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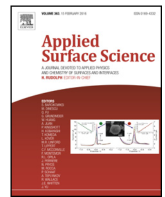

Nitridation of silicon by nitrogen neutral beam

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ABSTRACT

Silicon nitridation was investigated at room temperature using a nitrogen neutral beam (NB) extracted at acceleration voltages of less than 100 V. X-ray photoelectron spectroscopy (XPS) analysis confirmed the formation of a Si_3N_4 layer on a Si (1 0 0) substrate when the acceleration voltage was higher than 20 V. The XPS depth profile indicated that nitrogen diffused to a depth of 36 nm for acceleration voltages of 60 V and higher. The thickness of the silicon nitrided layer increased with the acceleration voltages from 20 V to 60 V. Cross-sectional transmission electron microscopy (TEM) analysis indicated a Si_3N_4 layer thickness of 3.1 nm was obtained at an acceleration voltage of 100 V. Moreover, it was proved that the nitrided silicon layer formed by the nitrogen NB at room temperature was effective as the passivation film in the wet etching process.

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1. Introduction

Silicon nitride is known to be an important material widely used in the semiconductor industry [1–3]. Silicon nitride (SiNx) film is more stable than SiO_2 film as the passivation film of Si nanostructures which can enhance the performance of the electronic device such as solar cell and bio sensor [4–11].

The silicon nitride film was fabricated by various plasma nitriding methods [12–19]. Hino et al. nitrided the silicon surface using an electron cyclotron resonance (ECR) plasma with bias voltage of −1 kV, with process time of 2 h, at substrate temperature of room temperature (RT) [12]. However, it is likely that this silicon nitride film was damaged due to the high energy ion bombardment. To generate the damage-free silicon nitride film, it is necessary to avoid the high energy ion beam irradiation.

Formation of a silicon nitride passivation film at the bottom of silicon nanostructured trenches is intensively required for fabrication of nano devices such as high density memories. However, it has been difficult to form the silicon nitrided film at the bottom of Si nanostructures by the conventional nitriding method and film deposition method. Recently, nitridation of the bottom of the silicon trench pattern bottom with aspect ratio 3 has been achieved by charge-free low energy nitrogen NB at the room temperature [20]. However, the detailed characteristics of the silicon nitridation by the nitrogen NB was not investigated sufficiently.

In the present study, the nitridation of the flat silicon surface using nitrogen NB has been investigated, with acceleration voltage less than 100 eV at room temperature. The characteristics of the nitrided silicon surface were investigated by the contact angle of the water droplet, X-ray photoelectron spectroscopy (XPS) and transmission electron microscope (TEM). Moreover, KOH wet etching characteristics of SiN film formed with NB nitridation were evaluated using the line & space pattern on Si substrate.

2. Experimental details

A schematic diagram of the neutral beam source equipped with a sample holder is shown in Fig. 1. The NB source consists of an inductively coupled plasma (ICP) source with an inner Cu electrode and two molybdenum electrodes. The detail of the NB source and sample setting method were described in the previous paper [20].

A positive potential was applied to the upper electrode against to the lower electrode which was grounded. The plasma potential of ICP was controlled by the potential of the upper electrode. Ions were extracted from the ICP by the potential difference between the two electrodes and injected into the process chamber. Purified nitrogen gas (99.9999%) was fed into the plasma chamber through the gas inlet near the copper electrode. The nitrogen gas flow rate was 34 sccm and the pressure of the process chamber was controlled by a gate valve. The process chamber pressure was set at

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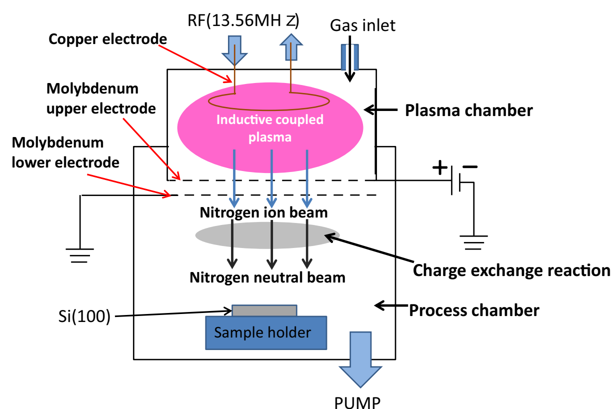

Fig. 1. Schematic of the neutral beam (NB) source equipped with the inductive coupled plasma (ICP) and sample holder.

0.5 Pa, since the nitrogen plasma could not be produced stable in the pressure lower than 0.5 Pa.

The nitrogen ion beam (IB) extracted from the ICP source was neutralized in the process chamber through a charge exchange reaction without energy loss. The flux ratio of nitrogen NB at the sample position is estimated to be 27.6% of the total amount of the extracted nitrogen IB and the generated NB [21].

The input inductively coupled power was 60 W. The acceleration voltage is changed from 20 V to 100 V. The sample for nitridation was Si (1 0 0) substrate. Silicon sample was set at floating potential. As electrons were not in the process chamber, nitrogen ions could not flow steadily into the silicon sample due to charging phenomenon.

Si samples were cleaned in H_2SO_4/H_2O_2 (sulfuric acid and hydrogen peroxide mixture, SPM; 4/1) for 10 min and then in diluted HF (DHF) for 15 min, respectively. In the first process, contaminants on Si surface were removed and oxidation of Si surface was carried out in SPM solution. In the second process, the Si oxide film was removed by 15 min treatment in 1% dilute hydrofluoric acid (DHF) solution. After these processes, Si samples were rinsed with the ultra-purified water and were prepared for the NB nitridation process.

Nitridation of Si surface using the nitrogen NB was investigated at various acceleration voltages. The nitridation time was set at 30 min and the sample was maintained at room temperature during the nitriding process. The hydrophilicity of Si surface was observed by contact angle measurement of water droplet. The surface composition of the nitrided Si sample was analyzed by XPS using monochromatic Mg K_α radiation. Detected energies were corrected in C—C binding energy at 284.5 eV. The cross section of the nitrided Si sample was observed by TEM.

3. Results and discussion

Fig. 2 shows the water contact angle, which indicates hydrophilicity, for Si surfaces prepared with nitrogen NB at various acceleration voltages. These samples were measured within 30 min after NB treatment. The contact angle for the untreated sample was 80°, and it decreased to 28° for the sample treated at the acceleration voltage of 20 V. The contact angle decreased with increasing acceleration voltage until 60 V, above which it became constant at 16°. The hydrophilicity of the Si surface was thus improved by irradiation with the nitrogen NB.

Fig. 3(a) shows high resolution Si 2p XPS spectra for the untreated and NB-treated samples. The untreated sample has a peak for the Si—Si bond at around 99 eV. A new broad peak was detected from 101.5 eV to 104.0 eV for the NB-treated samples, which indicates the formation of SiO_2 and Si_3N_4 at the Si surface. Representative Si_3N_4 peaks were detected in the region from 101.5 eV to 102.1 eV, while SiO_2 peaks were detected in the region from 103.0 to 104.0 eV. The intensity of the Si—Si peaks decreased with increasing acceleration voltage and was 65% of that for the untreated sample when the acceleration voltage was 40 V. In contrast, the intensity of the wide peak for the nitrided samples was constant over the range of acceleration voltage.

Fig. 3(b) shows the high resolution N 1s XPS spectra for the untreated and NB-treated samples. The Si_3N_4 peaks were detected in the region from 397.5 eV to 398.5 eV, while the Si_2=N—O peak was detected at 400 eV [22]. The Si_3N_4 peak intensity increased with acceleration voltage over 60 V. The FWHM of the Si_3N_4 peaks were constant against the increment of the acceleration voltage. The Si_2=N—O peak was observed when the acceleration voltage was 20 V. However, this peak disappeared when the acceleration voltage was higher than 40 V. It is considered that a pure silicon nitride layer can be produced by nitrogen NB with a kinetic energy higher more than 50 eV.

Fig. 4(a) shows high resolution N 1s XPS spectra at various Ar sputtered time for the sample treated with N_2 NB with an acceleration voltage of 100 V. The nitrided Si surface was etched by short-term Ar sputtering and the exposed Si surface was evaluated by XPS. Acceleration voltage of Ar sputtering is 400 V. Approximately 3 nm Si was etched by 10 s Ar sputtering. The Si_3N_4 peak was observed on the NB-treated Si surface. However, this peak was not observed from the 10 s etched Si surface. Instead, a new peak of $SiN_{0.82}$ was detected at 397.1 eV [23], and the intensity of that decreased with increasing depth and disappeared from the 120 s etched Si surface. These results suggest that the thickness of the silicon nitride layer was 36 nm when the acceleration voltage was 100 V. Fig. 4(b) shows the dependence of the silicon nitride layer thickness on the acceleration voltage. The thickness increased with acceleration voltage from 20 to 60 V, and then became saturated at 36 nm for higher acceleration voltages up to 100 V. It is considered

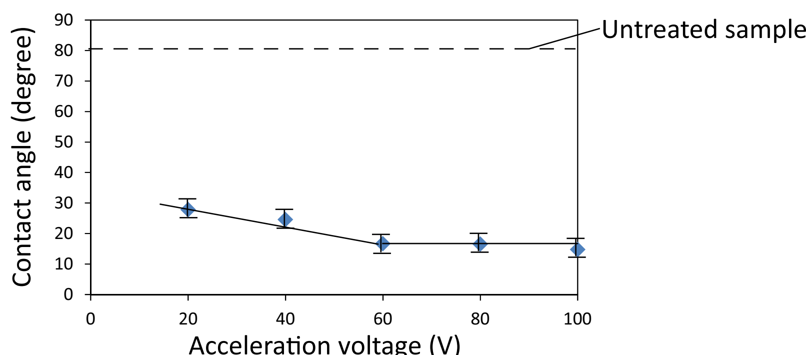

Fig. 2. Acceleration voltage dependence of water contact angle on the silicon surface treated with N_2 NB.

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