Structure and photoluminescence properties of the quasi-regular arrangements of porous silicon

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The morphology of porous silicon treated by electrochemical process depends sensitively on the anodization parameters, such as the current density and electrolyte concentration. In this work, the self-assembly quasi-regular arrangements porous silicon have been fabricated by controlling of the several important anodization parameters. The structure and luminescence characteristics of the etched porous silicon were studied. We discussed the influence of the current density on the morphology of the porous silicon layer and on the luminescence characteristics, and also investigated the effect of anodization time on the luminescence characteristics. Scanning electron microscopy (SEM) images showed that the pores have almost the same size and depth, grow perpendicular to the surface and parallel to each other. The pore diameter ranging from 500 nm to 1μm and pore depth being capable of reaching 20μm, fresh porous silicon can emit the red light at room temperature and be excited at 400 nm.

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1. Introduction

Porous silicon (PS) has attracted much attention because of its various applications in optical devices, chemical and biological sensors and so on [1, 2]. It can be made by several methods, ordered porous silicon can be obtained by using the standard lithography method [3-5], however, this method has some drawbacks such as low yield, high cost and complicated processing, therefore it is not suitable to produce the ordered structure for a large surface area (i.e. more than 1cm^2). Recently, the self-assembly method has attracted more and more attention because of its simplicity and quickness. Highly ordered pores can be fabricated by using the porous anodic alumina film as a mask [6-10], however, photoluminescence properties have not yet been reported in published papers. Electrochemical anodization is taken as another self-assembly method which commonly used to fabricate porous silicon. The macropores usually were formed on the low doped p-type silicon [11-15]. And recently S. Lust [16] reported the formation of macropore on the medium doped p-type silicon, but porous silicon normally arranges in an irregular morphology which fabricated by the electrochemical anodization.

In this paper, porous silicon has been fabricated by electrochemical etching. We used n-type silicon wafers with a resistivity of 2–4 Ω·cm and took a mixture of dimethylformamide (DMF) and hydrofluoric acid (HF) aqueous solution as electrolyte for porous silicon formation. The quasi-regular arrangement porous silicon can be fabricated by controlling of the anodization parameters, and the as-prepared fresh porous silicon can emit a red visible luminescence at room temperature. The morphology of the surface and cross-section of etched porous silicon were studied by the SEM. The effect of current density on the morphology of porous silicon layer and on the luminescence characteristics, the etching time on the luminescence characteristics have been also discussed in the paper.

2. Experimental

The starting materials were n-type (100) silicon wafers with resistivity of 2 - 4 Ω·cm and thickness of about 500 μm, and the wafers were cleaned by following procedures before electrochemical etching. Firstly, the samples were soaked in acetone for 15 minutes to remove grease and dust from the surface, and were immersed for 5 minutes into 10% hydrofluoric to remove native oxide, secondly the samples were dipped at 80 ^{o}C for 5 minutes to remove organic impurities with a mixed solution of $NH_3 \cdot H_2O$, H_2O_2, and H_2O at a volume ratio of 1:1:5, and were washed also at 80 ^{o}C for 5 minutes to remove inorganic impurities with aqueous solutions containing HCl, H_2O_2 and H_2O at a same volume ratio, finally the samples were stored in methanol after cleaning.

Porous silicon was fabricated by galvanostatic regime at room temperature with aqueous hydrofluoric acid (HF-40%: DMF-98% = 1:2) as electrolyte. The current density was in the range of 50 - 100 mA/cm^2. The voltage decreased fast and then stable during the etching process. Fig. 1 was the voltage-time curve for anodization of silicon at 75 mA/cm^2, we see from the figure that the voltage quickly decreased from 90V to 30V and then

stable at 30V. The electrochemical anodization process was lighted using a 300 W tungsten lamp. The PS samples were rinsed in ethanol after the anodization, then dried by blowing and finally stored in an atmospheric environment.

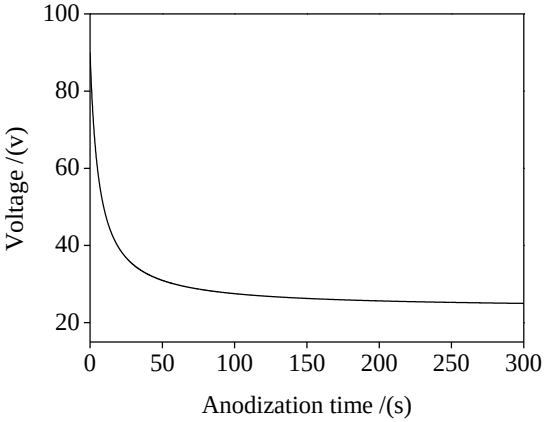

Fig. 1. Voltage-time curve for anodization of silicon at 75 mA/cm^2.

All the photoluminescence measurements have been performed by fiber-spectrometer (Ocean Optics, USB2000). Investigations of the morphology of porous silicon have been carried out by SEM (TESCAN, VEGA II LMU). The samples were observed in surface and cross-section. The cross-sectional views were obtained for the surfaces which were exposed by mechanically cleaving the sample after having scribed the back side with a diamond scriber.

3. Results and discussion

3.1 Morphology analysis

The SEM images of the samples prepared at an etching current densities ranging from 50 to 100 mA/cm^2 which were shown in Fig. 2. It is obvious that the morphologies varied significantly in different current density, and the different porosities achieved in the current densities varying from 50 to 100 mA/cm^2. The increasing current density lead to the increase of the pore diameter and the decrease of the inter-pore distance, and the average pore-diameter increased from 500 nm to 1μm. Anodizing with high current densities (>75 mA/cm^2) yields a rather homogeneous distribution of the pore diameters within the sample. From the SEM images, the self-organized arrangements obtained with current densities greater than the 75 mA/cm^2 provided quasi-regular arrangements. The pores closed together and almost had the same size. However, the samples were prepared with lower current densities the regularity vanished, the pores not only separated from each other but also exhibited a more and more random distribution. We also exhibited the cross-section SEM image of the sample which is prepared at the current density 100 mA/cm^2, Fig. 2(d) shows the cross-sectional views of the sample, the achieved pores with rough pore walls grown perpendicularly to the surface, and grew parallel to each other and shown almost the same depth. In this way, the better homogeneity of the pore diameter is achieved. The shape of the cross-section of individual pore is circular. The average pore length can be estimated from the SEM images and the depth is about 20 μm.

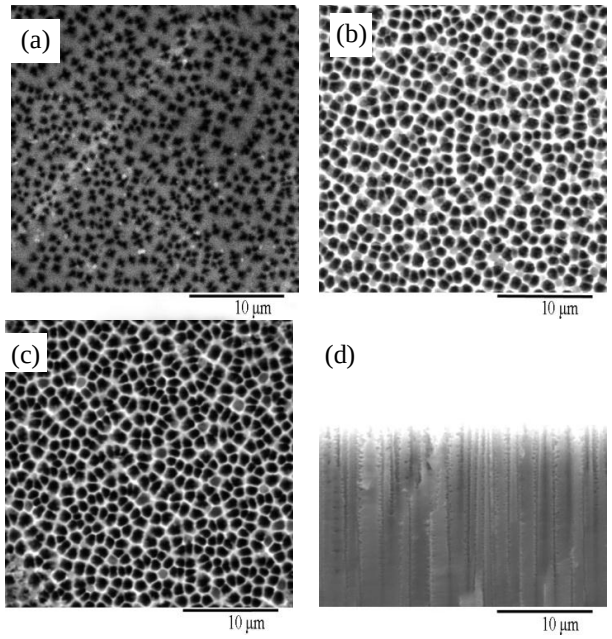

Fig. 2. (a)-(c) SEM showing the top view of porous silicon samples prepared with different current densities. (a): 50 mA/cm^2; (b): 75 mA/cm^2; (c): 100 mA/cm^2. (d): The cross-section SEM image of the sample which prepared by electrochemical at 100 mA/cm^2.

3.2 Photoluminescence studies

The fresh porous silicon can emit a red visible luminescence at room temperature by photoluminescence measurements, but the as-prepared pores are macropores, and macroporous silicon is not known to be luminescence, so what is the real cause for luminescence. From the cross-section SEM image we can see that the pore wall is very rough, and there have many small pores in it, we thought the real cause for the luminescence probably is the microporous silicon layer which is generally present at the pore walls, not the macropores. We under take an experiment to prove this point. First we measure the photoluminescence of the fresh sample without any treatment. We can see from Fig. 3 a that it can emit a red visible luminescence with a peak at 660 nm, then put the sample in an oven at 473 K for 1h and soak in 5% HF after that, finally we measure the photoluminescence again after this treatment. Fig. 3 b shows that the photoluminescence spectra of porous silicon after the thermally oxidize, and we can not see the luminescence phenomenon. This is because the fine microporous coverage would be first turned into oxide after thermally oxidize which is afterwards removed by HF, so we can see any

luminescence phenomenon after this thermally oxide treatment. As a result, we thought the microporous structures layer which is generally present at the pore walls is very important for the luminescence.

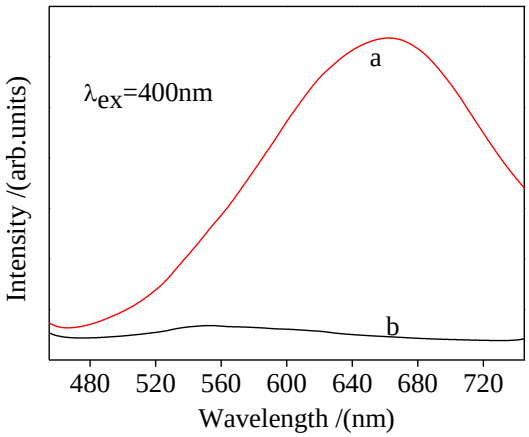

Fig. 3. Photoluminescence of porous silicon prepared by different treatment, a: before thermally o xidize; b: after thermally oxidize.

Fig. 4 shows that the photoluminescence spectra of porous silicon fabricated by an etching time of 5, 8 and 10 min, respectively. The current density was 100 mA/cm^2. When excited at the same wavelength (i.e. 400 nm), red luminescence is emitted from the porous silicon. The PS exhibited photoluminescence behave in a wavelength range of 610–670 nm and the maximum photoluminescence intensity is found about 10 minutes of an anodization with a peak at 610 nm. It is noticed from the spectra that photoluminescence peak intensity increases with the increase of the etching time, and a slight shift of the photoluminescence peak wavelength toward shorter wavelength. Fig. 5 shows the photoluminescence spectra of the porous silicon fabricated by etching current densities of 50, 75 and 100 mA/cm^2, respectively. The porous silicon emits red luminescence at the peaks position of 610 - 630 nm. The maximum photoluminescence intensity is found for the sample prepared by current density 100 mA/cm^2 with a peak at 610 nm. It clearly shows that the peak position shifts to lower energies with the increase of the current density, and accompanies by the increase of the photoluminescence intensity. The shift of photoluminescence peak position to shorter wavelengths as increasing the current density can be interpreted by the luminescence mechanism of quantum confinement model. At the same time, when the current density is heightened, the speed of anodic oxidation will be accelerated. This leads to the shrinkage of nanocrystallites and the increasing of porosity, so its effective band-gap will increase and the corresponding peak will be blue shifted.

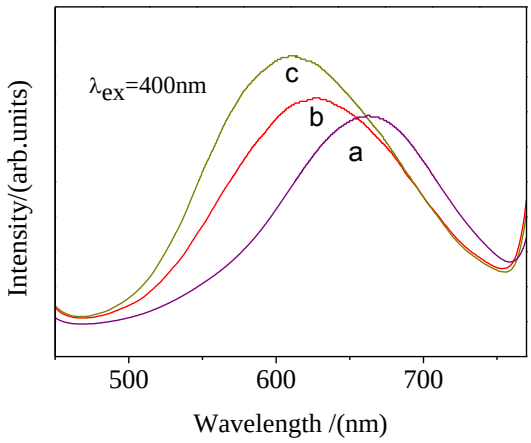

Fig. 4. Photoluminescence of porous silicon prepared by different anodization time, a: 5 min; b: 8 min; c: 10 min.

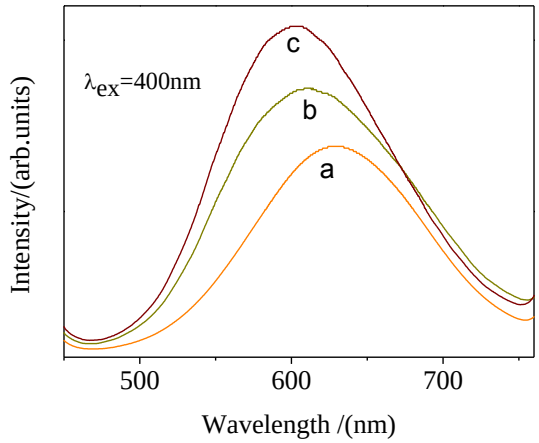

Fig. 5. Photoluminescence of porous silicon prepared by different current density, a: 50 mA/cm^2; b: 75 mA/cm^2; c: 100 mA/cm^2.

4. Conclusions

In summary, we have presented a useful technique for fabricating porous silicon which provides quasi-regular arrangements without pre-structuring. The variation of the electrochemical parameters changes greatly the morphology of the porous silicon layer. A heightening of the current density leads to an increase of the pore-diameter. The optimal condition has been obtained by discussing several important factors of the electrochemical anodization: V_{HF}: V_{DMF}=1:2, current density = 75 mA/cm^2, anodization time=10 min. The samples prepared in this condition successfully obtain the quasi-regular arranged pores. The shape of the cross-section of individual pores is circular. The pore diameter is ranging from 500 nm to 1μm and the pore depth is about 20 μm. Fresh porous silicon can emit a red luminescence at room temperature, the peak position shifts to lower energies with increasing current density, and accompanied by the increase of photoluminescence intensity. Photoluminescence peak intensity increases with the increase of the etching time,

and a slight shift of the photoluminescence peak wavelength toward shorter wavelength is observed.

Acknowledgments

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