si substrates anodized for 30 minutes and (b) porous Si layers formed from the p-type Si substrates anodized for 30 minutes and immersed in the H_2SO_4 solution.

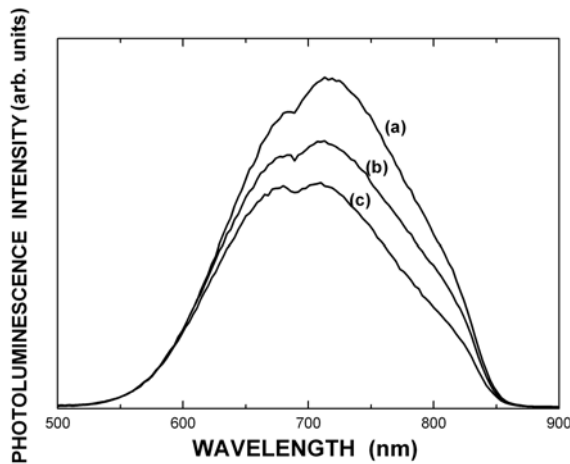


Fig. 4. Photoluminescence spectra for the porous Si layers formed from the p-type Si substrates anodized for 120 minutes immersed in the H_2SO_4 solution for (a) 30, (b) 60, and (c) 120 s.

Figure 3 shows PL spectra for the (a) as-formed PS layer formed from the p-type Si substrate anodized for 10 minutes and the (b) PS layer formed from the p-type Si substrate anodized for 10 minutes and immersed in the H_2SO_4 solution for 60 s. The PL intensity for the PS layer immersed in the H_2SO_4 solution for 60 s is ten times larger than that for the as-formed PS layer. The significant enhancement of the PL intensity after the H_2SO_4 treatment is attributed to the passivation of the defects which act as non-radiative recombination centers [21]. A similar enhancement of the PL intensity has been observed by adopting an appropriate solution concentration or an immersion time [15]. This result indicates that the proposed post-treatment method is very effective in the enhancement of the PL intensity in the PS layer. The dominant excitonic peak in the PS layer immersed in the H_2SO_4 solution for 60 s is shifted to higher energy in comparison with that in the as-form PS layer. The blue shift of the PL peak position for the H_2SO_4 treated PS layer in comparison with that for the as-form PS layer might be attributed to a decrease in the size of the nanocrystallites resulting from the oxidation of the PS layer [22]. Therefore, the post-treatment method using the H_2SO_4 solution is very effective for enhancing the PL intensity in the PS layer. PL spectra for the PS layers formed from the p-type Si substrate anodized for 120 minutes and immersed in the H_2SO_4 solution for 30, 60, and 120 s are shown in Fig. 4. While the PL intensity for the PS layers decreases with increasing H_2SO_4 treatment time, the PL peak position does not significantly change regardless of variations in the H_2SO_4 treatment time because the interfacial region between the Si nanocrystals and the surface oxide layer plays a critical role in the luminescence process [22].

Figure 5 shows the J-V current at 300 K for the ITO/ H_2SO_4 treated PS layer/n-Si/Al structure, and the J-V curve of the structure depicts the electrical properties of

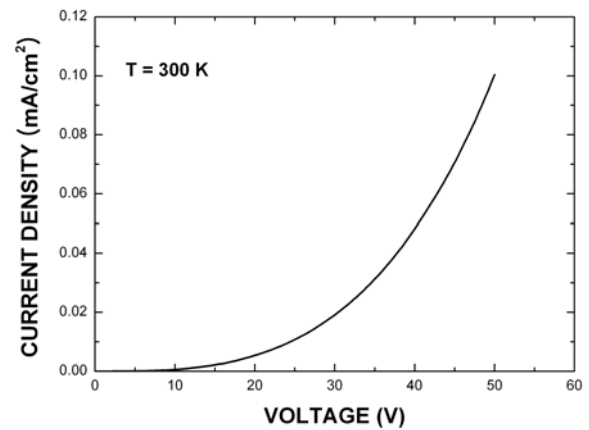


Fig. 5. Current density as a function of the bias voltage at 300 K for the ITO/ H_2SO_4 treated PS layer/n-Si/Al structure.

typical diode devices such as for the Au/PS layer/n-Si/Au structure. The J-V behavior for the ITO/ H_2SO_4 treated PS layer/n-Si/Al structure is similar to that reported elsewhere [23]. The turn-on voltage of the diode fabricated utilizing a H_2SO_4 treated PS layer is smaller than that of the diode fabricated utilizing a PS layer [23]. When the applied voltage is high, the current generated in the diode increases due to the creation of the electron and the hole resulting from the tunneling of the electron. However, since almost all of the electrons and the holes generated under a large electric field move in an opposite directions, the overlap of the electron and hole population decreases, resulting in degradation of the diode property in H_2SO_4 treated PS layer-based diodes.

Summary and Conclusions

The optical properties of the as-formed and H_2SO_4 treated PS layers were investigated, and the electrical properties of the diodes fabricated utilizing the H_2SO_4 treated PS layers were studied. SEM images showed that the PS layers were formed by anodization. While the PL intensity for the PS layer immersed in the H_2SO_4 solution was significantly improved in comparison with that for the as-formed PS layer, the PL peak position did not change regardless of variations in the H_2SO_4 treatment time due to the invariance of the crystal structure of the PS layer. The J-V curve for the ITO/ H_2SO_4 treated PS layer/n-Si/Al structure showed diode characteristics with a small turn-on voltage. The present results can help improve our understanding of the optical properties of the as-formed and H_2SO_4 treated PS layer together with the electrical properties of diodes utilizing the H_2SO_4 treated PS layers.

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