The Effects of Rapid Thermal Annealing on Photoluminescence Properties of Nanostructures Silicon

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Abstract

The photoluminescence spectrums (PL) of as-prepared and rapid thermal annealing RTA of nanostructures silicon have been investigated. p-Type porous silicon (psi) fabricated by electrochemical etching method .The (PL) of as-prepared sample, showed top of photoluminescence (PL) peak centered at about 540.9 nm. After the annealing process of nanostructures silicon in temperature 450°c, 600°c and 750°c at annealing time 15 sec, the (PL) peaks shifted,to 743.99nm, 747.49nm and 757.37 nm rspectively . The intensity of(PL) of annealed samples also shown a conspicuous decrease in intensity Compare with as-prepared sample .The intensity reach to (50%),(39%) and (29%)from its intial value whenthe temperature increase 450, 600°c and 750°c rspectively. This behavour is due to the increase in the average skeleton size.

Introduction

After the observation of efficient room-temperature photoluminescence (PL) from porous silicon (PSi) [1], research activities have been concentrated on obtaining an understanding of the luminescence mechanism, the structures and chemical states of the PSi crystallites, and the production of stable and controllable PSi devices [2, 3]. Thermal treatment in the gaseous, mostly oxygen, environment has been of great interest because thermal oxidation is one method to realize stable, efficient, and controllable luminescence [4, 5]. Annealing PSi at high temperature in vacuum has also been of interest because most microelectronic devices are processed at high temperature. Thermal treatments in vacuum and in an oxygen environment both have shown similar trends of rapid PL decrease around 400°c ~ 700°c [4,6, 7, 8]. Especially, in the case of annealing in vacuum, PL quenched completely near 500°c [9, 8]. The cause of PL quenching upon annealing in vacuum, which is also important in understanding the PL mechanism, however, is not yet understood. One phenomenon strongly related to PL degradation upon annealing was an observation of thermal hydrogen desorption from the dihydride (SiH_2) configuration at 400°c and the monohydride (SiH_2) configuration at 500°c [10]. It was thought that, through thermal hydrogen desorption, surface dangling bond defects (DB) were created at the PS crystallite surfaces [10] and that the defects formed surface energy states for non radiative recombination sites, resulting in a lower PL efficiency [4,7 and 11]. Changes in the chemical states, such as a change in the surface oxide state [12, 13] upon annealing, might be considered to explain the PL degradation, even though the role of the surface chemical states of the PS layer on the PL is still controversial [4,6,7,11,14 and 15]. Also, annealing PSi in vacuum results in an increased skeleton size. Consequently, both the skeleton size increase and the chemical-state change in the PS layer surface should be considered in explaining the cause of PL degradation upon annealing in vacuum. In this paper, we present the observation, performed to understand the PL degradation, of a skeleton size change of the PS layer and the oxide-state change upon annealing up to 550°c, where PL quenched completely. We used an atomic force microscopy (AFM), a scanning electron microscopy (SEM), and X-ray photoemission spectroscopy (XPS). The results show that the change in the sub-oxide intensity is not related to the PL degradation consistently up to 550°c annealing, even though the surface oxide-state changes may affect the PL efficiency. The skeleton-size increase, about a 5 ~ 10 times increase from the initial skeleton size, accompanied by surface reconfiguration at high temperatures is thought to be the main cause of the irrecoverable PL degradation[16, 17, 18, and 19].

Experimental Procedures

Photo luminescent porous silicon was fabricated by anodizing a boron-doped p-type <100>Si wafer (resistivity: 3.5 Ω.cm) in a 29 % HF-ethanol solution. Then, the anodized Si was rinsed with de-ionized water and carefully dried in a mild air blow. Two kinds of PS were investigated; the as prepared sample was fabricated for 60min at a 20mA/cm^2 current density, and annealed sample, these different rapid thermal annealing (RTA) temperature. The thicknesses of the PS layers, measured by using an optical microscope and a scanning electron microscope, (FIELD EMMISION SCANNING ELECTRON MICROSCOPE) (FESEM) type GEMINR-SUPRA™ 40 VP. SEM measurements were carries out in the school of physics /Nano – Sci Tech center Institute of Science University Technology MARA (UiTM) 40450 shah Alam, Selangor Malaysia. The PL was produced by a CW 400mW He-Cd laser (Liconix 3205N) and was measured with a CCD-equipped spectrometer (Acton 300). The wavelength of the laser was (450 - 900 nm), and the incident angle was 45 degrees. The spectrometer was placed normal to the sample surface.

The RTA process was carried by using 1000W halogen tungsten lamp in vacuum about 10^{-3} *par* at different temperature 450, 600°c and 750°c at annealing time about 15sec. these measurement carried out in Malaysia.

Results and Discussion

The (PL) spectrum show one broad PL peak centered at about 540.9 nm for the as-prepared sample. As shown in Fig.(1) as prepared psi before annealing process and Fig.(2) present (PL) After the annealing process of nanostructures silicon in temperature 450°c, 600°c and 750°c at annealing time 15 sec .The PL spectra of annealed samples show a red shift in peak position from 743.99nm, 747.49nm and 757.37 nm rspectively with incrasing temperature 450°c, 600°c and 750°c respectively.The (PL) of as-prepared sample and annealed samples, showed similar shapes but the intensity of as-prepared sample is higher than the annealed samples. With increasing the temperature of the annealing process the (PL) intensity drop gradually with temperature .The intensity reach to (50%),(39%) and (29%)from its intial value whenthe temperature increase 450°c, 600°c and 750°c rspectively. These results show that in both samples, the strong PL quenched completely after annealing at higher temperatures. Surface morphologies of the PS layers before and after annealing were investigated using an SEM and are shown in Fig.(3). The average skeleton size observed at the surface of the PS layer before annealing was on the order of about 10 nm. The reported crystallite size of the photo luminescent PSi measured with a SEM is typically ~5 nm [2, 20]. In the image, however, few crystallites were observed to have such a size, possibly due to the poor space-resolution of the SEM and possibly because the anodizing had smoothened the crystallite surface. After annealing at 750°c, the skeleton size became (23 ~ 42 Å) and the shape of the skeletons got smoother.

$$E_g^{\bullet} = E_g + \frac{88.34}{L^{(1.37)}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where $E_g^{\bullet}$ (eV) is the energy gap of PSi layer, E_g (eV) is the energy gap of bulk silicon and L (Å) is nanocrystallite size.[2]

These facts indicate that the PSi layer surface reconstructed to form larger skeletons.

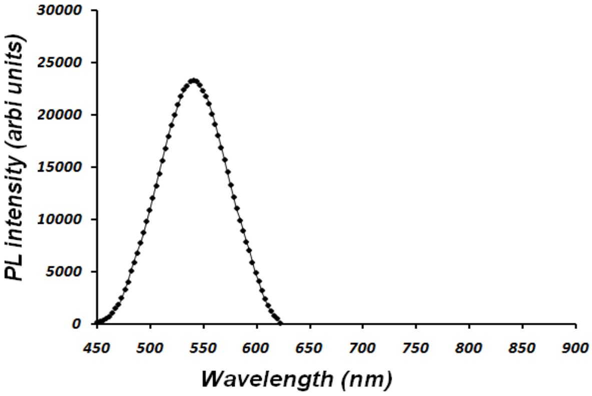

Fig.(1) Photoluminescence spectrum from as prepared porous silicon sample (psi) etching time 60 min and current density 20mA/sm^2.

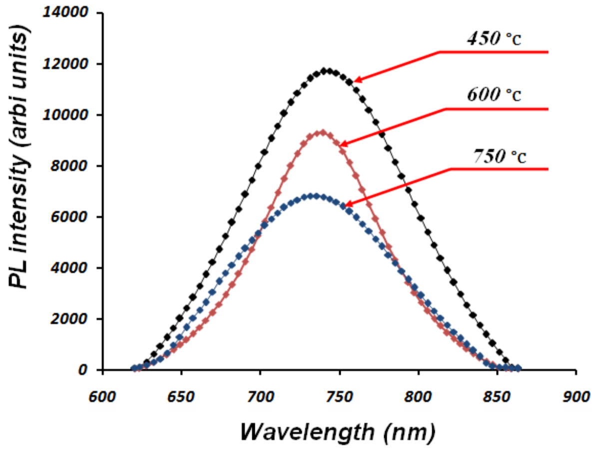

Fig.(2) Photoluminescence spectra from psi samples annealing at 450, 600 °c and 750°c.

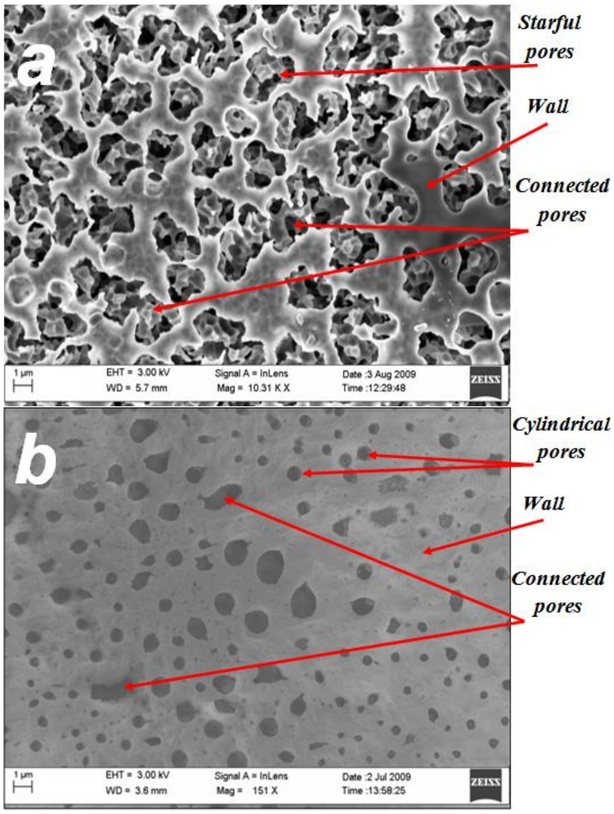

Fig.(3) Show the SEM image of (a) as prepared psi layer at etching time 60 min and (b) annealing at 750°c.

Fig.(3) shows SEM images of sample A before and after annealing. Before annealing, the skeletons in the images show the direction of anodization and have fine skeleton structures. After annealing, the images show smoothened and conglomerated skeletons. Further studies show that the skeleton size increases more or less uniformly in space inside the PS layer, with the skeletons at the top surface of the PS layer being slightly larger, until the skeletons at the top surface stick together. When the top surface-layer skeletons stick together, the skeleton size at the top surface is larger than those inside the PS layer, but the skeleton sizes inside the PS layer are still larger than the ones before annealing. For annealed samples the tendency was the same, except that its porosity was less than that of as-prepared sample the results indicate that the crystallites were smoothened to form larger skeletons. In explaining the PL mechanism, the skeleton size [1, 6, 21, and 22], the surface-oxide states, the dangling bond defects, and the quantum confinements luminescence center's (QCLC) placed at the interface or on the surface of the passivity layer [11,14,15, and 23] were proposed to play an important role in the PL efficiency. It was reported that thermal oxidation or natural oxidation showed better PL [4, 6, 10, and 24]. The results indicated that PL could be improved by increasing oxidation. The PL eventually quenched at 750°*c*. This observation is also contrary to expectation. Therefore, we can rule out the possibility that the density of oxide states is directly related to the PL degradation in this study. The other cause of the PL degradation might be an increase in the density of dangling bond defects (DB), which results in non-radiative recombination sites [4,7 and 11]. It was observed that, after annealing, the DB density increased, but the PL intensity decreased [9, 25]. *Prokes et al*. [25] observed that after annealing at 650°*c*, the DB density increased by a factor of 6-7 whereas the PL intensity dropped by a factor of 70 or more. However, *Bardeleben et al*. [9] observed that after annealing at 550°*c*, the DB density increased by a factor of about 100, but the PL intensity dropped by a factor of about 10. These observations indicate that there is little direct relation between the DB density change and PL degradation/ quenching. In the QCLC model, electron-hole pairs are produced inside the silicon nanocrystallites by the absorbing incident photons, tunnel to the surface luminescence centers, and recombine to produce visible wavelength photons. If visible wavelength photons are to be produced, the nanocrystallites size should be on the scale of nanometers so that the energy gap in the nanocrystallites, as well as the energy gap of the surface states, would be equal to or larger than the energy (~1.7 eV) of the PL peak. However, the observed skeleton size after annealing corresponds to the expected energy gap of ~1.1 eV, which is similar to that of bulk silicon [21, 26, 27, 28 and 29]. The transition and the recombination probabilities would then become similar to that of the bulk silicon where the PL efficiency is negligible compared to that for porous silicon. Therefore, it can be concluded that the skeleton-size increase is more likely the main cause of irrecoverable PL quenching upon annealing in vacuum [30, 31 and 25]. Tsai et al. [8] also mentioned that skeleton-size increase after surface reconstruction *Bardeleben et al*. [9] noticed that the increase in the DB density at 400°*c* is mainly accompanied by hydrogen adsorptions (from the dihydride configuration) at passivated DB sites, with less skeleton size change. Strong thermal hydrogen desorption of the monohydride configuration from the PS layer surface was observed to occur at 500°c [10]. It was mentioned that the surface reconfigures to form larger skeletons after the complete hydrogen desorption in order to lower the surface energy [20]. From these reports, we infer that strong surface reconfiguration occurs with hydrogen desorption, and this results in a larger skeleton-size increase in order to lower the surface energy [32, 33, and 34].

Conclusion

We investigated the photoluminescence (PL) degradation of p-type porous silicon PSi after annealing at different temperature in vacuum. The annealing gave rise to an increase in the skeleton-size. In this study, the skeleton-size increase, rather than the oxide state change, is attributed to irrecoverable PL quenching at higher annealing temperatures.

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