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Formation of Luminescence Porous Silicon by Two-Step Chemical Immersion and Role of NO_2 in Etching*

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Abstract The uniform luminescent porous silicon (PS) film on crystal Si wafer has been prepared by two-step chemical staining etching. The refractive index of the film ranges from 2.0 to 2.4. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra and Fourier transform infrared (FTIR) spectra have been measured. The features of chemically stained PS are consistent with those of anodized samples. It is found that the etching is induced by the electron transmitting through neutral NO_2. Both oxidization by HNO_2 and hydrogen action by HF make the chemically stained PS have similar FTIR spectra as anodized samples. The occurrence of bold spots during PS formation has been discussed. It is believed that there exists metasilicate acid in the PS film.

Keywords: porous silicon, luminescence, chemical staining.

The potential application of high effective visible luminescence from porous silicon at room temperature[1] in Si-based optoelectronics has aroused scientists' interest. At present, there are two main methods to prepare PS; one is electrochemical anodization[1-3], and the other is chemical staining etching[4,5]. The former has been extensively studied, and its formation technology has been well understood[6-8]. Several models have been proposed[1, 9-11] to elucidate its formation mechanism. However, none is proved flawless. The latter is less reported and its formation mechanism is still unclear. Archer reported the chemically stained Si film in 1960[12], suggesting that there were Si and Si-rich complex in the chemically stained PS film. In 1965, Bechmann studied the infrared transmission spectra of both chemically stained film and anodized film. He estimated that the over-all composition of chemically stained film varied between H_2SiO and $HSiO_{1.5}$ which was irrelevant to the type or conductivity of the substrate Si wafer[13]. In 1986, Beale *et al.* discovered that the microscope morphology of chemically stained film had a porous structure. And he further proposed that the formation of chemically

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stained PS resulted from a local anodized process[14]. In 1992, Fathaur *et al.* reported that PS had effective photoluminescence at room-temperature, which was similar to anodized PS. In the same year Shih studied the formation mechanism of the light-emitting chemically stained PS and gave out the reaction equations[5]. In 1993, he and his colleague analyzed the microstructure of stained PS and concluded that it comprised crystalline, poly-crystalline and amorphous phase crystalline[15].

Chemical staining process is simpler than anodization process. Shih's equation shows that chemical staining etching proceeds nonpreferentially, but in fact etching proceeds more easily at lattice-imperfect sites, such as dislocation and grain boundary. Furthermore, Shih pointed out that the prerequisite to start chemical staining etching is to maintain enough concentration of HNO_3 on the surface of Si wafer; and therefore a waiting time is necessary[5].

In this paper, we report the two-step immersion chemical staining etching method for preparing uniform porous silicon with visible luminescence, measure its refraction index, PL, PLE and FTIR spectra and discuss the role of NO_2 during chemical staining etching.

1 Experiments and Results

Both n-type and p-type Si wafers polished mechanically or chemically have been used in our experiments with B, Al, As, Sb as dopants.

The first step is to adhere a very thin layer of 40% to 50% HNO_3 on the surface of Si wafer flatly, then immerse the wafer into G. R. grade HF solution (solution A). There form a lot of gas bubbles and the surface of Si wafer is chemically stained turning ocher or blue rapidly. The second step is to insert the colored stained Si wafer into solution B which is mixed with HF (G.R.) and 50% HNO_3 to thicken the colored porous layer. The proportion of HF and HNO_3 can be adjusted in the range of 120:1 – 50:1 according to the growth rate and thickness.

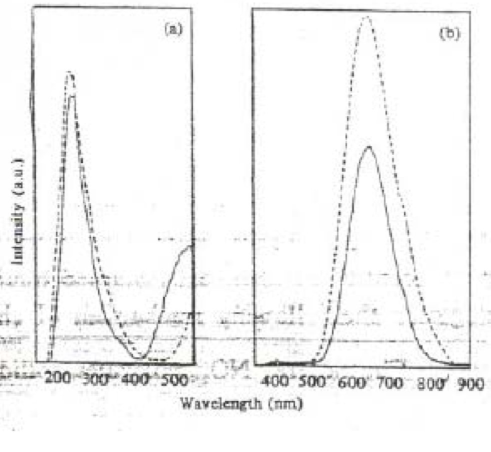

Fig. 1. The **PLE** and **PL** spectra of chemically stained PS and pulse anodized PS. (a) PLE spectra; (b) PL spectra. In (a) the solid lines represent the spectra of the chemically stained PS. The optimum exciting wavelength is about 254 nm. In (b), the solid lines with the PL peaks at 640 nm are the PL spectra of chemically stained PS excited by light of 254 nm with 5 nm width. For comparison, the corresponding spectra of pulse anodized PS[14] is drawn in dashed line which was excited by the optimum exciting wavelength 254 nm, and the peak of PL at 630 nm.

As the reaction goes on and the bubbles transpire continuously from the stained layer, the surface color changes repeatedly in the following order: dark blue, emerald green, dark green, grass green, light yellow, gold yellow, purple red and dark blue again. Since the stained porous film is hydrophobic in the solution, when it is taken out of solution B, no solution remains, and on the surface the color no longer changes. After it is inserted into solution B again, the color changes once more. When the proportion of solution B was settled, the PS film will have a stable thickness as previously reported[4, 5]. On the other hand, if the time of chemical staining etching lasts for a too long time, the porous layer will get dark and loses its luminescence property at last.

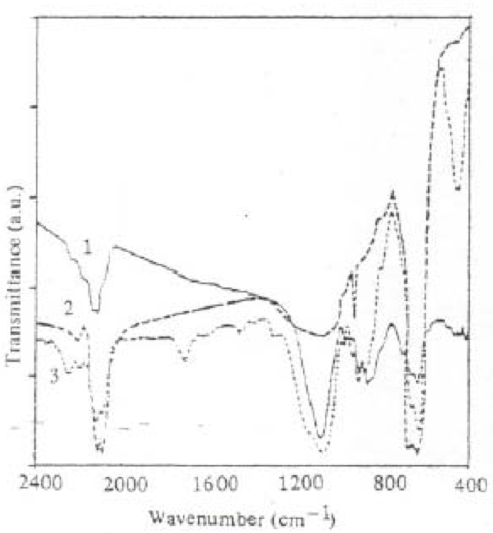

Fig. 2. The FTIR spectra of chemically stained PS and pulse anodized PS 1, as-prepared chemically stained PS; 2, as-prepared pulse anodized PS; 3, the anodized PS kept for 40 D.

The equivalent refractive indexes measured with ellipsometry ($\lambda = 6328$ Å) range from 2.0 to 2.4. PL and PLE spectra were recorded with Hitachi 850 florescence spectro-meter as shown in Fig. 1, in which (a) is the PLE spectra and (b) is the PL spectra. We can see that PLE and PL peaks of the two kinds of PS are similar. Fig. 2 shows the FTIR spectra gauged with Nicolet FTIR 170SX. Solid line (Fig. 2-1) is for chemically stained PS and dashed lines (Fig. 2-1, 2) for the pulse-anodized one. On the three spectra, all the peaks in range of 628 − 664 cm^{-1}, 864 − 907 cm^{-1} and 2190 − 2250 cm^{-1} are composed of two mini peaks except the wide peak from 1000 cm^{-1} to 1250 cm^{-1}. These peaks reveal the features of infrared absorption corresponding with the bonds of SiH, SiH_2, SiH_3, Si-O-Si and Si-O-H indicating that the two types of PS are almost the same except for the difference in absorption intensity.

2 Discussion

The uniformity of chemical staining in the first step in preparing PS with two-step chemical immersion method is impertant. If the stained is incomplete, "bold spots" phenomenon, i.e. unstained areas will appear, and these "bold spots" cannot be chemically stained again. We have studied this phenomenon and suggested the following mechanism of chemical staining.

(1) The neutral NO_2 molecules collide with the Si lattice giving rise to a lot of

electron-hole pairs. Then NO_2 is reduced to NO_2^- after capturing an electron, and Si is oxidized to form SiO_m group, such as SiO and SiO_2 when its atoms get the holes (Eq. (1)).

(2) The reaction between the SiO_m and HF generates the metasilicate acid mixture of H_xSiO_y, such as H_2SiO_3 and H_2SiO_5, as shown in Eqs. (5) − (9). The existence of H_xSiO_y and the adsorption effect of H^+ on dangling bonds of PS surface bring about the characteristic FTIR spectra of the chemically stained PS layer.

(3) Porous structure is caused by a series of factors, such as the randomization of collision of NO_2 with Si lattice, the retarding function of the gas bubbles to the reaction during the etching, anisotropic etching, preferential chemical staining at defect sites of Si lattice. All these lead to a fractal porous structure. The porous structure may be further developed to form nanometer silicon islands or silicon granules.

The reaction equations of chemical staining etching process are summed up as below:

Reaction occurring on the surface of Si wafer:

$$Si + mH_2O + h = SiO_m + 2mH^+. \quad (m = 1,\ 2) \tag{1}$$

Reaction occurring in the solution near surface of Si wafer:

$$NO_2 + e = NO_2^- \qquad (2)^{[18]}$$

$$NO_2^- + H^+ = HNO_2 \qquad (3)^{[18]}$$

$$HNO_3 + HNO_2 = H_2O + 2NO_2 \qquad (4)^{[18]}$$

$$SiO + 2HF = SiF_2 + H_2O \tag{5}$$

$$SiF_2 + 2HF = SiF_4 + H_2 \uparrow \qquad (6)^{[7]}$$

$$SiO_2 + 4HF = SiF_4 + 2H_2O \qquad (7)^{[19]}$$

$$3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6 \qquad (8)^{[19]}$$

$$6SiF_4 + 5H_2O = H_2Si_2O_5 + 4H_2SiF_6 \qquad (9)^{[19]}$$

The above equations seem complicated, but the products deposited on the surface of Si wafer are mainly the mixture of H_2SiO_3 and $H_2Si_2O_5$. This coincides with Bechmann's results, calculated from the infrared absorption spectra, that the overall components of the chemically stained film vary between H_3SiO and $HSiO_{1.5}$[13]. As to other products such as SiF_4 and H_2SiF_6, the former can react with water to form the latter, while the latter is stable only in the water. After Si wafer is taken out of the solution, it will decompose into[19]

$$H_2SiF_6 = 2HF\uparrow + SiF_4\uparrow \quad (10)$$

NO_2 molecules steadily attack the surface of Si wafer, entering the holes on the surface. So the oxidization process will proceed continuously. Eqs. (2)−(4) show that the quantity of NO_2 is fixed if the escaping NO_2 was neglected. Actually NO_2 plays the role of catalyst in the chemical stain process[18]. During the formation of the porous layer, the surface of porous structure area will increase rapidly[17]. As a result: (i) the probability of oxidization on the chemically stained area will surpass that on the "bold spots" area, and (ii) the concentration of NO_2 in the chemically stained porous area is higher than that on the "bold spots" area. These two effects give rise to a much higher growth rate in the chemically stained area.

When the concentration of HNO_3 in the solution B and the condition of temperature and illumination are definite and the concentration of NO_2 in the solution is given, the thickness of the porous layer will reach its maximum. We have repeated Shih's experiment with identical Si wafers at three different temperatures (0℃, 20℃ and 50℃). During the etching, the proportion of solution was HF (40%) : HNO_3 (20%) : H_2O = 1 : 3 : 5. We found that Si wafers could not be stained at 0℃. At 50℃, although it could be stained rapidly, the stained layer would disappear again at once. Only at 20℃ could it be stained normally. It is well known that HNO_2 is stabler at 0℃ than at 20℃[19]. This fact is incomprehensible in Shih's model. We further compared the chemical staining processes with and without illumination at 23℃, with the wafers and solution being the same. The result shows that the illuminated wafer will first form an ocher chemically stained film. Based on the fact that HNO_3 decomposes into NO_2 more easily under illumination or at high temperature, we believe that NO_2 is the key to chemical staining etching: NO_2 takes part in the reaction through transmitting electrons, functioning as the catalyst. At 50℃, the stained film disappeared because the decompose rate is higher than the growth rate[5].

The formation of porous silicon during chemical staining etching is preferential, i.e. the chemical staining process proceeds easily at lattice imperfect sites, such as dislocation, grain boundary because these places may act as the recombination center and be able to generate electron-hole pairs when they are colliding with NO_2 molecules. The chemical staining etching process was divided into two steps in order to restrain the preferential etching. In the first step, a thin layer of 40%−50% HNO_2 is adhered to silicon surface evenly to provide uniform possibility of oxidization, in order that the silicon surface may be chemically stained uniformly in solution A. However, since the proportion of HNO_3 and HF is indefinite in solution A, it is hard to control the growth rate and thickness in solution A. Therefore, it is required to thicken the chemically stained porous layer in solution B.

3 Conclusion

We have prepared uniform luminescent PS film on crystal Si wafer by means of two-step chemical immersion. The equivalent refractive index of film ranges from 2.0 to 2.4. Both PL and PLE spectra of the chemically stained film are similar to that of anodized samples. And its FTIR feature spectra are corresponding with that of anodized film, too. We believe that there is metasilicate acid in the chemically stained PS film. Our new formation mechanism suggests that the agent of chemically stained film formation is due to neutral NO_2 instead of HNO_2. The cause of the "bold spots" has been discussed.

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