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Germanium oxynitride gate dielectrics formed by plasma nitridation of ultrathin thermal oxides on Ge(100)

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Germanium oxynitride (GeON) gate dielectrics with surface nitrogen-rich layers were fabricated by plasma nitridation of thermally grown oxides (GeO_2) on Ge(100). Insulating features of ultrathin GeO_2 layers of around 2-nm-thick were found to improve with plasma treatment, in which leakage current was drastically reduced to over four orders of magnitude. Consequently, Au/GeON/Ge capacitors of an equivalent oxide thickness down to 1.7 nm were achieved while keeping sufficient leakage reduction merit. The minimum interface state density values of GeON/Ge structures as low as 3×10^{11} $cm^{-2}\,eV^{-1}$ were obtained for both the lower and upper halves of the bandgap without any postnitridation treatments. These results were discussed based on the effects of plasma nitridation on a degraded GeO_2 surface for recovering its electrical properties by creating stable nitride layers. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3171938]

As the bulk-Si-based metal-insulator-semiconductor (MIS) field effect transistor approaches its physical limitation, novel materials and innovative device structures are highly required for continuous progress in information technology. Germanium (Ge) has attracted tremendous attention as an advanced substrate and channel material due to its higher hole and electron mobility compared with that of Si.[1,2] Various candidate materials for gate dielectrics of Ge-based devices have been investigated in terms of insulating and interface properties. Also, compatibility with integration processes of conventional Si-based devices, such as wet cleaning and thermal treatment, is a key issue that should be addressed for material selection. GeO_2 is known as a fundamental insulator for Ge-MIS devices and also considered as a buffer layer between modern high-permittivity (high-k) dielectrics and Ge substrates. Although electrical and physical properties of a GeO_2 dielectric and a GeO_2/Ge interface have not been fully understood, recent experimental and theoretical studies have indicated good electrical properties of thermally grown GeO_2/Ge interfaces, which exhibits a low interface state density (D_{it}) of less than the mid 10^{11} $cm^{-2}\,eV^{-1}$ without any defect termination techniques.[3–7] However, the intrinsic nature of GeO_2, such as water solubility and poor thermal stability in contact with a Ge substrate, is a serious problem for implementation of high-mobility Ge-based devices. Previously, dielectric and interface qualities at the GeO_2/Ge have been mainly examined for thick oxide layers typically over 10 nm or stacked structures with high-k gate dielectrics, and the scalability of GeO_2 insulators has not been clarified for ultrathin regions down to a thickness of a few nanometers.

Nitrogen incorporation into GeO_2, which causes GeON, has proven to improve its stability against thermal and wet treatments, thus providing distinct advantages in designing device fabrication processes.[8,9] It was also found that nitridation of Ge surfaces prior to high-k film deposition is effective in suppressing Ge diffusion in metal oxides and leads to improved performance of Ge-based devices.[10] Annealing in NH_3 ambient is widely used for surface nitridation and formation of GeON dielectric layers. This method results in nitrogen piling up at the GeON/Ge interface and sometimes deteriorates interface properties. Recently, pure nitrides (Ge_3N_4) formed by nitrogen plasma have shown to exhibit superior physical stability over GeO_2.[11–13] Moreover, the use of nitrogen plasma treatment for gaining carbon-free Ge surfaces owing to selective C–N bond formation and subsequent desorption at low temperatures has been demonstrated.[14]

Based on this research and recent findings on pure Ge oxides and nitrides, we believe that scaled GeON gate dielectrics fabricated using surface nitridation of ultrathin GeO_2 layers by plasma exposure is one of the most reasonable solutions for future Ge-MIS devices. In addition, this method for controlling the nitrogen profile in GeON insulators will provide guidelines for designing high-k/Ge gate stacks. For these purposes, we first studied the basic properties of ultrathin GeO_2 dielectrics grown by thermal oxidation of Ge(100) surfaces and investigated the effects of nitrogen plasma treatment on the electrical properties of Ge-MIS devices.

The starting substrates are commercially available (100)-oriented p-type and n-type Ge wafers with resistivity of $0.1-0.5$ Ω cm. After removing surface-damaged layers by sacrificial oxidation and subsequent wet treatment with 10% HF solution, ultrathin GeO_2 layers were formed by dry oxidation at 550 °C using a conventional furnace. Plasma nitridation of the oxide surfaces was conducted using ultrahigh vacuum-based plasma equipment less than 1×10^{-7} Pa at a substrate temperature of 350 °C.[12,13] Physical characterization of ultrathin oxides and oxynitrides was performed using x-ray photoelectron spectroscopy (XPS) with a monochromated Al $K\alpha$ line. The nitrogen depth profile was also estimated by angle-resolved XPS analysis. Ge-MIS capacitors

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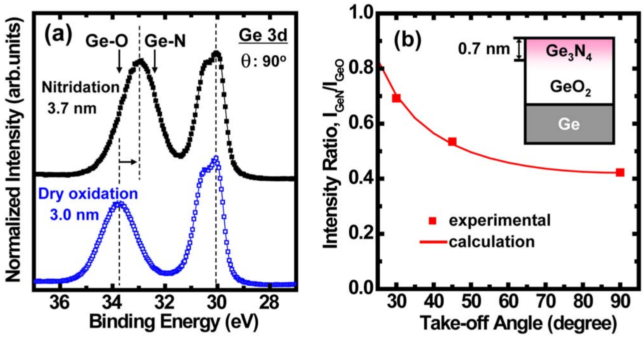

FIG. 1. (Color online) XPS analysis of thermally grown oxide on Ge(100) substrate and oxynitride formed by subsequent plasma nitridation. (a) Ge 3*d* photoelectron spectra taken after oxidation and plasma nitridation. (b) Intensity ratio of Ge–N to Ge–O components (I_{GeN}/I_{GeO}) in Ge 3*d* spectra acquired from oxynitride surface. The intensity ratio estimated at each take-off angle fits well with simple stacked structure consisting of 0.7-nm-thick Ge_3N_4 layer on GeO_2 base-oxide.

were constructed by Au electrode deposition on the oxides or oxynitrides by vacuum evaporation. Capacitance-voltage (*C*-*V*) and current-voltage (*I*-*V*) measurements were conducted at room temperature to study the equivalent oxide thickness (EOT) versus leakage current (J_g) characteristics. A low temperature conductance method was used to evaluate D_{it} of the Au/GeON(GeO_2)/Ge capacitors at a temperature range from 112 K to room temperature.

Figure 1(a) shows the Ge 3*d* photoelectron spectra obtained from the oxide and nitrided surfaces. Thermal oxide on the Ge substrate was formed at 550 °C for 3 min and subsequent plasma nitridation was preformed at 350 °C for 30 min. As indicated by the open square, a chemical shift peak originating from the thermal oxide was observed at a binding energy of around 34 eV. The physical thickness was estimated to be 3.0 nm. After plasma nitridation (see filled squares), the chemical shift peak shifted toward a lower binding energy due to nitrogen incorporation, and the thickness increased 0.7 nm. We also examined the nitrogen depth profile using angle-resolved XPS. The chemical shift peak from the oxynitride was deconvoluted into two components from the Ge–N and Ge–O bonds, and the intensity ratio (I_{GeN}/I_{GeO}) was plotted as a function of the take-off angle [Fig. 1(b)]. The intensity ratio was found to increase with decreasing take-off angle, and these experimental data fit well with a simple stacked structure composed of a 0.7-nm-thick pure nitride layer and a bottom GeO_2 layer, as indicated by the solid line in Fig. 1(b). These results imply that high-density plasma nitridation of GeO_2 surfaces allows us to form an ultrathin Ge_3N_4 capping layer without piling up nitrogen at the interface. Moreover, a slight increase in the physical thickness is attributed to the growth of the bottom oxides (BOs), probably due to residual oxygen during plasma treatment or that emitted by an exchange reaction during nitrogen insertion into the oxide network.

Figures 2(a) and 2(b) show typical *C*-*V* and *I*-*V* curves of Ge-MIS capacitors measured at room temperature, respectively. To understand the scalability of GeO_2 dielectrics, we examined the insulating properties of the oxides for the ultrathin region, in which 2.3- and 3.0-nm-thick oxides were formed on *p*-type Ge(100) substrates by thermal oxidation at 550 °C for 1 and 3 min, respectively. As indicated by the black-filled and open squares, maximum capacitance in *C*-*V* curves was hardly observed because of the large leakage current. The black squares in Fig. 2(c) indicate EOT-J_g plots of the capacitors. The EOT values were extracted from the physical thickness and reported permittivity of GeO_2 (ε=5.5).[3] The poor insulating property of ultrathin oxides indicates difficulties in EOT scaling of pure GeO_2 gate dielectrics. Considering that the GeO_2 layer is highly reactive and vulnerable to humidity and hydrocarbon contamination during air exposure,[12] a possible explanation for the increased leakage current is the deteriorated insulating feature caused by surface reaction with hydroxides and hydrocarbons, as revealed with infrared absorption spectroscopy study.[15]

It is noted that plasma nitridation of ultrathin GeO_2 layers significantly improved the electrical properties of Ge-MIS capacitors, and ideal *C*-*V* curves were obtained from Au/GeON/Ge capacitors. The red open and filled circles in Figs. 2(a) and 2(b) represent improved properties after plasma treatment. The leakage current was drastically suppressed, typically by four to six orders of magnitude, at the small expense of an increase in EOT [see Fig. 2(c)]. When using a thinner oxide (BO: 2.3 nm), the EOT value and average permittivity were estimated to be 1.7 and 6.5 nm, respectively. Since pure Ge_3N_4 dielectrics show higher permittivity than oxides, the increased average permittivity by nitridation is simply attributed to the formation of pure nitrides at the uppermost surface, as we confirmed from angle-resolved XPS analysis. Consequently, although the band off-

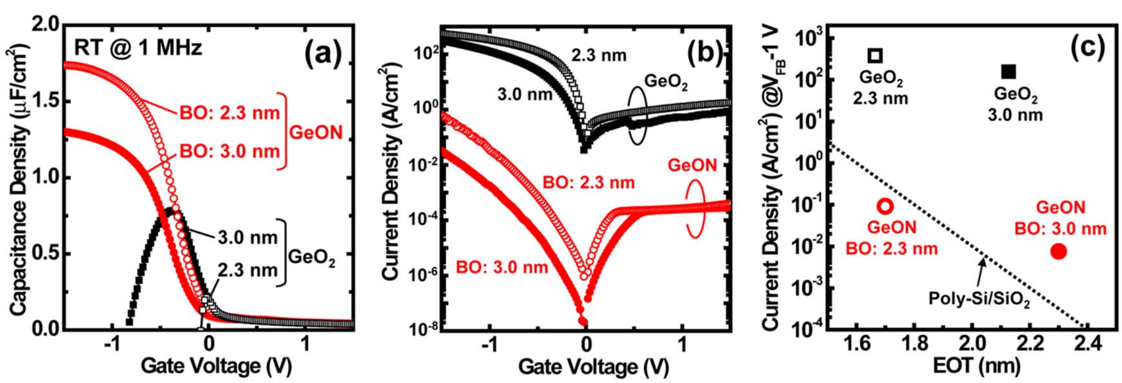

FIG. 2. (Color online) Electrical properties of Au/GeO_2/Ge and Au/GeON/Ge capacitors measured at room temperature. (a) *C*-*V* curves obtained at frequency of 1 MHz. Physical thickness of GeO_2 dielectrics and that of BOs for preparing GeON dielectrics are indicated. (b) *I*-*V* curves obtained from GeO_2 and GeON gate dielectrics. (c) EOT vs J_g plot of capacitors. EOT value of GeO_2 was estimated from physical thickness and reported permittivity of pure oxides, and that of GeON was determined by maximum capacitance in *C*-*V* curves. Typical trend of conventional poly-Si/SiO_2 stacks is also indicated by dotted line.

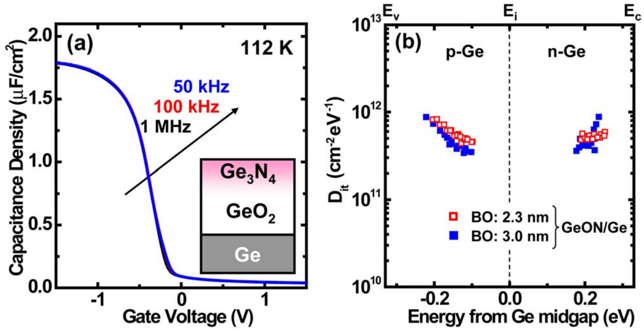

FIG. 3. (Color online) Evaluation of interface quality of GeON/Ge structures. (a) *C-V* curves of Au/GeON/Ge capacitor measured at 112 K. Measured frequency ranged from 50 kHz to 1 MHz. (b) Energy distribution of D_{it} for GeON/Ge structures obtained using low temperature conductance method. Thickness of initial BOs is also indicated.

set of the Ge-MIS stack is smaller than that of the Si-based system, the trend of the EOT-J_g characteristic can be extended to the ultrathin region. A small *C-V* hysteresis of about 70 mV was observed for as-nitrided GeON dielectrics, which could be reduced to less than 10 mV by postnitridation annealing at 500 °C under nitrogen ambient (data not shown).

Figure 3(a) shows the *C-V* characteristics measured at 112 K for Au/GeON/Ge capacitors fabricated by the plasma nitridation of a 2.3-nm-thick GeO_2 layer without any postnitridation treatment. Although a considerable gate leakage current prevents reliable accumulation capacitance under lower frequency conditions, small frequency dispersion was confirmed in the range from 50 kHz to 1 MHz, suggesting that the excellent interface quality at the GeO_2/Ge interface was preserved even after exposure to plasma. The energy distribution of the D_{it} for GeON/Ge stacks was also determined with a low temperature conductance method using *p*-type and *n*-type substrates to examine state density in the lower and upper halves of the bandgap. As shown in Fig. 3(b), the D_{it} distribution follows a symmetric U-shape, and there was no distinct difference in the D_{it} value and its distribution depending on the physical thickness of the BOs. The minimum D_{it} values were estimated to be 3.3×10^{11} and 3.4×10^{11} cm^{-2} eV^{-1} in the lower and upper halves, respectively, which are comparable to those of thermally grown GeO_2/Ge interfaces.[3]

These experimental results clearly demonstrate the effectiveness of plasma nitridation of GeO_2 layers, especially for the ultrathin region. Nitride capping will act as barrier layers to provide flexibility in the device fabrication process. Moreover, considering the physical and electrical characterizations mentioned above, it seems that plasma nitridation effectively converts the degraded uppermost layer on reactive GeO_2 surfaces into highly stable nitride layers, while maintaining superior electrical properties at the bottom interfaces. Therefore, we believe that a GeON gate insulator with nitride capping is the most promising method for obtaining EOT scaling, a high-quality interface, and flexibility in the device-integration process. Moreover, it is concluded that careful attention is required for designing high-*k*/Ge gate stacks because conventional ultrathin GeO_2 layers of less than a few nanometers that are exposed to air will not work as an interface passivation layer. Thus, nitridation and/or oxynitridation of Ge surfaces prior to high-*k* deposition and additional oxide growth at the interface may be a possible method for improving the interface quality of the gate stacks. However, for the latter case, material selection to avoid intermixing between high-*k*/Ge is the key issue. Although further studies are required to understand both exchange reaction between surface contamination and incoming nitrogen atoms and the most suitable atomic configuration at high-*k*/Ge interfaces, our results revealed the intrinsic problem of ultrathin GeO_2 and demonstrated the use of nitrogen incorporation into the oxides by nitrogen plasma treatment.

In summary, we proposed a method for fabricating GeON gate dielectrics with nitride capping layers on thermally grown BOs. Plasma nitridation was found to recover insulation properties of the degraded GeO_2 uppermost layers by forming stable and high-quality nitride layers. As a result, the EOT value was scaled down to 1.7 nm, and leakage current was significantly reduced. The minimum D_{it} value of the GeON/Ge interfaces was estimated as low as 3.3×10^{11} cm^{-2} eV^{-1}, which suggests that excellent interface properties of thermally grown GeO_2/Ge structures were preserved by selective surface nitridation or newly formed by the emitted oxygen. These results clearly demonstrate the use of GeON with nitride capping for the gate dielectric and interface layer for high-*k*/Ge gate stacks.

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