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Author(s)	Sato, Hidekazu; Izumi, Akira; Matsumura, Hideki
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Description	

Japan Advanced Institute of Science and Technology

Ultrathin silicon nitride gate dielectrics prepared by catalytic chemical vapor deposition at low temperatures

Hidekazu Sato
FUJITSU Limited, 1500, Mizono, Tadocho, Kuwana-gun, Mie 511-0192, Japan, and JAIST (Japan Advanced Institute of Science and Technology), 1-1 Asahidai, Tatsunokuchi, Ishikawa 923-1292, Japan

Akira Izumi[a] and Hideki Matsumura
JAIST (Japan Advanced Institute of Science and Technology), 1-1 Asahidai, Tatsunokuchi, Ishikawa 923-1292, Japan

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The feasibility of using ultrathin silicon nitride (SiN_x) films, prepared by catalytic chemical vapor deposition (Cat-CVD) method, as an ultrathin gate dielectric is reported. The effects of postdeposition treatments carried out using hydrogen (H_2)-decomposed species or NH_3-decomposed species formed by catalytic cracking of H_2 and NH_3 are also studied. A small hysteresis loop is seen in the $C-V$ curve of as-deposited Cat-CVD SiN_x films. The leakage current in the case of these films with equivalent oxide thickness (EOT) of 3 nm is slightly larger than that in the conventional thermal SiO_2 films of similar EOT. However, it is found that the properties of Cat-CVD SiN_x films are markedly improved by the postdeposition H_2 or NH_3 treatments, that is, the hysteresis loop disappears and the leakage current decreases by three orders of magnitude. © *2000 American Institute of Physics.* [S0003-6951(00)01943-4]

As semiconductor devices are scaled down to submicron dimensions, the conventional processing temperatures of approximately 900 °C will be incompatible with the desired device structure. For example, the conventional high-temperature formation process of gate dielectrics changes the impurity profile formed in the substrate. Thus, the gate dielectric must also be formed at temperatures below 550 °C.[1] Because the dielectric constant of SiN_x is about twofold that of SiO_2, the SiN_x film is one of the candidate films for replacing the SiO_2 gate dielectric.[2] Therefore, the lower growth temperature of SiN_x films is a key for the fabrication of future ultralarge-scale integrated circuits (ULSI).

The catalytic chemical vapor deposition (Cat-CVD) method is a new technique, in which deposition gases are decomposed by catalytic cracking reactions with a heated catalyzer placed near substrates so that SiN_x films are deposited at substrate temperatures of approximately 300 °C without the aid of plasma or photochemical excitation.[3,4] Thus, the surfaces of the substrates and the films do not sustain plasma damage. In effect, we have already succeeded in depositing high-quality SiN_x films as thick as 300 nm as passivation films by this method using a gas mixture of SiH_4 and NH_3.[5] When the flow rate of NH_3 exceeds 50–100 times that of SiH_4, nearly stoichiometric (Si_3N_4) films are formed in which the hydrogen content is as low as a few at. %. Under these conditions, the Si_3N_4 films have adequate insulating properties, that is the resistivity and breakdown electric field are larger than $10^{14}\ \Omega$ cm and several MV/cm, respectively. Additionally, it is known that Cat-CVD is useful not only for film deposition but also for surface modification of semiconductors, such as direct nitridation of Si[6] and GaAs.[7]

In the present letter, the feasibility of using Cat-CVD SiN_x films as ultrathin gate dielectrics for ULSI devices is studied. Particularly, the effects of postdeposition treatments by using the H_2-decomposed species or NH_3-decomposed species formed by catalytic cracking of H_2 and NH_3 are studied.

The Cat-CVD apparatus is schematically illustrated in Fig. 1. A tungsten wire (diameter 0.5 mm ϕ and total length 1300 mm) is used as the catalyzer and placed beneath the substrate at a distance of 40 mm. A catalyzer is coiled, pinned by molybdenum wires and spread parallel to the substrate with an area of 65 mm×70 mm. The deposition chamber (diameter 200 mm, height 200 mm) is made from stainless steel. The sample substrates are attached to a substrate holder which is heated by a heater. A thermocouple is mounted just beside the substrate on the substrate holder to measure the holder temperature (T_h). This includes the effect of thermal radiation from the catalyzer, which is heated electrically. The temperature of the catalyzer (T_{cat}) is estimated by both an electronic infrared thermometer placed outside a quartz window (emissivity is 0.4) and from the temperature dependence of the electric resistivity of the cata-

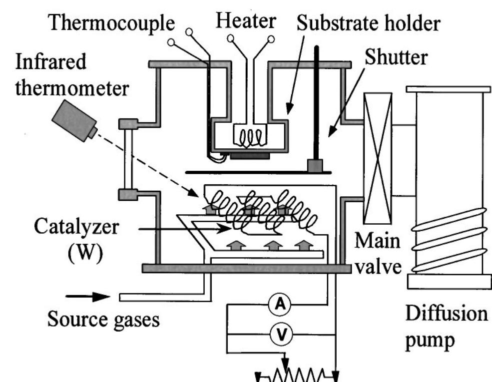

FIG. 1. Schematic diagram of a Cat-CVD apparatus.

[a]Electronic mail: a-izumi@jaist.ac.jp

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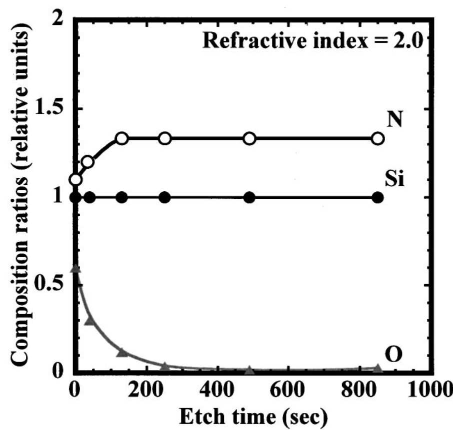

FIG. 2. Distribution of Si, O and N in the depth direction measured by XPS with as-deposited Cat-CVD SiN_x.

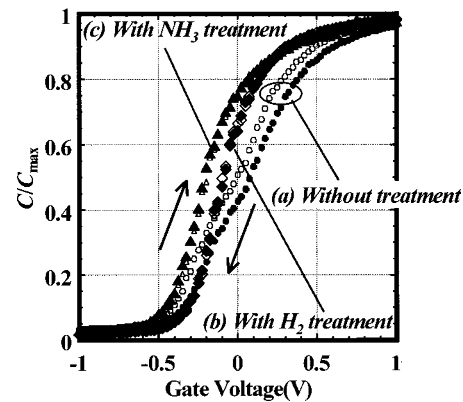

FIG. 3. $C-V$ characteristics with Cat-CVD SiN_x. (a) Without postdeposition treatments, (b) with postdeposition H_2 treatments and (c) with postdeposition NH_3 treatments.

lyzer. The SiH_4 and NH_3 gas mixture is introduced into the chamber from many stainless steel nozzles placed below the catalyzer. These gases were decomposed at the heated catalyzer. The gas pressure (P_g) is measured by an electronic capacitance manometer and it is kept at several mTorr. The chamber is pumped down to about 5.0×10^{-7} Torr by a rotary and an oil diffusion pump before deposition. The chamber pressure during deposition is controlled by the main valve between the diffusion pump and the chamber.

An *n*-type Czochralski (Cz)-Si(100) wafer with a resistivity of 0.85–1.50 Ω cm is degreased and cleaned by the RCA method.[8] Then, it is dipped in 0.5% diluted HF for 0.5 min. After the cleaning, the wafer pieces are immediately loaded into the Cat-CVD chamber. Then, the chamber is evacuated to 5×10^{-7} Torr. The deposition conditions of the SiN_x, the flow rate of SiH_4 gas, FR(SiH_4), and that of NH_3, FR(NH_3), are 1.1 and 60 sccm, respectively. FR(H_2) is kept at 50 sccm when H_2 is used for post SiN_x deposition treatments, and FR(NH_3) is 60 sccm when NH_3 issued. In both the deposition and post SiN_x deposition treatments, T_{cat} and T_h are 1800–1900 °C and 300 °C, and the gas pressures of deposition and postdeposition treatments are 0.01 Torr, respectively.

The electrical properties of the deposition films are evaluated by fabricating a metal-insulator-semiconductor (MIS) (Al/SiN_x/Si) capacitor structure with the electrode area of 3×10^{-2} mm^2. In these samples, no postmetal annealing treatments are performed. The capacitance–voltage ($C-V$) characteristic is measured at the frequency of 1 MHz and with the sweep rate of 0.1 V/s using a SANWA model MI-319A. The leakage current density–voltage ($J-V$) characteristics are measured using a Hewlett-Packard semiconductor parameter analyzer model 4156A. The measurement of the refractive index of SiN_x is carried out by the ellipsometry method using a helium-neon laser of 632.8 nm wavelength. The conditions of SiN_x films are characterized by *ex situ* x-ray photoelectron spectroscopy (XPS) using monochromatic Al $K\alpha$ radiation. The binding energies are calibrated to the adventitious carbon peak at 284.6 eV. Measurements of the depth profile of each atom are carried out using XPS by etching using the argon sputtering.

Figure 2 shows the as-deposited Cat-CVD SiN_x films, the depth profiles of Si, O and N are measured by XPS. The horizontal axis shows the sputter etch time by argon, corresponding to the depth, and the vertical axis shows the composition ratio of N and O in normalizing Si as 1. It is found the composition ratio of Si to N is 1.33 at a certain depth and O is not detected. This means that the stoichiometric SiN_x(Si_3N_4) films are formed. A high density of oxygen that exists at the film surface appears to be caused by adsorption of the atmosphere because the evaluation is carried out by *ex situ* XPS. The refractive index of this film is 2.0.

The $C-V$ characteristics of the Cat-CVD SiN_x films measuring diodes are shown in Fig. 3. A small hysteresis loop is seen in the $C-V$ curve as-deposition sample. However, the hysteresis loop disappears from the $C-V$ curve following the postdeposition H_2 or NH_3 treatments for 60 min. The interface trap density (D_{it}) calculated by the Terman method[9] of the as-deposited sample is $4.2\times10^{12}\,cm^{-2}\,eV^{-1}$. However, the value of D_{it} is reduced to $1.2\times10^{12}\,cm^{-2}\,eV^{-1}$ following the postdeposition H_2 or NH_3 treatments, but is still much larger than that of conventional thermal SiO_2 films. On the other hand, the flatband voltage is shifted to a negative value following the postdeposition NH_3 treatments. We consider that the SiN_x film is nitrided by the postdeposition NH_3 treatments.

The EOT measured using MIS diodes with the Cat-CVD SiN_x films is shown in Fig. 4. The thickness of the SiN_x films measured using an ellipsometer is about 4.3 nm while the

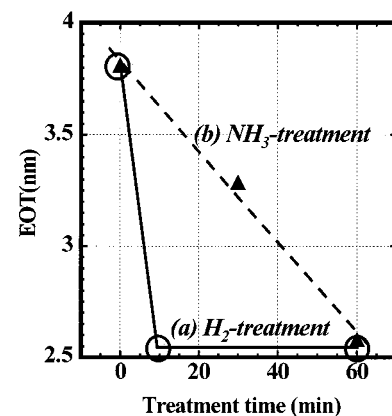

FIG. 4. EOT measured on MIS diodes at different treatment times with Cat-CVD SiN_x. (a) With postdeposition H_2 treatments and (b) with postdeposition NH_3 treatments.

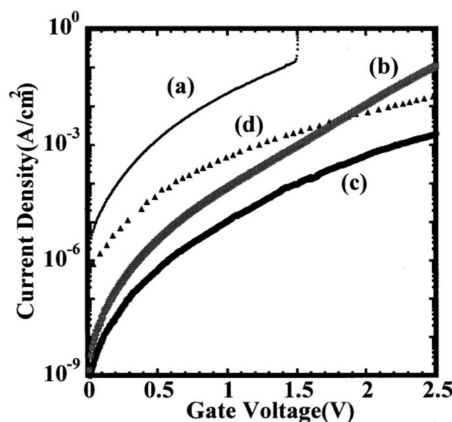

FIG. 5. The $J-V$ characteristics with Cat-CVD SiN_x. (a) Without post-deposition treatments (EOT=2.97 nm), (b) with postdeposition H_2 treatments (EOT=2.91 nm), (c) with postdeposition NH_3 treatments (EOT=2.78 nm) and (d) thermal SiO_2 (EOT=2.8 nm) (see Ref. 10).

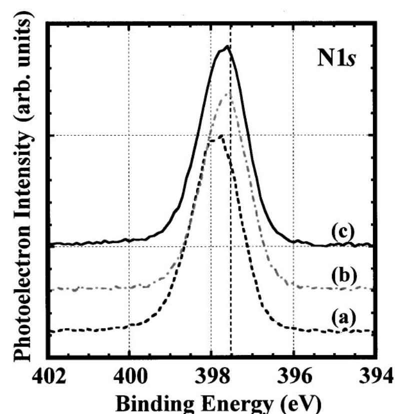

FIG. 6. N 1s XPS spectra from (a) without postdeposition treatments, (b) with postdeposition H_2 treatments and (c) with postdeposition NH_3 treatments.

EOT measured using MIS diodes in the accumulation mode is about 2.5–3.8 nm. The EOT decreases since the dielectric constant of the films is likely to increase following these treatments, but the refractive index remains unchanged.

Figure 5 shows the leakage currents measured for Cat-CVD SiN_x films and for conventional thermal SiO_2 films[10] of about 2.9 nm of EOT. It is found that the leakage currents are significantly decreased following the postdeposition treatments for 60 min. This is also increases the dielectric constant and reduces the trap-assisted tunneling currents. The postdeposition treatments for Cat-CVD SiN_x films reduce the leakage currents by several orders of magnitude compared with that of conventional thermal SiO_2 films of similar EOT.

Figure 6 shows the N 1s XPS spectra measured for Cat-CVD SiN_x films. The postdeposition treatments for 60 min results in the formation of $N\equiv Si_3$ bonds as shown in the spectrum, because the N 1s peak energy (397.5 eV) is the same as that of the conventional thermal CVD Si_3N_4.[11] Without postdeposition treatments, nitrogen atoms may form $N=Si_2$ bonds, since the N 1s peak energy (398.0 eV) is higher than that of the conventional thermal CVD Si_3N_4.[12]

The preparation of high quality ultrathin SiN_x films can be realized at 300 °C using the Cat-CVD system. In particular, the postdeposition treatments of Cat-CVD SiN_x films play a remarkable role in reducing the leakage currents by several orders of magnitude, compared with that of conventional thermal SiO_2 films of similar EOT, and in improving the quality of the films. The results demonstrate that ultrathin Cat-CVD SiN_x films can be used as gate dielectrics for ULSI devices. This technology is highly promising for fabricating future SiN_x gate MIS field effect transistors.

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