



Multiple UV-blue luminescence emissions in electrochemical anodic etched n-type silicon wafer

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ABSTRACT

This very paper is focusing on the preparation of porous nanostructures in n-type silicon (1 1 1) wafer by chemical etching technique in alkaline aqueous solutions of 5 M NaOH, 5 M K₂CO₃ and 5 M K₃PO₄, and particularly, on its ultraviolet-blue photoluminescence emission. The anodic chemical etched silicon wafer has been characterized by means of optical microscopy, scanning electron microscopy, fluorescence spectroscopy, atomic force microscopy and Fourier transform infrared spectroscopy. This very surface morphology characterization has been clearly shown – the effect of anodic-chemical-etching procedure processed in K₂CO₃ or K₃PO₄ was much vigorous than that processed in NaOH. The FTIR spectra indicate that the silicon oxide was formed on the surface of electrochemical etched n-Si (1 1 1) wafers, yet not on that of the pure chemical etched ones anyhow. And an intense ultraviolet-blue photoluminescence emission is observed, which then differs well from the silicon specimen etched in alkaline solution with no anodic potential applied. The proper photoluminescence mechanism is discussed, and hence there may be a belief that the intense ultraviolet-blue photoluminescence emission would be attributed to the silicon oxide coating formed on silicon wafer in anodic-chemical-etching process.

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1. Introduction

In the recent few decades, the micro electronic device manufactory has been advanced in the level of “all system on a chip”. Hereby little progress has been, so far, made for the preparation of optoelectronic device with bulk crystalline silicon (Si) yet. In fact, Si (cheap, abundant, with many desired electrical and mechanical properties) is the mainstay semiconductor of the modern microelectronics industry. However, being an indirect-band-gap semiconductor with narrow band gap ($E_g = 1.12$ eV), bulk crystalline Si can give only rise to poor illumination efficiency at near-infrared range. It is not until the reports on visible light emission in porous Si [1] and in nanometer-scaled Si structures (Si-NS) [2] that there has been an ongoing motivation to build nano Si-based optoelectronics. The luminescence mechanism has been studied and ascribed to the quantum confined effect [3] or the oxygen-related defects luminescence centers [4]. Based on the quantum confinement theorem, on one hand, it is believed that the luminescence emission in Si-NS owes a great deal to the recombination of confined excitons in the Si-NS [5]. And on the

other, if the fine Si-NS is dispersed in a dielectric matrix of Si oxide, the defect-assisted recombination mechanism should be involved, for instance. In this case, the luminescence is reckoned as being caused by the recombination of carriers trapped at radiative recombination centers, which form at the interface between Si-NS and the dielectric [6], or in the dielectric itself [7]. Therefore, Si-NS has been paid much close attention because of the potential compatibility between the technology of preparing Si-NS and that of micro electronic device manufactory. Many alternative technologies have been recently developed to make Si-NS [8]. From the viewpoint of technology, there are basically two general routs for us to prepare Si-NS [9]. One approach (top-down) starts from crystalline Si wafer, in which Si wafer is disintegrated into small pieces either mechanically or chemically. The other (bottom-up) is based on the growth of Si-NS from atomic constituents either by Si aggregation in annealed SiO_x or by silane (SiH₄) combustion. The photoluminescence (PL) spectra of all the Si-NS, now, are in near-infrared and visible spectra regions except those of the Si-NS specimens treated by thermal annealing and HF etching procedures [10], whose PL spectrum covers from 330 nm to 430 nm in the spectrum. In order to utilize the luminescence as the light source for data storage, full color display and solid-state lighting engineering, a shorter light (UV-blue emission for instance) is more desirable.

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Both p- and n-type Si are widely used in optoelectronic device manufacture. The preparation of Si-NS on n-type Si wafer is widely studied for their luminescent properties. Nevertheless, to date, it is difficult to achieve a Si-NS preparation, taking porous Si on n-type Si wafer for example, unless either the surface illumination or lateral electrical potential applied. To our knowledge, the anodic-chemical-etching (ACE) procedure of Si wafer in alkaline aqueous solution differs greatly from that in HF-based electrolytes. Although there is still some debate on the finer details of the mechanism of ACE treating Si wafer in HF-based electrolytes, the availability of an electric field at the silicon/electrolyte interface is known to be an important factor [11]. And it is the only pathway for the electrochemical dissolution of Si atoms. The issue of Si-NS fabricated in this way comprises rather different porous structures ranging from micron-large pores to sponge-like layers with pores of several nanometers in diameter. In fact, the ACE treating Si wafer in alkaline aqueous solution is a complex process in which two mechanisms are involved [12]. According to the chemical mechanism, Si atoms are dissolved in a thermally hydroxide-catalysed chemical reaction, in which water is the reactive species, and simultaneously, an electrochemical dissolution pathway may take place. Most of the silicon dissolves, and hillock-like structures are formed on the surface.

The ACE treating Si wafer in KOH or NaOH aqueous solutions have been widely made in the past decades [12,13]. Because of partial hydrolysis of K_2CO_3 or K_3PO_4 , the etching Si wafer in these basic aqueous solutions is more inhomogeneous, whereas the ACE treating Si wafer in basic salt aqueous solutions has been merely reported. And this paper has demonstrated a much easy method for Si-NS preparation by means of ACE in alkaline aqueous solutions. On this purpose several alkaline aqueous solutions, such as NaOH, K_2CO_3 or K_3PO_4 , were used so as to etch the n-type Si (1 1 1) wafers under anodic bias to form the photo active Si-NS. The ACE samples were characterized by optical microscopy, scanning electron microscopy (SEM), atomic force microscopy

(AFM) and Fourier transform infrared spectroscopy (FTIR). The PL emission was also investigated; it is quite interesting that the intense UV-blue emissions are obtained with excitation of the wavelength 260 nm.

2. Experimental

The mirror polished n-type (1 1 1) Si wafers ($\rho = 20 \Omega \text{ cm}$, 12 mm by 12 mm) were used hereby. They were firstly degreased using sulfuric peroxide mixture (SPM) cleanings [14], and then followed by an oxide removal process in 5% HF, and finally rinsed in de-ionized water getting rid of the residual contamination. The ACE procedures were conducted respectively in three kinds of alkaline aqueous solutions of 5 M NaOH, 5 M K_2CO_3 or 5 M K_3PO_4 for 20 min. The current density for anodization was maintained at 80 mA cm^{-2} . After the ACE, all samples, referring to the ACE samples, were rinsed in de-ionized water and brown dry in the air. For comparisons, some ACE samples were etched with 5% HF and at the same time some Si wafers were only chemically etched in 5 M NaOH for 20 s or 20 min, respectively, without anode bias applying, referring to the PCE procedure and PCE samples, respectively.

The surface morphology was characterized by optical microscopy, scanning electron microscope (SEM, JEOL JSM-5900LV) and atomic force microscopy (AFM Veeco Instruments Nanoscope Multimode & Explore). The PL measurements were performed using fluorescence spectrophotometer (Hitachi F-4500, xenon lamp). In addition, the infrared absorption spectra were taken with Fourier-transformation infrared spectroscopy (Nicolet Magna 560). All the measurements were carried out at room temperature.

3. Results and discussion

Fig. 1 shows the optical microscope images of Si-NS samples. As in Fig. 1(a) and its inset, there are many etching pits regularly distributed on the surface. With respect to the surface morphology,

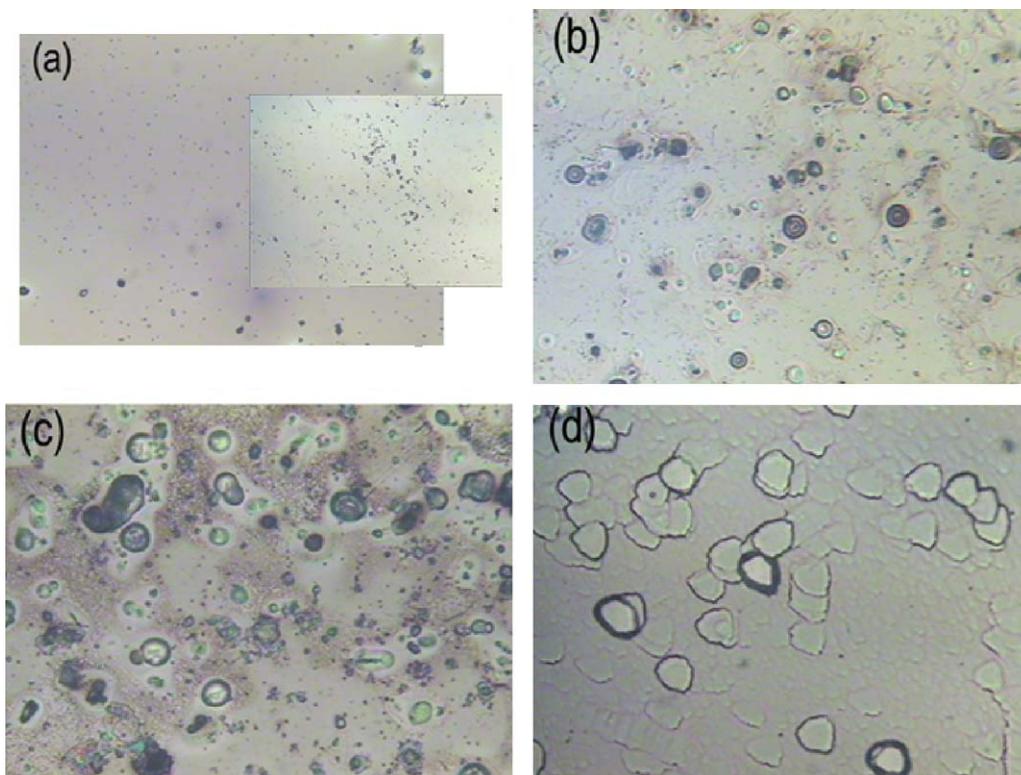


Fig. 1. Optical microscopy images ($\times 900$) of ACE samples prepared in (a) 5 M NaOH, (b) 5 M K_2CO_3 and (c) 5 M K_3PO_4 . (d) Optical microscopy images of PCE sample in 5 M NaOH for 20 min. The inset is the surface image of PCE sample in 5 M NaOH for 20 s.

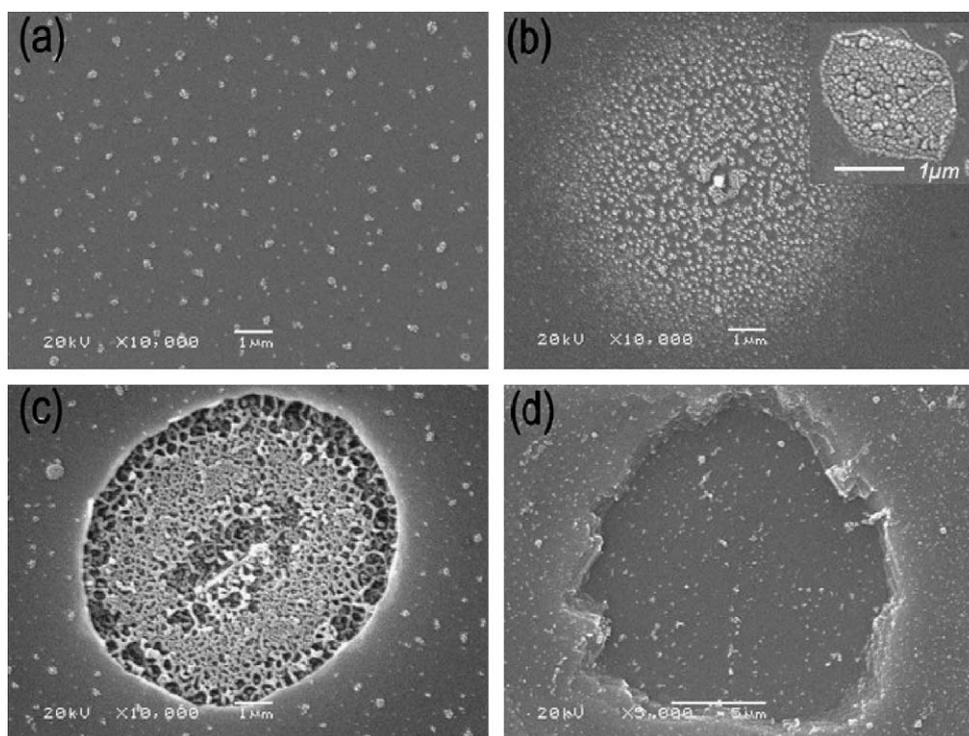


Fig. 2. Typical SEM images of ACE samples prepared in (a) 5 M NaOH, (b) 5 M K_2CO_3 , (c) 5 M K_3PO_4 and (d) that of PCE sample etched in 5 M NaOH. The chemical etching time was fixed for 20 min.

there is no clear difference between the ACE sample and the PCE samples prepared in NaOH. However, when the PCE procedure in NaOH was fixed for a longer time, the etching pits were disappeared and terrace-like steps appeared (Fig. 1(d)). As for the ACE samples prepared in either K_2CO_3 or K_3PO_4 , some disordered etching spotty patterns were formed (Fig. 1(b) and (c)). Therefore, it is certain that the various surface structures on n-type Si wafers result from the ACE procedures in different alkaline aqueous solutions.

Typical SEM images of Si-NS samples are demonstrated in Fig. 2. Fig. 2(a) displays the SEM image of the ACE sample prepared in NaOH. It can be found that there are many hillocks distributed homogeneously on the surface. However, as for the samples prepared in either K_2CO_3 or K_3PO_4 , some assembled hillocks can be found (Fig. 2(b) and its inset) and even the bird nest-like structures were formed (Fig. 2(c)). As in Fig. 2(d), when the sample was directly immersed in NaOH for 20 min under PCE condition, then anisotropic etched inverted plateau appeared.

Fig. 3(a) and (b) shows the AFM images of ACE and PCE samples prepared in 5 M NaOH for 20 min. The AFM images represent that there are many hillocks and voids on the samples' surfaces (Figs. 3(a) and (b)). The roughness obtained from the images is estimated to be 6.5 nm or 3.9 nm, respectively. Fig. 3(c) displays the AFM image of PCE sample prepared in NaOH for 20 s and its roughness is 0.8 nm, which is quite different from samples treated for 20 min.

It is known to all that in either NaOH, or K_2CO_3 , or K_3PO_4 both hydrolysis process and partial hydrolysis one would take place, depending on the alkaline compounds used, and schematically express below:

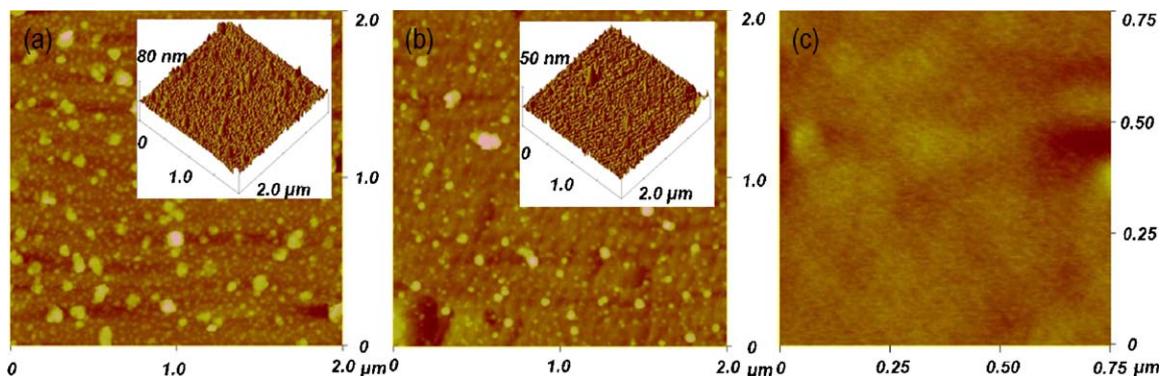
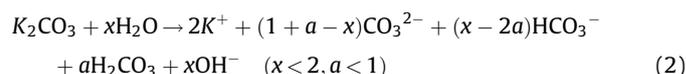
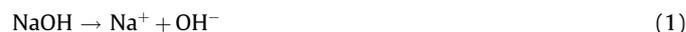
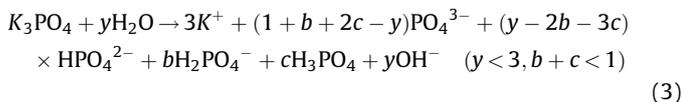
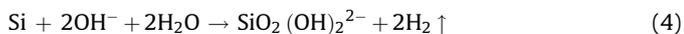


Fig. 3. AFM images of the samples prepared in 5 M NaOH for 20 min with (a) ACE, (b) PCE. (c) The AFM image of PCE sample prepared in 5 M NaOH for 20 s. The roughness is (a) 6.5 nm, (b) 3.9 nm and (c) 0.8 nm, respectively.



The ACE procedure in alkaline aqueous solution involves a number of sequential reactions, including chemical etching, electrochemical etching and even oxide formation when the local anodic potential drop in the space charge layer exceeds a threshold value [15]. The rate of etching Si is dependent on alkaline concentration; yet pure H₂O does not etch at an appreciable rate. Therefore, alkaline etching of Si involves, at least, three species—OH⁻, H₂O and Si. The possible net-etching reactions, here, in alkaline aqueous solution can be expressed as follows [12]:



Upon these equations, when etching procedure is conducted, the OH⁻ concentration is gradually decreased in NaOH; however, it will be compensated by the hydrolysis process of K₃PO₄ or K₂CO₃ in the aqueous solutions (Eqs. (2) and (3)). Thus, the etching rate in the K₃PO₄ or K₂CO₃ is expected to be much more vigorous than that in NaOH.

As for the ACE samples prepared in the K₂CO₃ or K₃PO₄, the partial hydrolysis is inhomogeneous near the initial etching pits, thus the hydrolysis rate is rather uneven and finally forms the disordered etching spotty patterns which differs greatly from the homogeneous etching pits in NaOH (Fig. 1(a–c)). As for the similar optical images between the ACE sample and the PCE sample prepared for 20 s (Fig. 1(a) and its inset), it can be deduced that the anodization must be triggered off by some chemical reaction.

Curves 1–3 in Fig. 4 give the room-temperature PL emission spectra of the ACE samples. For comparison, the emission spectrum of the PCE sample has also been measured and illustrated (Curve 4 in Fig. 4). It can be found that the PL spectra from the ACE samples exhibit several UV-blue emissions peaking at 310–320 nm, 340 nm, 370 nm or 470 nm together with a shoulder at 400 nm. Conversely, there might be no clear PL emission in UV-blue region for PCE sample.

So far, the quantum confinement model is the most popular theorem to explain the visible luminescence emission from Si–NS [1]. Meanwhile, many other alternative models have also been proposed [8,16]. Except for the quantum confinement model, the other ones assume an extrinsic origin of the photoluminescence.

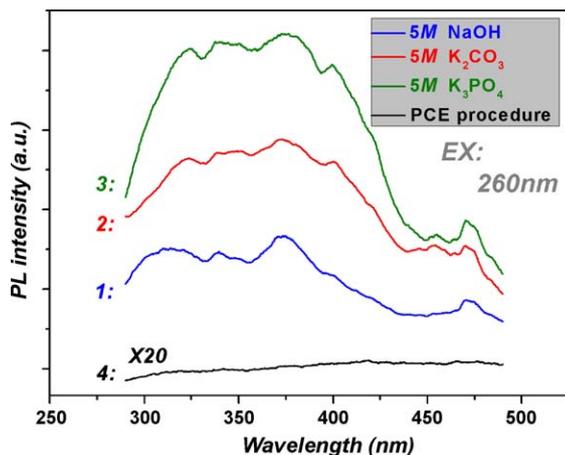


Fig. 4. PL spectra of the ACE samples prepared in (Curve 1) 5 M NaOH, (Curve 2) 5 M K₂CO₃, (Curve 3) 5 M K₃PO₄ and (Curve 4) the spectrum of PCE sample in 5 M NaOH for 20 min. The excitation wavelength was 260 nm for all the spectra.

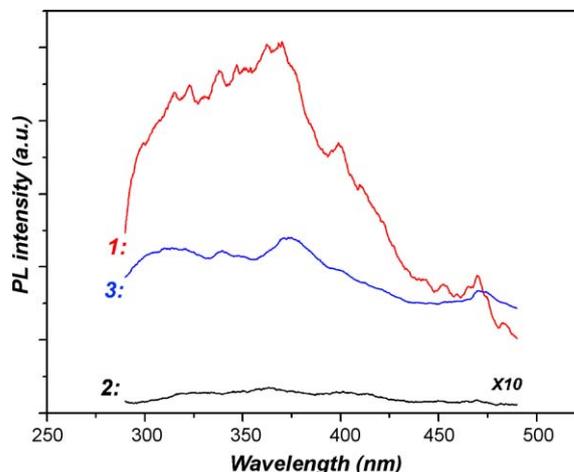


Fig. 5. PL spectra of (Curve 1) annealed ACE sample in 5 M NaOH, (Curve 2) HF-etched ACE sample in 5 M NaOH, (Curve 3) as-prepared ACE sample in 5 M NaOH.

The little difference in sizes between the ACE samples and the PCE ones (insets of Figs. 4(a) and (b)) suggests that the strong UV-blue emission observed only in the ACE sample is not due to quantum size effects. On the other hand, the roughness of the PCE sample immersed in 5 M NaOH for 20 s is about 0.8 nm, comparable to those of HF-etched Si (1 1 1) wafers [17]. And no PL emission is observed from such shiny flat PCE sample.

To further investigate the performance of the UV-blue PL emission, one ACE sample was annealed at 1000 °C in oxygen atmosphere for 10 min and another one was etched in 5% HF, respectively. The corresponding PL spectra are plotted in Fig. 5, in Curve 1 of which, PL spectrum, taken from annealed ACE sample, also exhibits several emissions peaking at 310–320 nm, 340 nm, 370 nm or 470 nm together with a shoulder at 400 nm, which is similar to, but more intense than that of, the as-prepared ACE sample (Curve 3 in Fig. 5). However, there is no UV-blue emission in HF-etched ACE sample (Curve 2 in Fig. 5). When the Si wafer is etched in the ACE, a local potential will drop in the space charge layer. As the local potential exceeds the threshold value, the condensation of neighboring surface Si–OH bonds by the formation of Si–O–Si bridges is predominated and then oxidation happens [18]. It is well known that the passivation layer is easily released in HF-based solution. Thus, the oxide layer must be the origin of the UV-blue luminescence.

Fig. 6 shows the FTIR spectra of ACE samples prepared under different conditions, and the absorption spectrum of the PCE sample is also plotted. The FTIR spectra of as-prepared ACE samples exhibit strong absorptions near 1107 cm⁻¹ (Curves 1–3 of Fig. 6). Adachi [19] thought that the relatively distinct peak at ~1107 cm⁻¹ may be due to a multi-phonons band. It should be noted, whereas, that the band of 1040–1240 cm⁻¹ is largely obscured by residual impurities. In fact, the peak at about 1107 cm⁻¹ has been assigned to the bulk Si–O–Si mode [20]. And a weak shoulder at about 1065 cm⁻¹ is attributed to the Si–O–Si stretching mode, originating from oxidation of porous silicon surface [21]. Conversely, the annealed ACE sample (5 M NaOH anodization followed by thermal annealing procedure) exhibits a distinct peak at about 1065 cm⁻¹ (Curve 4), the typical absorption band can be assigned to the surface Si–O–Si stretching mode and particularly found in thermal oxidized porous silicon [19]. However, the PCE samples and the HF-etched ACE samples do show no Si–O–Si stretching mode (Curves 5 and 6), accompanying together with no UV-blue PL. Thus, it can be concluded that the intense UV-blue emissions in the ACE samples must be ascribed to

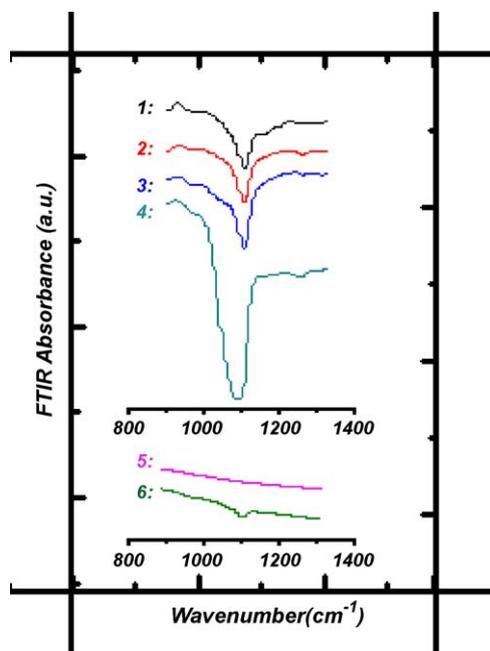


Fig. 6. FTIR spectra of ACE samples prepared in (Curve 1) 5 M NaOH, (Curve 2) 5 M K_2CO_3 , (Curve 3) 5 M K_3PO_4 , (Curve 4) 5 M NaOH and then followed annealing process. (Curve 5) FTIR spectrum taken from PCE sample prepared in 5 M NaOH and (Curve 6) FTIR spectrum of HF-etched ACE sample prepared in 5 M NaOH.

multiple oxygen-related luminescent centers induced by the anodic etching procedure.

The ACE procedure is widely used to achieve the oxidation reaction. And the enhanced OH^- concentration in the aqueous solution results in a much vigorous reaction. Because of the hydrolysis effect, the OH^- concentration in NaOH, K_2CO_3 or K_3PO_4 aqueous solution must be varied, i.e., $C_{NaOH(OH^-)} < C_{K_2CO_3(OH^-)} < C_{K_3PO_4(OH^-)}$, here $C_{NaOH(OH^-)}$, $C_{K_2CO_3(OH^-)}$ or $C_{K_3PO_4(OH^-)}$ are denoted to the OH^- concentration in NaOH, K_2CO_3 or K_3PO_4 , respectively. It is believed that, in the ACE process, the Eqs. (5) and (6) are the major reactions and finally the surface would be passivated. This is also in consistent with the intensity changes of the PL emissions, as shown above in Fig. 4.

The 310–320 nm, 340 nm and 370 nm UV PL emissions have been frequently observed in silicon oxides and thermally oxidized porous Si [6,22–24]. It is known that the origins of these UV PL bands are defect-related luminescence centers in Si oxide but the structure of the centers has not yet been identified. Qin et al. [22] studied thermally oxidized anodic porous Si samples and observed almost the same UV emissions as those seen in the PL spectrum of SiO_2 powders. They thought that the similar luminescence centers in silicon oxide are responsible for UV emission in both P-Si and SiO_2 powders. On the other hand, Kim et al. [23] believed that the UV PL band at 365 nm is ascribed to the hole-trapped E' centers. Yang et al. [6] also observed UV PL emission from Si oxide nanostructures anodically formed in alkaline solution on n-type silicon and suggested that the ~370 nm emission originates in the “ $-SiO_3^-$ ” group which bonds to Si structural surface. More recently, Uchida et al. [24] have fabricated UV luminescent Si-NS by photosynthesized in alkali fluoride aqueous solutions. Spectral analyses suggest that both quantum confinement and surface passivation effects enable the observation of UV emission. Thus, it is believed that the UV-blue emissions in our n-type ACE samples are attributed to the oxygen-

related luminescent centers induced by the ACE procedure, and the detailed luminescence mechanism would be further investigated. The 400 nm band has been extensively studied in silica and oxidized porous silicon, which is deduced to be originated from the $B_2\beta$ band in SiO_2 [10,25]. The blue 470 nm PL band has been thoroughly studied in silica glass and ion-implanted SiO_2 , which has been assigned to the optical transitions in neutral oxygen vacancies [26,27].

4. Conclusions

In conclusion, the Si-NS samples have been prepared on the surface of n-type Si wafers by means of the ACE procedure and the PCE one in alkali aqueous solutions, 5 M NaOH, 5 M K_2CO_3 or 5 M K_3PO_4 , at room temperature. The structure and the property of the samples prepared have been characterized by optical microscopy, SEM, AFM, PL, and FTIR technologies. SEM and AFM images reveal that there are many hillocks of tens nanometers randomly distributed on the surface of the ACE treated Si wafers. An intense UV-blue photoluminescence emission is found in the ACE samples, which differs well from the PCE etched sample in alkali aqueous solution and the HF-etched ACE sample. Hence, it is believed that the UV-blue PL emissions can be attributed to oxygen-related centers in oxide coating formed in the electrochemical anodic etching procedure.

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