Ge metal-insulator-semiconductor structures with Ge$_3$N$_4$ dielectrics by direct nitridation of Ge substrates

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We have fabricated Ge metal-insulator-semiconductor structures with ultrathin pure germanium nitride (Ge$_3$N$_4$) films by the direct nitridation of germanium (Ge) substrates. The plasma-enhanced nitridation technique was used with dc plasma source at low temperatures. Capacitance–voltage characteristics with no hysteresis and capacitance equivalent thickness of 1.23 nm have been achieved. © 2004 American Institute of Physics. [DOI: 10.1063/1.1805194]

A Ge channel metal-oxide-semiconductor field-effect transistor (FET) has been considered as one of promising devices for future high-speed complementary metal-oxide semiconductor (CMOS) technology, because it offers high carrier mobilities for larger drive current and a small band-gap for supply voltage scaling. To make surface channel devices, the formation of gate dielectrics is a challenging issue, because of the lack of stable germanium oxide. The germanium oxide, which is water soluble, hinders the fabrication of Ge CMOS devices under conventional processes. Direct nitridation of Ge can be one of plausible techniques to make dielectrics on Ge with good interface properties. In comparison with Si nitridation, Ge nitridation has been scarcely investigated as yet. Previously, the trials of direct thermal nitridation of Ge substrates have been reported. However, the results have shown that oxygen incorporation in these films was unavoidable, attributed to native oxide and residual oxygen in the reactor. As a result, only germanium oxynitride (GeON) films were obtained. In respect to deposited films, several authors reported on chemical vapor deposition (CVD) of Ge$_3$N$_4$ films on various semiconductors with good electrical properties. On the other hand, direct nitridation can provide a clean, simple, and convenient method for fabricating dense, uniform, and water-insoluble dielectric films on Ge substrates with high thermal stability. In this work, we present a demonstration of pure nitridation of clean Ge substrates using a plasma process at low temperatures and Ge metal-insulator-semiconductor (Ge-MIS) structures with germanium nitride films.

Starting substrates were commercially available (100)-oriented, n-type Ge wafers with a resistivity of 0.1–0.3 Ω cm. Surface cleaning was carried out in a reaction chamber with a UHV system operating at base pressures in the 10$^{-10}$ Torr range. In order to realize the pure nitridation of Ge, we have chosen the plasma-enhanced nitridation technique with dc plasma source, instead of the thermal nitridation, because a clean Ge surface without any incorporation of oxygen is totally inert to NH$_3$ up to 600 °C. The plasma nitridation conditions were as follows: total pressure of 10 m Torr, nitrogen flow rate of 50 sccm, dc power of 45 W, and substrate temperature from room temperature to 300 °C. The surface cleaning of Ge substrate and subsequent nitridation were performed in the same chamber. Ge nitrided films were analyzed by in situ Auger electron spectroscopy, x-ray photoelectron spectroscopy (XPS), transmission electron microscope (TEM), and spectroscopic ellipsometry. Ge-MIS structures with germanium nitride were fabricated to evaluate electrical characteristics by depositing Au films.

Preparation of a clean surface of a Ge substrate is very important for the pure direct nitridation without any incorporation of oxygen or carbon. Figure 1(a) shows the Auger spectrum of a Ge substrate. Oxygen (O$_{KLL}$) and carbon (C$_{KLL}$) transitions at kinetic energies of 276 and 514 eV indicate the existence of chemical oxides and carbon contamination. A two-step cleaning process, out-gassing at low temperatures and subsequent thermal decomposition of chemical oxide at high temperatures in UHV chamber, is necessary to prepare a oxide- and contamination-free clean surface of Ge substrates. Figure 1(b) shows the Auger spectrum of the Ge surface after the thermal cleaning at 600 °C. Both oxygen and carbon were undetectable, confirming that this two-step cleaning process causes thermal desorption of

![Auger spectra](image)

**FIG. 1.** Auger spectra of (a) a Ge substrate, (b) the clean Ge surface after thermal cleaning at 600 °C and (c) the nitrided Ge surface by plasma-enhanced nitridation of the clean Ge surface.
chemical oxides and carbon atoms, leading to the clean Ge surface. The plasma-enhanced nitridation of Ge surface was performed immediately after this cleaning process. Figure 1(c) indicates the existence of nitrogen (N_{3LL}) at kinetic energies of 388 eV on the nitrided Ge surface without any oxygen and carbon, meaning the realization of pure direct nitridation of clean Ge substrates.

XPS analysis was performed for nitrogen chemical states of the nitrided Ge surface using N 1s and Ge 3d core level spectra, as shown in Figs. 2(a) and 2(c). The N 1s component at a binding energy of 397.0 eV, close to that of nitrogen in the Si nitride environment as previously determined, was detected for the nitrided Ge surface. The N 1s spectrum of Si_{3}N_{4} film is also shown as a reference in (b). Figure 1(d) shows the core level spectra of (d) the thermal GeO_{2} and (e) the clean Ge surface after thermal cleaning at 600 °C. N 1s spectrum of Si_{3}N_{4} film is also shown as a reference in (b).

In summary, we have fabricated pure Ge_{3}N_{4} dielectrics by the plasma-enhanced direct nitridation of clean Ge substrates. The high-frequency (1 MHz) C_{g}–V_{g} and J_{g}–V_{g} characteristics of a Au/Ge_{3}N_{4}/Ge MIS structure with are shown in Fig. 4. The C_{g}–V_{g} curve indicates good accumulation and inversion regions. No significant hysteresis and kinks is observed in the bidirectional C_{g}–V_{g} curves, suggesting low surface states and trap states in Ge_{3}N_{4}/Ge interface. From the 3-nm-thick C_{g}–V_{g} data, the capacitance equivalent thickness extracted from the accumulation capacitance is 1.23 nm. The dielectric constant is estimated to be 9.5, which is close to the value of CVD-deposited Ge_{3}N_{4} film. The J_{g}–V_{g} characteristics exhibit normal asymmetrical leakage behavior with respect to the gate bias polarity. The leakage current density, measured under accumulation and inversion condition, are 42 A/cm^{2} at 0.5 V gate bias and 0.15 A/cm^{2} at −0.5 V gate bias, respectively. This large leakage current can be solved by combining with other insulating films such as high-k dielectrics deposited on top of a Ge_{3}N_{4} layer, in addition to the optimization of the film fabrication process.

In summary, we have fabricated pure Ge_{3}N_{4} dielectrics by the plasma-enhanced direct nitridation of clean Ge substrates.
strates. We have demonstrated excellent $C_g - V_g$ characteristics for Au/Ge$_3$N$_4$/Ge MIS structures. Pure direct nitridation of Ge substrate is one of the clean, simple, and convenient methods for fabricating Ge-MIS gate stacks. The pure Ge$_3$N$_4$ films have a possibility to be used as not only a passivation layer but also a diffusion barrier of oxygen and impurities. Therefore, this insulator fabrication technology will open a possible pathway for realizing Ge MISFETs.

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