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Nanostructured silicon formations as a result of ionized N$_2$ gas reactions on silicon with native oxide layers

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Nanostructured silicon was formed by means of the ionized N$_2$ gas reaction on SiO$_2$/Si, and the electronic structure, surface morphology, and optical properties were investigated. The physicochemically modified thin layers were resolved to Si$_x$N$_y$ and SiO$_x$N$_y$ through the observation of Si 2$p$, O 1$s$, and N 1$s$ core-level spectra in x-ray photoelectron spectroscopy. The formations of SiO$_x$N$_y$ and SiO$_2$ nanostructures (3–4 nm in size), performed by the etching process followed by adsorption of ionized nitrogen, were confirmed by atomic force microscopy. The nanocrystalline Si (6 nm in size) distributed within the modified layer (approximately 10 nm thick) was observed after the in situ rapid thermal annealing processes, using high-resolution transmission electron microscopy. Photoluminescence with a wavelength peaking at around 400 nm was emitted from the nanocrystalline Si formed from the SiO$_x$N$_y$/SiO$_2$/Si structures. This work suggests that the nanocrystalline-Si formation and the nanostructured surface modification method, using the methods requiring low energy and low temperatures. © 2003 American Institute of Physics.

Recently, many researchers have reported on the potential applications of Si-based devices in optoelectronics.\textsuperscript{1–3} Since the visible photoluminescence (PL) in porous Si (p-Si) was reported at room temperature (RT), many scientists have endeavored to understand the structure, electronic properties, luminescence mechanisms, etc.\textsuperscript{4–6} P-Si can be produced by anodic oxidation of a crystalline silicon anode, typically for visible light emissions. However, the mechanism of light emission from p-Si is not fully understood. Various nanostructures, such as amorphous silicon (a-Si) and nanocrystalline silicon (nc-Si), were also reported for the light-emitting device applications.\textsuperscript{7,8} Plasma-enhanced chemical vapor deposition was utilized mostly in the production of a-Si and nc-Si.\textsuperscript{9} A typical formation mechanism for the nanostructured Si (ns-Si) is based on a self-organized mechanism: The transformation from nonstoichiometric thin layers of Si$_x$ or SiO$_x$/Si into ns-Si embedded in a stoichiometric Si$_x$N$_y$ or SiO$_x$ through the postgrowth thermal annealing processes.\textsuperscript{10} However, the primary flaw in such a formation mechanism is that the size and distribution of ns-Si are difficult to control. Hydrogen atoms that are introduced by ion implantation, plasma, and thermal dissociation of H$_2$ or NH$_3$, etc., can be good candidates for a nanometric control medium.\textsuperscript{11,12}

In this article, a feasible method for the formation of ns-Si using ionized N$_2$ gas reactions on SiO$_2$/Si at RT is reported. Since the ionized gas reaction method is a type of low-energy plasma exposure with no emission of photons, it has many advantages, e.g. easy control, low surface damage, low-temperature process, etc.

The silicon substrates used in this work had Sb-doped (001) orientation with a resistivity of 0.01 Ω cm and were commercial products of Nilaco Corporation. The native oxide layer on Si was cleaned using the Radio Corporation of America process in an air atmosphere. Samples were put into the ultrahigh-vacuum (UHV) chamber (background pressure 1×10$^{-10}$ torr). The vacuum system was composed of an analysis chamber for the x-ray photoelectron spectroscopy (XPS) experiment, and an ion beam treatment chamber for the surface modifications. Samples were exposed to the ionized N$_2$ gas (N$_2$ 99.999%) using an AG5000 cold cathode ion gun of the VG microtech at room temperature. The sample holder was voltage biased to −1 kV. The exposing gas pressure was typically maintained at 4.0×10$^{-6}$ torr. The exposure time varied from 5 to 180 min. The typical sample current density was approximately 0.15 μA/cm$^2$. Typical fabrication yields are high because the process conditions are reliable. Physicochemically modified silicon surfaces were investigated by XPS and atomic force microscopy (AFM). The Si 2$p$, O 1$s$, and N 1$s$ core-level spectra and the binding energy 99.3 eV of Si 2$p_{3/2}$ for the clean silicon were obtained by referencing core-level Au 4$f_{7/2}$. The structural analysis was performed, and the luminescent properties of the ns-Si were determined using high-resolution transmission electron microscopy (HR-TEM) and PL measurement, respectively.

Figures 1(a)–1(c) show Si 2$p$, O 1$s$, and N 1$s$ core-
level spectra for the samples, with ionized N$_2$ gas exposure times ($t_e$) of 30, 60, 120, and 180 min. The peak position of native silicon oxide is marked by an arrow at 102.9 eV, which is at a higher binding energy than the main bulk-Si peak observed at 99.3 eV, as shown in Fig. 1(a). The spectral weight in between the arrow mark and the main peak position increases with increasing $t_e$. In Fig. 1(b), it is apparent that the binding energy of O 1s is 533.0 eV for an as-received sample, and it shifts toward a lower value with increasing $t_e$. It should also be noted that the N 1s core-level spectrum was not apparent before ionized N$_2$ gas exposure. However, the peak intensity of the N 1s core-level was enhanced with increasing $t_e$. The peak position of the O 1s core-level was consistently shifted to a low binding energy and the peak intensity became conspicuous as the $t_e$ increased. The shifts of peak positions were due to the creation of intermediate states such as SiO$_3$N$_y$ and SiN$_x$ between SiO$_2$ and Si. This means that the N 1s core-level spectra have several phases of chemical composition, resulting from the ionized N$_2$ gas exposure onto the SiO$_2$/Si surfaces. In addition, the spectral intensity of the Si 2$p$ core level, denoted by an arrow mark [Fig. 1(a)], increased with $t_e$, also indicating the chemical modification of SiO$_2$/Si surfaces.

Figures 2(a)–2(d) show the AFM surface morphology of the ionized N$_2$ gas-exposed surface at various $t_e$. For the sample at $t_e$ = 30 min, it was found from the AFM data analysis that nanostructures with an average height of 3.7 nm were distributed over the surface. This means that the native SiO$_2$ thin layers were partially etched by ionized N$_2$ gas exposure and transformed into roughened surfaces, i.e., $ns$-SiO$_2$. The chemical reaction should be as follows:

$$\text{SiO}_2(\text{layer}) + N^+_2 \rightarrow ns$-SiO$_2 + NO^\uparrow.$$  \hspace{1cm} (1)

At 30$\leq t_e \leq$60 min, the root-mean-square (rms) roughness decreases abruptly due to both etching and adsorption processes. However, for the sample of $t_e \geq 60$ min, the rms roughness is diminished as the $t_e$ increases. On the basis of XPS analysis, it can be confirmed that the adsorption of ionized nitrogen results in the $ns$-SiO$_2$ surface being covered with Si$_3$N$_4$ and SiO$_y$N$_z$ compounds through the following chemical reactions:

$$\text{Si} + N^+_2 \rightarrow \text{Si}_3\text{N}_4 + \text{Si},$$ \hspace{1cm} (2)

$$ns$-SiO$_2 + N^+_2 \rightarrow ns$-SiO$_2N_y + ns$-SiN$_x.$ \hspace{1cm} (3)

In particular, the chemical reaction (2) is normally observed on the clean Si surface under ionized nitrogen exposure, resulting in the preferable formation of Si$_3$N$_4$ islands. In Fig. 2(e), the average rms of the morphology is summarized as a function of the exposing time $t_e$. In the range of the dominant etching process (i.e., 0$\leq t_e \leq$40 min), the maximum roughness of $ns$-SiO$_2$ is approximately 3.7 nm corresponding to the thickness of the native SiO$_2$ layer on a Si substrate. The adsorption process is not initiated until the clean Si surface begins to appear due to the removal of the SiO$_2$ layer from Si at around $t_e$ = 40 min. Following this, the abrupt chemical reaction to form nitride compounds such as SiN$_x$, SiO$_y$N$_z$, and Si$_3$N$_4$ occurs with increasing $t_e$. Thus, it is proposed that the physicochemically modified structures are
mainly composed of $n$-SiO$_2$/$n$-SiO$_2$/Si as illustrated in Fig. 2(f). It should also be noted in this process that the SiO$_2$ and SiN$_x$ compounds are formed at a nanometer scale, due to the formation of $n$-SiO$_2$ at the initial stage of the chemical etching reactions. Thus, it is suggested that the ionized N$_2$ gas exposure is a simple, reproducible, and low-temperature process for fabricating the $n$-SiO$_2$/Si structures, which differ from the common methods, such as chemical vapor deposition or sputtering techniques, that have been used for the formation of those structures.

A sample of $t_a = 180$ min was adopted for the PL measurements. Figure 3(a) shows the PL spectra taken from the as-prepared sample and the rapid thermal annealed samples in an UHV chamber at 1000 °C for 1 min. In addition, 2–3 nm thick SiO$_2$ cap layers on top of the $n$-SiO$_2$/$n$-SiO$_2$/Si structure were prepared and annealed under the same conditions, for comparative purposes. As shown in Fig. 3(a), RT-PL peaking at a wavelength of around 400 nm was obtained in the annealed samples, whereas no emission peak was observed in the as-prepared sample. Although the luminescent intensity is not as strong due to the single layer structure, the emission peak is clearly seen after the rapid thermal annealing (RTA) processes. Moreover, the higher PL intensity is observed for the SiO$_2$-capped sample. Better confinement of carriers is expected to enhance the PL efficiency for the SiO$_2$-capped sample. This reflects the fact that the PL spectra are related to the creation of $n$-Si from the $n$-SiO$_2$/Si structures through the RTA processes. No other chemical bonding states related to the PL spectra can be reasonably ruled out because all of the processes were performed in situ in the UHV chamber. Therefore, the RTA process performed in the UHV chamber results in the formation of $n$-Si from the physicochemically modified $n$-SiO$_2$/Si structures, affecting the appearance of PL spectra.

In order to confirm the formation of $n$-Si, a HR-TEM image of the plane view of the annealed sample was taken, as shown in the inset in Fig. 3(a). As expected from the AFM and PL measurements, the distribution of $n$-Si was observed for all areas on the sample. The areal density of $n$-Si is $4.6 \times 10^{12}$ cm$^{-2}$ with an average size of 6 nm. Figure 3(a) also shows an enlarged view of a local $n$-Si region. The cross-sectional HR-TEM is provided in Fig. 3(b), indicating that the nearly single layer structure of $n$-Si was formed in between nanostructures such as SiO$_2$ and SiO$_2$. The typical height of nanostructures were found to be less than approximately 5 nm which is in good agreement with the results of AFM measurement. It can be confirmed from the HR-TEM measurement that the nanostructures played a role of barrier against the random formation of $n$-Si during the RTA processes.

In summary, the structure of $n$-Si has been fabricated from in situ etching and adsorption processes on SiO$_2$/Si, using ionized nitrogen gas exposure at RT. The chemical reactions on the surface were monitored and analyzed quantitatively in situ by XPS. Both the etching process for $n$-SiO$_2$/Si and the adsorption for $n$-SiO$_2$/Si followed by in situ RTA, were the main procedures for the formation of a single layer structure of $n$-Si. A typical $n$-Si size of 6 nm and an areal density of $4.6 \times 10^{12}$ cm$^{-2}$ were obtained in a thin layer (10 nm in thickness), resulting in a PL peak of around 400 nm. It is, therefore, suggested that the present method can be applied to nanostructure formation using a low-energy and low-temperature process suitable for nanodevice applications.

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