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Optical emission from silicon-based SiO_2 islands fabricated by anodic alumina templates

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We have investigated the photoluminescence spectra of silicon-based nanoscale SiO_2 islands obtained by anodization of silicon-based aluminum membranes in a 0.3m sulfuric acid solution under a constant voltage of 25 V. Two ultraviolet emission bands were observed at 290 and 370 nm. After annealing the samples in 900 °C in O_2, the 290 nm band vanishes, but the 370 nm band still exists. We suggest that the 290 nm band originates from optical transition in the E' centers in the SiO_2 islands according to its annealing behavior. The 370 nm band is considered to be from Al-related luminescence centers, $[AlO_4]^0$, because a decrease of intensity of the 370 nm band is in agreement with that of amount of the Al ion impurities located in the SiO_2 islands. This work shows a clear understanding of the light-emitting mechanism of silicon-based SiO_2 island array. The obtained result can be expected to have important applications in modem optoelectronics. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1767980]

I. INTRODUCTION

In recent years, a kind of Si-based material, Si-based porous anodic alumina (PAA), has attracted increasing interest because of its favorable applications as a template in fabricating Si-based nanostructures and nanomaterials.[1–8] This template can easily be obtained by anodization of Si-based Al membrane. After the Al membrane is completely anodized, anodic process will continue and lead to anodization of the Si-substrate. As a result, a nanoscale SiO_2 island array is formed on the Si substrate.[9] This layer of SiO_2 islands would influence the performance of the devices fabricated by the Si-based PAA templates. However, on the other hand, the SiO_2 islands themselves may widely be used in semiconductor industry such as integration circuit. Thus, further investigations on optical properties of the SiO_2 island array are necessary for the future applications in optoelectronics. In this work, we first fabricate the Si-based nanoscale SiO_2 island arrays and then investigate the corresponding light-emitting properties. Our work shows a clear understanding of the light-emitting mechanism of this kind of Si-based SiO_2 island array and the obtained result can be expected to have important applications in modern optoelectronics.

II. SAMPLES AND EXPERIMENTS

⟨100⟩-oriented *n*-type Si wafers with a resistivity of 5 Ω cm were used as substrates. Al membrane with a thickness of about 800 mm was evaporated onto the Si wafer in vacumm. Prior to evaporation, the Si wafer was rinsed and immersed in a dilute HF solution for 1 min to remove natural oxide. Before anodization, the Si-based Al membrane was annealed at 400 °C in N_2 for 30 min to improve the homogeneity of the Al membrane. Anodization with a platinum plate as a cathode and the Al/Si system as an anode was carried out in a solution of 0.3 M sulfuric acid under a constant dc voltage of 25 V. The electrolyte solution was mechanically stirred during anodic process. To obtain Si-based SiO_2 island array, a real-time-controlled anodic method was employed with the help of anodic *I-t* curve.[8,10] Anodic process lasted for 120 s after the Al membrane was completely anodized. Then, the PAA membrane was entirely removed by immersing the sample in 5 wt % phosphoric acid at 60 °C for more than 5 h. The surface morphology and microstructure of the Si-based SiO_2 islands were characterized using atomic force microscope (AFM, Digital Instruments Nanoscope IIIA) observation and x-ray photoelectron spectroscopy (XPS, ESCALB MK-II). Photoluminescence (PL) spectra were taken on a FluoroMax-2 fluorescence spectrophotometer (Jobin-Yvon Company) with a 150 W Xe lamp as light source. All the measurements were carried out at room temperature.

III. RESULTS AND ANALYSES

Figure 1(a) shows the AFM image of an as-made sample. Nanoscale island array can clearly be observed in the surface of the Si wafer. The SiO_2 island sizes are almost identical, about 40 nm. Figure 1(b) illustrates the Si 2*p* XPS spectrum for the surface of the sample. The peak centered at 103.2 eV corresponds to stoichiometric SiO_2. No peaks from the Si substrate were observed. This is understandable because the SiO_2 islands distribute over whole surface of the substrate, as seen in the AFM image. Therefore, the XPS

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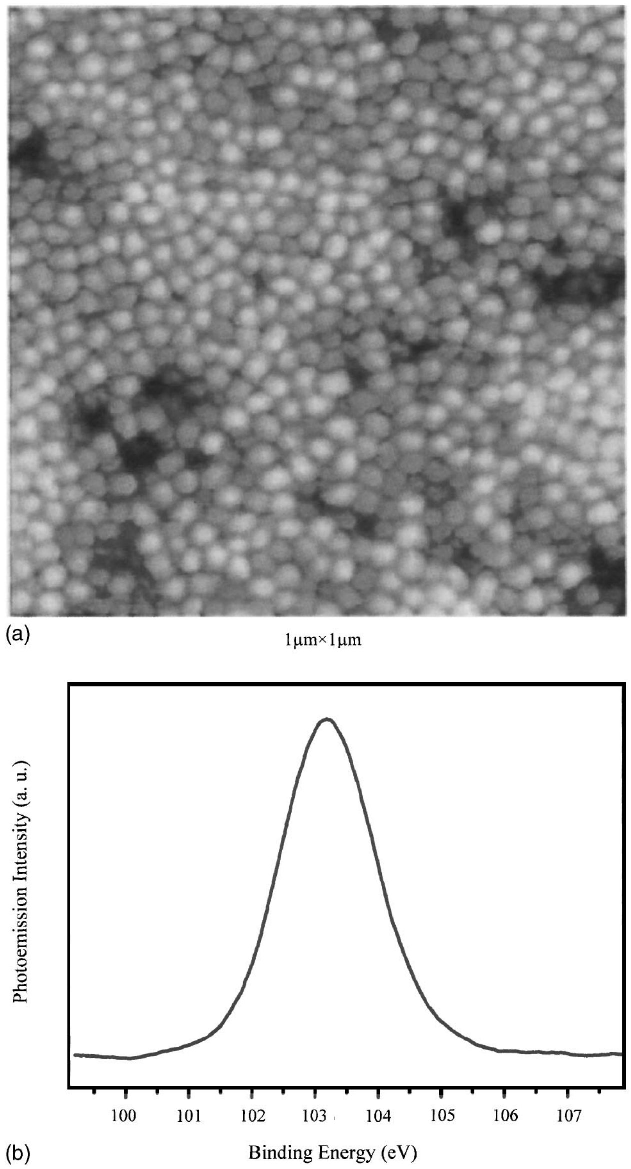

FIG. 1. (a) AFM image of the Si-based nanoscale SiO_2 islands. (b) Si 2*p* XPS spectrum of the surface of the SiO_2 islands.

results clearly show that the islands consist of SiO_2. When anodic process reaches the Al/Si interface, Al is exhausted but the anodization will last.[11] The Si substrate beneath the PAA nanopore channels will be anodized. Hence, the SiO_2 islands appear at each bottom of the PAA channels. Their ordering depends on that of the nanopore arrangement in the PAA membrane. Due to thin thickness of the Si-based Al membrane and resultant short anodic time, the pore ordering is not as good as that in Al-based PAA.[12,13] In our experiments, we further found that the sizes of the SiO_2 islands increase with anodic time. Therefore, we can obtain the Si-based SiO_2 islands with different sizes by setting the anodic voltage and time.

The PL spectra of the Si-based SiO_2 island and array are shown in Fig. 2, taken under excitation with the 220, 230, 240, and 250 nm lines of a Xe lamp. One can see that a broad PL band appears at 370 nm. The band is accompanied with a shoulder band at about 290 nm. The positions of the two bands hardly change with excitation wavelength. This

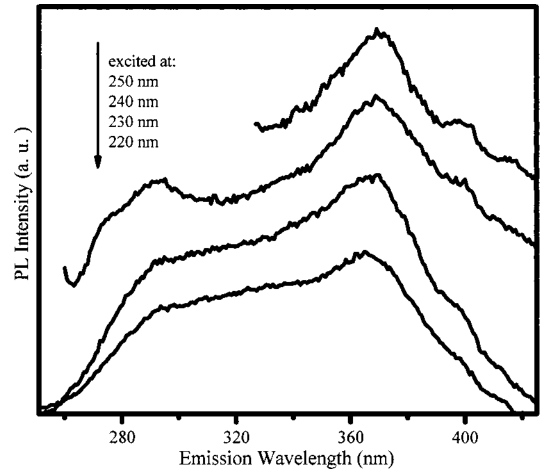

FIG. 2. PL spectra of the Si-based SiO_2 islands, taken under excitation with the 220, 230, 240, and 250 nm lines of a Xe lamp.

result indicates that the PL band is not due to the band-to-band recombination in the quantum confined SiO_2 nanoparticles. The luminescence centers may be impurities/defects related. Anodization of the Si substrate cannot lead to the appearance of the two PL bands. Similarly, anodization of the Si wafer obtained by removing the Al membrane of the annealed Al/Si system cannot also produce such PL bands. So the Si-based PAA plays an important role in producing the light-emitting property of the SiO_2 islands. To clarity the origins of the two ultraviolet PL bands, we investigated their annealing behaviors. We divided the Si-based SiO_2 island samples into two groups. One group was annealed at 500 and 900 °C in O_2 and the other at the same temperatures in N_2. The PL spectra of the two groups of samples are shown in Figs. 3(a) and 3(b). Annealing behaviors of the 370 nm band are identical in O_2 and N_2, showing an obvious decrease with increasing the annealing temperature. However, the shoulder band at 290 nm has different annealing behavior. It vanishes in the sample annealed at 900 °C in O_2 but still exists in the sample annealed at 900 °C in N_2. According to anodic process of Si-based Al membrane,[8,9] the oxygen content in the SiO_2 islands comes from oxygen ion transformation from OH^- in electrolyte solution and then migration into the Si substrate through the barrier layer under a high electric field (vacancy mechanism, similar to the growth of PAA membrane).[14,15] Thus, partial oxygen vacancies will remain in the formed SiO_2 islands and make these islands oxygen deficient. The annealing behavior of the 290 nm PL band suggests that the band is connected with oxygen-deficient defects in the SiO_2 islands. In the previous literature,[16,17] the 4.28 eV (290 nm) band has been observed in SiO_2 thin film and assigned to the radiative recombination in the E' centers, which can be greatly decreased by annealing at 926 °C in O_2 because of the filling of oxygen vacancies during annealing.[17] Based on our experiment results, we believe that the shoulder band at 290 nm should originate in the E' centers.

Due to different annealing behavior, we cannot simply attribute the 370 nm band to optical transition in the E' centers. Previously, Alonso *et al.*[18] reported a 380 nm emission

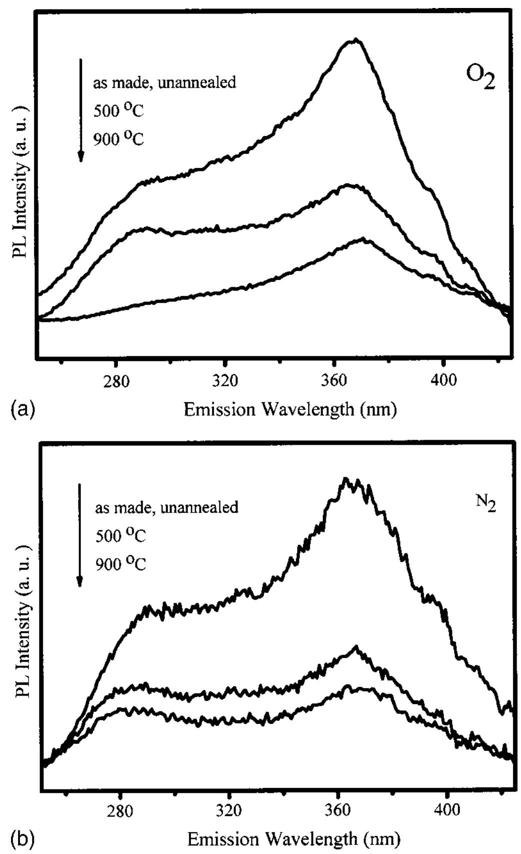

FIG. 3. PL spectra of the Si-based SiO_2 islands unannealed and annealed at 500 and 900 °C in different atmospheres, taken under excitation with the 230 nm line of a Xe lamp: (a) O_2 and (b) N_2.

band in quartz, which was considered to be from Al impurities. Our PL band may have a similar origin in view of the microstructure similarity between the quartz and the SiO_2 islands obtained. When anodic process proceeds to the Al/Si interface, the Si^{4+} ions may drift to the PAA/SiO_2 interface under a high electric field and thus a mixture of Al, Si, and O may come into being near the interface. To check this mechanism, we chemically etched a sample (1×1 cm^2) in a dilute HF aqueous solution of about 0.8 wt % for 4 s to remove partial surface layer. Al amount in the SiO_2 islands was quantitatively determined using inductively coupled plasma analysis (ICP J-A1100). In our experiment, the Al amounts of the as-grown and chemically etched samples were obtained to be 0.95 and 0.27 μg, respectively. The corresponding PL spectra of the two samples are shown in Fig. 4. A notable decrease in intensity can be observed for the chemically etched sample. We found that in the chemically etched sample, the intensity of the 290 nm band is reduced by a factor of about 1/3, while that of the 370 nm band by about 1/4.6. The decrease of the 370 nm band intensity tracks well with that of Al impurities in the etched sample. This provides a good argument that the 370 nm PL band is intimately associated with Al impurities. Al impurities usually exist at the PAA/SiO_2 island interface i.e., the surfaces of the SiO_2 islands and so a large decrease of Al impurities in the etched sample is reasonable.

Many kinds of Al-impurity-related luminescence centers exist in quartz and amorphous SiO_2. In anionic model, an

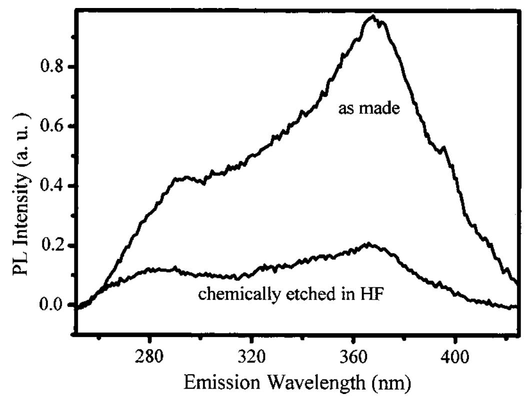

FIG. 4. PL spectra of the Si-based SiO_2 islands before and after chemically etched in dilute HF aqueous solution of about 0.8 wt % for 4 s, taken under excitation with the 230 nm line of a Xe lamp.

Al^{3+} ion replaces a Si^{4+} ion. The resulting charge imbalance is usually neutralized by an alkali metal ion M^+ or a hydrogen ion H^+. These neutral complexes are indicated, respectively, with $[AlO_4/M]^0$ or $[AlO_4/H]^0$.[19] Hole h^+ can also be trapped to form $[AlO_4]^0$ center, which is the most prominent impurity center in SiO_2. The $[AlO_4/M]^0$ or $[AlO_4/H]^0$ centers are not so stable under irradiation,[19] or high temperature annealing.[20] In our annealing experiments, they will transfer to the $[AlO_4]^0$ centers.[20] Since the 370 nm band can still be observed in the samples annealed at 900 °C in O_2 and N_2, the corresponding luminescence centers in the SiO_2 islands should be thermally stable. The $[AlO_4]^0$ centers meet this condition and therefore are the most promising candidate for the 370 nm PL band origin.

According to the above analyses, we can attribute the 290 and 370 nm bands to optical transitions in defect and impurity centers in the SiO_2 islands, respectively. Obviously, change of the sizes of the PAA channels or SiO_2 islands will not influence the peak positions of the two ultraviolet PL bands, but the peak intensities can be strengthened by increasing the concentration of related luminescent centers in the SiO_2 islands. Since the luminescence centers are mainly localized at the bottoms of PAA channels, that is, at the surfaces of SiO_2 islands, an increase of the porosity of the PAA membrane will increase the SiO_2 island area. This correspondingly increases total amount of the luminescence centers. Therefore, we may control the PL intensities by selecting various anodic conditions to obtain the Si-based PAA membranes with different porosities. Further work in this aspect is currently in progress.

IV. CONCLUSION

We have fabricated the Si-based nanoscale SiO_2 islands by anodizing the Si-based Al membrane in 0.3 M sulfuric acid under a constant dc voltage of 25 V. Two ultraviolet emission bands centered at 290 and 370 nm were observed. Based on annealing behavior of the 290 nm PL band, we have suggested that the E' centers in the SiO_2 island matrix are responsible for this luminescence band. Since the decrease of the 370 nm band intensity tracks well with the decrease of Al impurities in the sample partially etched in dilute HF aqueous solution, we have attributed the 370 nm band to optical transition in the $[AlO_4]^0$ centers, which still exist during high-temperature annealing. This work shows a clear understanding of the light-emitting mechanism of Si-based SiO_2 island array.

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