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Ultrathin Silicon Oxynitride Layers with a Low Leakage Current Density Formed by Plasma Nitridation Using Low Energy Electron Impact and Chemical Oxidation

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1. Introduction

Under recent rapid down scaling of metal-oxide-semiconductor (MOS) technology, ultrathin dielectric layers with thickness less than 2 nm are required for 0.10 μm design rule. It is well known that in the practical use of ultrathin silicon dioxide layers as gate insulators, the following obstacles arise, i) the penetration of boron from poly-Si gate electrodes, ii) insufficient charge to breakdown voltage, and iii) high density leakage current. Nitrogen-containing dielectrics such as silicon oxynitride and silicon nitride have attracted much attention, since these materials have excellent properties to solve these problems.

We have recently developed a low temperature formation method of silicon oxynitride layers using nitrogen plasma generated by low energy electron impact [1]. This method can form oxynitride layers with a nitrogen concentration, N/(N+O) as high as 29 %, but a density of the leakage current flowing through the layers is considerably high. In the present study, we have succeeded in the formation of ultrathin silicon oxynitride layers with a lower leakage current density by the combination of this nitridation method with a chemical oxidation method.

2. Experimental

n-type Si(100) wafers with a resistivity of 10 ~ 20 Ωcm were cleaned using the RCA method, followed by the immersion in a 5 % hydrofluoric acid solution for 5 min. Then, the wafers were immediately introduced into a vacuum chamber (base pressure of 2×10^{-6} Pa) and exposed to nitrogen plasma generated by low energy electron impact at the nitrogen pressure of 0.5 Pa. The specimen temperature during the nitridation was maintained at 670 °C. The specimen was then oxidized chemically in boiling (113 °C) concentrated nitric acid (HNO_3) for 10 min, followed by annealing in nitrogen at 980 °C for 25 min (*sample #1*). For some nitrided specimens, chemical oxidation was not performed (*sample #2*). Aluminum dots of 0.15 mm diameter were formed on the oxynitride layer, followed by post-metallization annealing in nitrogen at 320 °C for 15 min, resulting in the <Al/oxynitride layer/n-Si(100)> MOS structure. Current-voltage (I-V) and high-frequency (1 MHz) capacitance-voltage (C-V) measurements were performed with an HP 4140B pA meter/DC voltage source and an HP 4192A LF impedance analyzer, respectively. X-ray photoelectron spectroscopy (XPS) spectra were measured using a VG Scientific ESCALAB 220i-XL spectrometer with a monochromatic Al Kα radiation source.

3. Results and Discussion

Electrical Characteristics

The I-V curves for *samples #1* and *#2* are shown in Fig. 1. A leakage current density of *sample #1* is considerably low (2×10^{-1} A/cm^{-2} at a gate voltage of 1.5 V). On the other hand, the leakage current density of *sample #2* is fifty times as much as that of *sample #1*, indicating that the chemical oxidation treatment after the nitridation is important for the reduction in the leakage current density.

From the C-V curves shown in Fig. 2, an equivalent oxide thickness, T_{ox}, for *sample #1* is estimated to be 1.3 nm assuming that the oxynitride layers possess a relative dielectric constant of 2.1 which is the same as that for ultrathin SiO_2 layers [2]. It is clearly seen from Fig. 1 that the oxynitride layers with the 1.3 nm equivalent thickness

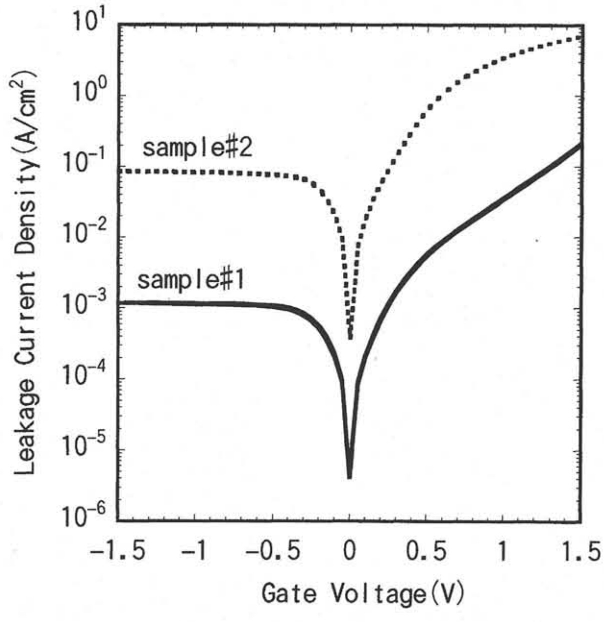

Fig. 1 Current-Voltage (I-V) curves for the <Al/oxynitride/Si(100)> structure: *sample #1* (oxynitride); *sample #2* (oxynitride with no chemical oxidation treatment).

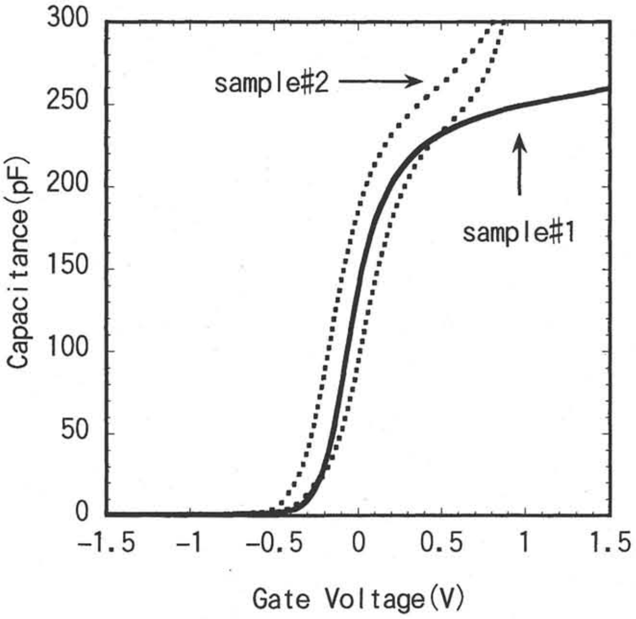

Fig. 2 High frequency capacitance-Voltage (C-V) curves for the <Al/oxynitride/Si(100)> MOS structure. Notations are same in Fig. 1.

possess a leakage current density much lower than that of good quality thermally grown SiO_2 layers of 1.4 nm thickness [3]. Furthermore, the flat band voltage lies around 0 V, showing the absence of fixed charges in the present dielectric layer. The C-V curve of the sample without chemical oxidation treatment (*sample #2*) has hysteresis with the magnitude of 0.2 V, while such hysteresis is not present in the C-V curve for *sample #1*, indicating that densities of slow interface states and mobile ions are low. These results imply that the silicon oxynitride layer formed by use of the low energy electron impact plasma method together with the chemical oxidation method is a promising candidate as an alternative of ultrathin oxide layers.

Nitrogen Concentration and Chemical Species

When the bare Si surface was exposed to nitrogen plasma generated by low energy electron impact for 5 min, an oxynitride layer of ~1 nm thickness was formed on the Si surface. This layer was found to contain 50 % nitrogen, i.e., N/(N+O)=0.5, as shown in Fig. 3a. For this oxynitride layer, a main N 1s peak was observed at 397.9 eV (spectrum a in Fig. 3) and this peak was attributed to oxynitride phase, i.e., nitrogen atom to which three Si atoms are bound. The weak peak at 398.8 eV was attributable to Si_2N-O, i.e., nitrogen atom to which one oxygen and two Si atoms are bound [4].

After immersing the oxynitride layer in HNO_3, the N/(N+O) ratio decreased to 14 %, indicating that the layer was oxidized by HNO_3. The thickness of the layer was increased to 1.7 nm by the oxidation with HNO_3. The

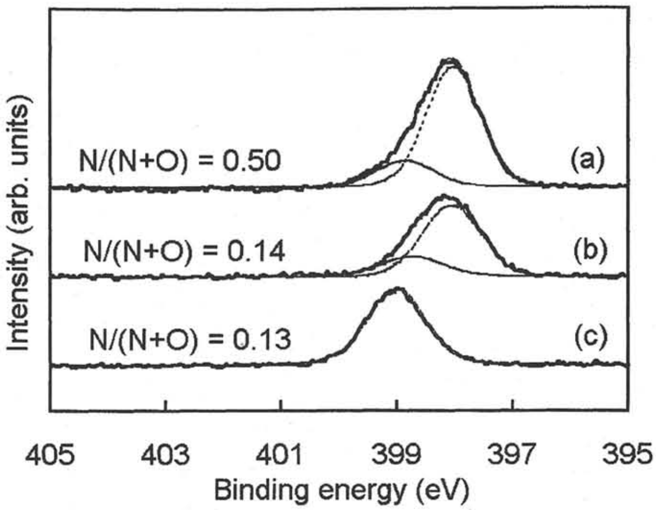

Fig. 3 N 1s energy region of XPS for *sample #1*: (a) as-nitrided; (b) after the chemical oxidation; (c) after the annealing of chemically oxidized specimen.

oxidation hardly shifted the N 1s peaks (spectrum b).

When heat treatment at 980 °C was performed after oxidation with HNO_3 (*sample #1*), the main peak at 397.9 eV completely disappeared, and the intensity of the shoulder peak at 398.8 eV greatly increased (spectrum c). Consequently, the N/(N+O) ratio slightly decreased to 13 %. This nitrogen concentration is much higher than those for oxynitride layers formed by the reaction of Si or SiO_2 with NO or N_2O (less than a few %). The high concentration nitrogen is expected to act as an effective barrier for the boron penetration, and to increase the dielectric constant.

4. Conclusion

We have succeeded in the formation of ultrathin (T_{ox} = 1.3 nm) oxynitride layers with a low leakage current density (i.e., 2×10^{-1} A/cm^2 at the gate voltage of 1.5 V) by the combination of the low energy electron impact plasma method and chemical oxidation process. The formed oxynitride layers possess a nitrogen concentration, N/(N+O) as high as 13.0 % together with a low fixed charge density, low interface state density, and low mobile ion density.

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