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Improvement of Photoluminescence Uniformity of Porous Silicon by using Stirring Anodization Process

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***Abstract*—**The electrolyte stirring method of anodization etching process for manufacturing porous silicon (PS) is reported in this work. Two experimental setups of nature air stirring (PS-ASM) and electrolyte stirring (PS-ESM) are employed to clarify the influence of stirring mechanisms on electrochemical etching process. Compared to traditional fabrication without any stirring apparatus (PS-TM), a large plateau region of PS surface structure is obtained from samples with both stirring methods by the 3D-profiler measurement. Moreover, the light emission response is also improved by both proposed electrolyte stirring methods due to the cycling force in electrolyte could effectively enhance etch-carrier distribution while the electrochemical etching process is made. According to the analysis of statistical calculation of photoluminescence (PL) intensity, lower standard deviations are obtained from PS-samples with studied stirring methods, i.e. the uniformity of PL-intensity is effectively improved. The calculated deviations of PL-intensity are 93.2, 74.5 and 64, respectively, for PS-TM, PS-ASM and PS-ESM.

***Keywords*—**Porous Silicon, Photoluminescence, Uniformity Carrier Stirring Method

I. INTRODUCTION

POROUS silicon (PS) consisted of many nano pores and pillars has been demonstrated to be a possible silicon-based material to yield efficient visible photoluminescence at room temperature [1]-[2]. Such optical property of light emission is attributed to the electron confinement in the nanocrystals that constitute the PS membrane [3]-[5]. Based on its unique porous nanostructure, PS material could simultaneously exhibit a high impendence, wide band-gap energy and high surface to volume ration (SVR) that are larger than conventional bulk Si. Therefore, many researches have widely carried out the PS technique development of electronic device design including the bio-sensor [6]-[7], hydrogen gas/photo detector [8]-[9], thermal sensor/isolator [10]-[12] and integrated circuit (IC) [13]-[14].

For PS manufacture, there are many techniques have been developed including electrochemical anodization [1], [15]-[16], spark erosion [17], stain etching [18]-[19], sol-gel [20] and vapor etching methods [21]-[22]. Especially, the electrochemical anodization etching is the most popular method for PS manufacture.

It is because of the low-cost and convenience of wet-etching process. In general, the illustrative equation of the overall process during PS electrochemical etching process can be expressed as [23]:

$$Si + 2HF + 2h^+ \rightarrow SiF_2 + 2H^+ \quad (1)$$

$$SiF_2 + 4HF \rightarrow H_2 + H_2SiF_6 \quad (2)$$

According to the chemical reaction equation, there are two major parameters to affect the etching rate of fabricated PS film; one is the hole (h^+) concentration of used Si-wafer, and another is the electrolyte concentration of HF-based soultion. According to the reaction mechanism of h^+, an improved manufacturing process of PS film with the application of Hall-effect was firstly proposed by Lin *et al* [16]. Based on its extra magnetic field, not only film uniformity of PS film but also a pattern-able profile is achieved in this report.

Thus, it should be found that the third interesting parameter of the etching carrier distribution surrounding the region between Si-surface and electrolyte is emerged. It is owing to the total current path of applied bias for electrochemical etching process is constituted by above two parameters of h^+ and HF concentration. Therefore, we report the stirring method of anodization process for PS manufacture in this work. The experimental setup and procedures of our stirring method will be described in following section. In the section of experimental results, the statistic calculation is employed to analyze the influence of stirring process on PS manufacture. Finally, conclusions are made.

II. EXPERIMENTS

In the present study, a vertical-design of experimental setup is employed to fabricate PS film (referred to the central-part of Fig. 1(a) or (b)). The Teflon materials are adopted to form the main-body of HF-based electrolyte container. Here, a mixture of HF : C_2H_5OH = 1 : 3 is used as the etching solvent for all studied PS samples. A copper (Cu) disk is set as the anode, while the cathode is made of platinum (Pt). It should be noted that the bottom reaction area was about 1.21π cm^2. Here, the vertical arrangement of setup design could effectively reduce

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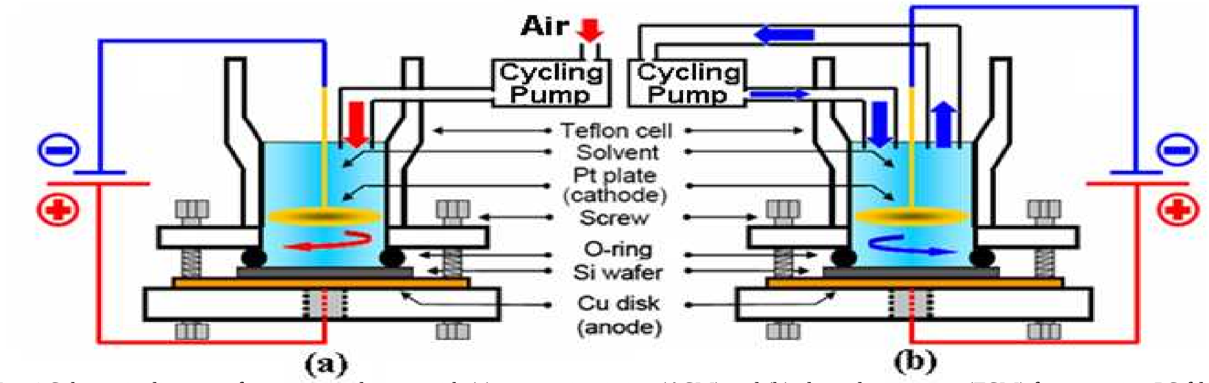

Fig. 1 Schematic diagram of experimental setup with (a) nature air stirring (ASM) and (b) electrolyte stirring (ESM) for preparing PS film

the hydrogen bubbles accumulation on PS surface while the electrochemical etching is made, and therefore improve the uniformity of fabricated PS samples. On the other hand, the (100)-oriented n-type Si-wafer with a resistivity of 1-10 Ωcm is used for preparing all studied PS samples. Before the electrochemical anodization etching process, an aluminum (Al) film is deposited on the backside of Si-wafer as a contact electrode and annealed as ohmic-contact to allow a homogeneous anodization current flow. The anodization etching current is supplied by an external constant current source which is kept at 60 mA.

To investigate the stirring influence on PS manufacture, two apparatus designs of nature air stirring (ASM) and electrolyte stirring (ESM) are added into the traditional setup as shown in fig. 1 (a) and (b), respectively. The employee of cycling pump is the key part used to create an extra force in HF-based electrolyte, and therefore induce a stirring distribution of hole etching carrier.

III. Results And Discussion

To optimize the electrochemical etching process, the PS film made by traditional method (TM) with a fixed anodiztion current (I = 60 mA) and various etching times (from 10 min to 30 min with 5 min/step) is firstly performed. Fig. 2 shows the measured PL-spectra of fabricated PS films. Obviously, the obtained peak value of PL-intensity is depended on the electrochemical etching time in this work. The corresponding wavelength of intensity peak for all PS-TM samples with different etching time are around 600 nm.

Such optical properties of orange-red light emission are believed to that the quantum confinement effect in the nanostructure of fabricated PS film. The related effect for illustrating the luminescence on PS structure has bee reported by [4], [24]. On the other hand, the increase in peak value is with the increase in etching time. Especially, the maximum intensity is obtained from PS-TM sample with etching time of 30 min. It is attributed to the deep size effect of fabricated PS film [24].

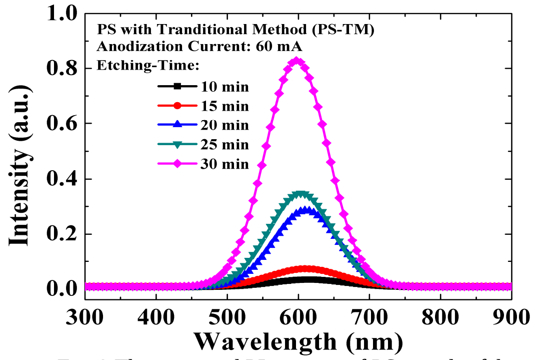

Fig. 2 The measured PL-spectra of PS samples fabricated by traditional method with various etching times (10 min to 30 min, 5 min/ step) at fixed anodization current of 60 mA

Based on this optimum etching time condition of 30 min with fixed etching current of 60 mA, the stirring methods of ASM and ESM are following performed to comprehend the related influences. Fig. 3 shows the measured PL-spectra for PS films fabricated with methods of TM, ASM and ESM. Here, a blue-shift and red-shift of light emission properties are observed from PS-ASM and PS-ESM, respectively. Such behavior is believed to the etching reaction is affect by the stirring forces of both studied methods. For PS-ESM, the force is mainly created by cycling electrolyte. Then, the etching carrier distribution between the electrolyte and Si-wafer is enhanced without any concentration loss.

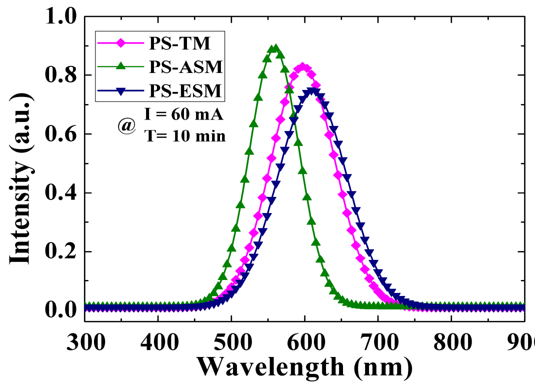

Fig. 3 The measured PL-spectra of PS-TM, PS-ASM and PS-ESM (excitation wavelength of 325 n He-Cd laser). The etching condition are fixed at T = 10 min and I = 60 mA

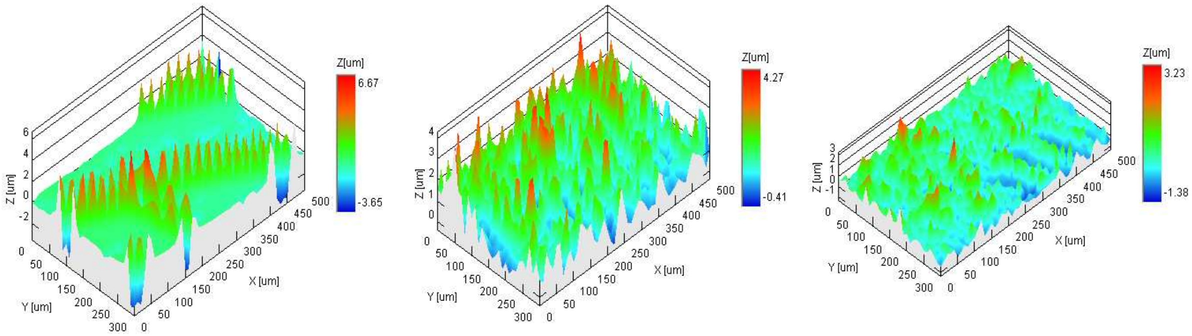

Fig. 4 The measured 3D profiles of studied samples of PS-TM, PS-ASM and PS-ESM (T = 10 min and I = 60 mA)

Therefore, a more complete anodization etching property is obtained from sample with electrolyte stirring method.

On the contrary, the manufacture of PS-ASM would bring the some extra nature air into the electrolyte and thus induce a loss in electrolyte concentration that compared with PS-ESM. However, the carrier distribution of anodization current is still stronger than PS-TM. Based on such mechanism, a few differences in deep-size of PS nanostructure are occurred on studied samples with different etching method. The corresponding wavelength of PL-intensity peak are 597 nm, 560 nm and 609 nm for PS-TM, PS-ASM and PS-ESM, respectively. To further clarify the influence of PS sample with/without stirring method, the statistic calculations of obtained PL-spectra are utilized to analyze uniformity improvement. The formula of standard deviation is expressed as below:

$$S = \sqrt{\frac{\sum_{i=1}^{n}(Xi - \overline{X})^2}{n}} \tag{3}$$

Where S is the roughness of PL intensity, Xi is the wavelength of intensity peak, $\overline{X}$ is the mean value of PL intensity and n is the sampling number. In general, the smaller S means the uniformity of PL intensity of studied PS sample is better. The calculated S values are 93.2, 74.5 and 64 for PS-TM, PS-ASM and PS-ESM, respectively. Calculated results indicated that the obtained S of PS samples with both stirring method are lower than traditional method. Therefore, the uniformity of PL property could effectively improved by stirring anodization method. On the other hand, the 3D-profiler is utilized to observe the surface roughness of PS sample with/without stirring method. Obviously, a flattest PS surface is obtained from PS-ESM. It's attributed that there is no any unnecessary parameter such as a loss of electrolyte concentration appeared during the etching reaction.

IV. Conclusion

The comparative study of stirring anodization process for PS fabrication by using the nature air stirring and electrolyte stirring were present in this work. It is found that the proposed stirring methods could effectively create an extra cycling force in electrolyte, and therefore enhance the hole (h^+) carrier distribution of electrochemical etching process. The corresponding wavelength of PL-intensity peak are 597 nm, 560 nm and 609 nm for PS-TM, PS-ASM and PS-ESM, respectively. Experimental results demonstrate that the uniformity improvements of structure profile and PL-intensity are obtained from studied PS sample with process of ASM or ESM. The calculated deviations of PL-intensity are 93.2, 74.5 and 64, respectively, for PS-TM, PS-ASM and PS-ESM. For the further applications of PS-based material such as electronic device, optical device and biosensor, the proposed stirring methods could provide an interesting approach to yield a high quality PS film.

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