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Atomic-layer doping in Si by alternately supplied NH_3 and SiH_4

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Low-temperature Si growth on the atomic-layer order nitrided Si(100) surface with N amount of $1-6\times10^{14}$ cm^{-2} formed by NH_3 reaction at 400 °C were investigated using an ultraclean low-pressure chemical vapor deposition system. The epitaxial growth of Si film on the nitrided Si(100) with the initial N amount as high as about 3×10^{14} cm^{-2} is realized at 500 °C, although the film becomes amorphous in the case at the initial surface N amount of 6×10^{14} cm^{-2}. By the analysis of the x-ray photoelectron spectroscopy, it is observed that the surface structure of the atomic-layer order nitrided Si(100) is changed into Si_3N_4 structure by the increase of the surface N amount. It is suggested that the crystallinity of Si film deposited on the atomic-layer order nitrided Si(100) is degraded by the existence of Si_3N_4 structure. Depth profile of N atomic-layer doped Si film clearly shows that most of the N atoms are confined within about 1-nm-thick region. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1576910]

Atomically controlled processing such as atomic layer-by-layer growth[1,2] becomes increasingly attractive for creating functional nanostructures and superlattice structures in Si-based semiconductor devices. High-concentration N doping in Si changes the energy band structure of Si[3] N delta doped Si is expected to be applied to the Si-based epitaxial tunneling structure. In our previous works,[4,5] atomic-layer order NH_3 reaction on Si(100) and possibility of subsequent Si epitaxy at low temperatures were demonstrated in an ultraclean low-pressure chemical vapor deposition (CVD). In this work, the relationship among the N amount on atomic-layer order nitrided Si(100), the surface structure and the crystallinity of Si film deposited on the nitrided Si(100) has been investigated in order to clarify the epitaxial growth condition of N delta doped Si film.

The ultraclean hot-wall low-pressure CVD system, which have been described previously,[6] was used for nitridation on Si(100) and subsequent deposition of Si. The substrates used were *p*-type Si(100) wafers of 2–20 Ω cm with a mirror-polished surface. The wafers were cleaned in three cycles in a 4:1 solution of H_2SO_4 and H_2O_2, rinsed with high purity de-ionized water, dipped into a 2% HF solution followed by de-ionized water, and were loaded to the reactor. In order to prepare an atomically flat and contamination-free Si(100) surface, a 6.5-nm-thick Si buffer layer is grown in the SiH_4 pressure of 25 Pa at 500 °C before the nitridation. Atomic-layer order nitridation of the Si(100) was performed in the NH_3 pressure of 500 Pa at 400 °C.[7] After the nitridation, the residual NH_3 was reduced by purging H_2 gas in the reactor and then capping Si growth is carried out in the pressure of 25 Pa at 500 °C.

The surface structure and the crystallinity of the deposited film were evaluated by reflection high-energy electron diffraction (RHEED). The nanometer order deposited film thickness after removing the patterned SiO_2 films and the surface roughness on Si(100) were measured by atomic-force microscope (AFM). The binding energy and the surface N amount were estimated by x-ray photoelectron spectroscopy (XPS) with the take-off angle of 90°. The depth profile of the N concentration in N atomic-layer doped Si film was characterized by combination of XPS measurement and wet chemical etching of subnanometer-thick Si layer. The etched thickness x is obtained from AFM measurement. Then, the average N concentration (n_N) in the depth region of $x_i \leqslant x \leqslant x_{i+1}$ can be calculated by the following equation with taking the photoelectron escape depth in Si into consideration:

$$n_N(x_i \leqslant x \leqslant x_{i+1}) = \frac{I(x_i) - I(x_{i+1})\exp\left(-\frac{x_{i+1}-x_i}{\lambda}\right)}{\beta\lambda\left[1-\exp\left(-\frac{x_{i+1}-x_i}{\lambda}\right)\right]} \quad (cm^{-3}), \tag{1}$$

where $I(x)$ is the total intensity of N 1*s* measured at the etched thickness of x, λ, is the photoelectron escape depth in Si, β is the overall conversion factor calibrated by standard atomic-layer order nitrided sample, $I(x_i)$ and x_i are for ith cycle.

RHEED patterns for the deposited Si film surfaces are shown in Fig. 1. 2×1 streak and Kikuchi lines originated from a flat epitaxial Si(100) are clearly observed even in the case of the initial surface N amount as high as 3×10^{14} cm^{-2} [Fig. 1(a)]. The 1×1 streak is weakly observed in the case at the N amount of 4×10^{14} cm^{-2} [Fig. 1(b)]. In the case at the N amount of 5×10^{14} cm^{-2}, the spot pattern is weakly observed [Fig. 1(c)]. The halo patterns are observed in the case at the N amount of 6×10^{14} cm^{-2} [Fig. 1(d)], and it is found that amorphous Si grew. From these results, it is suggested that the crystallinity of the Si film deposited on the atomic-layer order nitrided Si(100) is degraded by the increase of the N amount larger than 3×10^{14} cm^{-2}.

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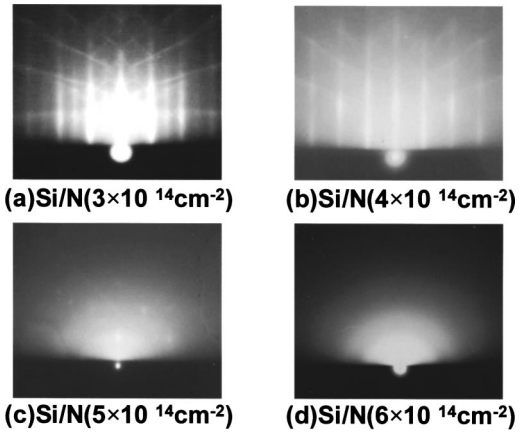

FIG. 1. RHEED patterns taken from the [011] azimuth for the N atomic-layer order doped Si film on Si(100). The capping Si thickness is about 3 nm. Before the capping Si growth, the initial surface N amount on the Si surface is (a) 3×10^{14} cm^{-2}, (b) 4×10^{14} cm^{-2}, (c) 5×10^{14} cm^{-2}, and (d) 6×10^{14} cm^{-2}.

The XPS spectra of N 1*s* for the atomic-layer order nitrided Si(100) is shown in Fig. 2. In the case of low N amount below 3×10^{14} cm^{-2}, N 1*s* peak of 397.0 eV is dominant compared to that of 397.4 eV. However, in the case of high N amount of 6×10^{14} cm^{-2}, N 1*s* peak of 397.4 eV corresponding to Si_3N_4 structure is dominant. Therefore, it is considered that the crystallinity of Si film grown on the atomic-layer order nitrided Si(100) is degraded [Figs. 1(b)–1(d)] by the existence of Si_3N_4 structure.

The SiH_4 exposure time dependence of the capping Si thickness deposited on the atomic-layer order nitrided Si(100) at 500 °C is shown in Fig. 3. It is found that an incubation time increases with increasing the initial N amount on the surface. Therefore, it is expected that the incubation time is caused by lowering of SiH_4 adsorption and/or reaction rates at the nitrided site than that at the pure Si site at the surface. The deposition rate after the incubation time on the surface with N amount below 3×10^{14} cm^{-2} is almost the same as that of the Si epitaxial growth without

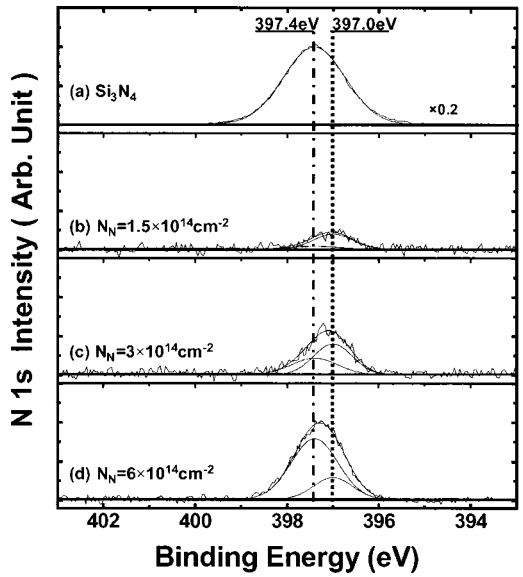

FIG. 2. N 1*s* spectra as a function of atomic-layer order nitrided Si(100). Two N 1*s* peaks at 397.4 and 397.0 eV are also shown.

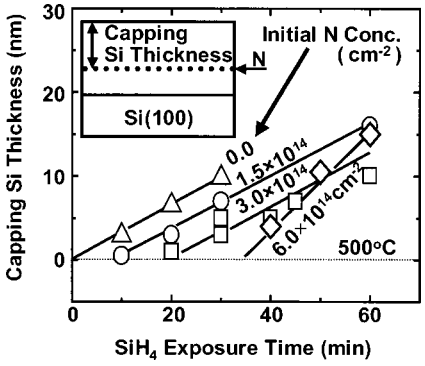

FIG. 3. The capping Si thickness as a function of SiH_4 exposure time at 500 °C on the nitrided Si(100). The SiH_4 pressure is 25 Pa.

nitridation. On the other hand, the deposition rate of amorphous Si on the surface with the N amount of 6×10^{14} cm^{-2} is higher than the others. This result may be caused by the change of surface structure as well as the increase of the surface area, because the surface roughness (2 nm) of the film with N amount of 6×10^{14} cm^{-2} was larger than that (0.1 nm) of 3×10^{14} cm^{-2}. From these results, it is suggested that epitaxial growth at pure Si site gets over the nitrided site on the surface with N amount below 3×10^{14} cm^{-2}.

Depth profile of the N delta-doped Si is shown in Fig. 4. It is found that most of the N atoms are confined within 1 nm depth region at depth of 5 nm. The highest average concentration of N in the doped region is as high as about 5×10^{21} cm^{-3}. Here, measurement accuracy for N concentrations is about 3×10^{20} cm^{-3}. Within such accuracy, the total amount of N atoms in the N doped region was in good agreement with that of the as-nitrided surface. Therefore, in the present Si growth condition, N desorption and segregation during the capping Si growth may be suppressed. On the other hand, thinning the capping Si thickness below 1 nm for N doped epitaxial Si film with the N amount of 3×10^{14} cm^{-2}, N 1*s* spectrum was measured. N 1*s* peak of 396.4 eV was mainly observed. Even after the heat treatment at 750 °C, the binding energy of N 1*s* in the Si did not

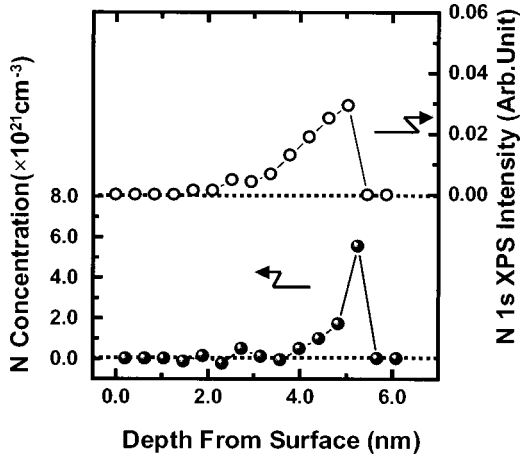

FIG. 4. Depth dependence of the N 1*s* intensity measured by XPS and the depth profile of the N concentration for the N atomic-layer order doped Si film with the N amount of 3×10^{14} cm^{-2}. The concentration is calculated using Eq. (1). The total N amount for N atomic-layer order doped region is estimated about 3×10^{14} cm^{-2}.

change.[8] Additionally, the diffusion coefficient (2×10^{-19} cm^2/s) of N in the Si[8] was lower than that (5×10^{-11} cm^2/s) of the N–N pair site.[9] The diffusion coefficient (6×10^{-17} cm^2/s) of substitutional N in Si was reported for the N ion implanted sample with damage.[10] The value without damage can be lower than the reported value. Therefore, it is considered that N atoms mainly occupy substitutional sites in the epitaxial film. In case of the N amount of 6×10^{14} cm^{-2}, the peak was observed at 397.4 eV. This result suggests that N atoms existing with the binding energy of 397.4 eV affect the crystallinity of deposited film.

In conclusion, the formation of N delta doped Si film on Si(100) has been investigated using ultraclean low-pressure LPCVD system. The epitaxial growth of the N atomic-layer order doped Si film with the N amount of 3×10^{14} cm^{-2} was achieved. It is found that most of N atoms are confined within 1 nm thick. It is suggested that the crystallinity of deposited Si film on the atomic-layer order nitrided Si(100) is degraded by the existence of Si_3N_4 structure.

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