

Gate Stack Integration of Germanium Oxynitride for Germanium MOSFETs

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1. Introduction

Recently, the requirements for high electron and hole mobilities and the advancement in high-k gate dielectrics have made germanium a promising channel material for CMOS devices. Among the many challenges, gate stack integration has been a major hurdle in the realization of germanium MISFETs. Unlike thermal silicon oxide, germanium oxide is hygroscopic and is volatile at high temperatures, making it unsuitable for gate dielectric application. Hymes and Rosenberg have demonstrated germanium oxynitride formed by nitridizing germanium oxide, and the resulting films are less susceptible to moisture than GeO_2 [1]. A reasonable fixed charge ($< 3 \times 10^{10} / \text{cm}^2$) and interface charge density ($< 4 \times 10^{11} / \text{cm}^2$) [2] also make germanium oxynitride an ideal choice as an interfacial layer between the germanium substrate and the high-k gate dielectric. On the other hand, poly-Si electrode which is widely used for Si CMOS processes is not suitable for germanium MISFETs due to the poly depletion effect and its high process temperatures. Metal gate electrodes are therefore necessary. Since there is not much reported research on metal-gate gate stack for Ge MISFETs, in this work, systematical studies on the electrical properties of metal gate electrode/germanium oxynitride/germanium systems and their thermal stability were carried out.

2. Experimental Procedures

MOS capacitors were fabricated on 4" n-type ($3 \times 10^{16} / \text{cm}^3$ Sb) germanium wafers in the (100) orientation. After rinsing in DI water to remove the native oxide, the wafers were thermally oxidized in a RTA furnace at 550°C for 2 to 10 minutes. Immediately following oxidation, rapid thermal nitridation (RTN) was performed at 600°C with 2-min soak time in an ammonia (NH_3) ambient. The germanium oxynitride has refractive index of around 2.3 at 635 nm wavelength, determined by spectrometer measurement. Subsequently, various 100 nm thick metal gate electrodes such as aluminum (Al), tungsten (W), tantalum (Ta), and molybdenum (Mo) were deposited at room temperature using an e-beam evaporator. Some of the samples received a further RTA treatment at 400°C for 3 minutes in order to examine the gate-stack's thermal stability. Finally 500 nm Al were deposited for probing purposes, and the samples were patterned into $200\mu\text{m} \times 200\mu\text{m}$ capacitors for C-V measurement. High resolution transmission electron microscope (HRTEM) was employed to inspect film integrity.

3. Results and Discussions

Comparison of various metal gate electrodes

Illustrated in figure 1 are C-V and I-V characteristics of the capacitors with germanium oxynitride and different metal gate electrodes. The difference in the accumulation capacitance is possibly due to batch variation and various delay time before metal deposition. We have observed that germanium oxynitride tends to yield higher equivalent oxide thickness (EOT) after being exposed to atmosphere. Thus, immediate metal deposition is essential to have a better control of the dielectric thickness. Among the four metals, Ta yields the smallest flat band voltage shift of -0.215 V , compared to the largest of -0.812 V with Al gate electrode. Al samples had the longest waiting time before metal deposition, and the degraded dielectric film might account for this serious flat band voltage shift.

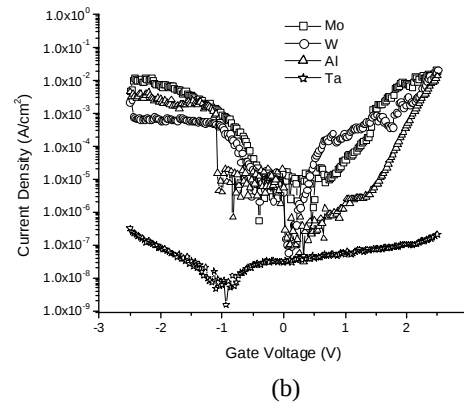
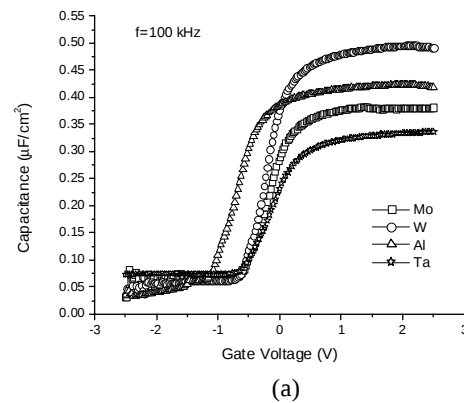


Fig. 1 C-V (a) and I-V (b) characteristics of germanium oxynitride with different metal gate electrodes.

The samples with higher EOT yield lower leakage current as would be expected. If comparison is made to the thermal silicon oxide baseline at each corresponding EOT, tungsten electrode shows a higher reduction in leakage current among these four groups. Nevertheless, germanium oxynitride with high EOT ($> 22\text{\AA}$ for Mo and $> 28\text{\AA}$ for Al) exhibits higher leakage current than thermal silicon oxide, but less leakage current than that of silicon oxide for smaller EOTs, consistent with the observation reported in [3] ($> 25\text{\AA}$ for W).

Thermal stability of molybdenum gate electrode

To realize germanium MISFETs, the proposed gate stack should withstand high temperature ($\sim 400^\circ\text{C}$) annealing without serious degradation. After 400°C 3 minutes RTA, metal peeling was observed for the Ta samples and further evaluation could not proceed. W group showed abnormal C-V curve after annealing. For Al samples, accumulation capacitance goes down by a factor of 5, and XTEM indicated strong interaction between the Al and Ge substrate resulting in a rough interface which inhibits accurate determination of the dielectric film thickness. Mo gate electrode, however, demonstrates a relatively high thermal stability against germanium oxynitride and germanium substrate.

Figure 2 compares the C-V characteristics of annealed and un-annealed Mo samples at different scan frequencies. After RTA, there is a negligible change of accumulation capacitance. The flat band voltage shifts toward the theoretical value, indicating a reduction of fixed charges. We calculated the fixed charge density to be $6 \times 10^{12} / \text{cm}^2$ and further process optimization can minimize this density. The C-V hysteresis increases slightly from 26 to 50 mV at 1 MHz, inferring increase of oxide trapped charges. It is unclear as to whether these trapped charges are from mobile ions or electron injection. Most interestingly, distinctive kinks appeared near inversion in lower frequency C-V curves suggesting increase of interface states after thermal annealing. This observation is contradictory to the common practice in which thermal annealing is believed to reduce interface charges. More in-depth studies on the interface charges are underway using conductance method.

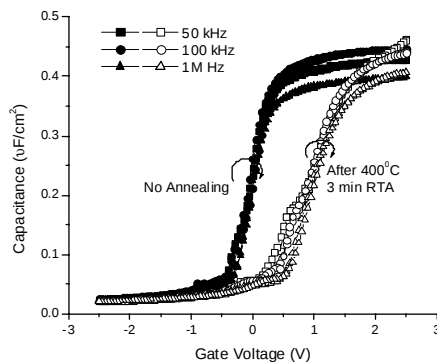


Fig. 2 The C-V characteristics of Mo/germanium oxynitride/Ge MOSCAP before and after 400°C 3 minutes annealing.

Based on the optimistic C-V results, HRTEM were performed on Mo gate electrode samples to inspect the film integrity. The physical thickness of germanium oxynitride was measured and the dielectric constant of germanium oxynitride film is calculated to be 3.9, same as that of thermal silicon oxide. This lower-than-expected value is possibly due to insufficient nitridation. There is no observable change of film integrity for the sample subjected to annealing, as shown in figure 3. The voids in the germanium oxynitride film appear in the un-annealed samples as well. These voids however are artifacts from TEM inspection due to long exposure to the electron beam. The interface roughness increases during longer electron irradiation, as is reported in [4].

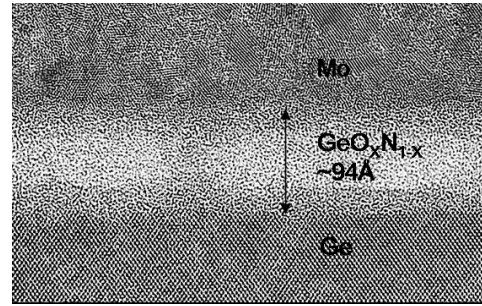


Fig. 3 HRTEM of Mo/germanium oxynitride/Ge gate stack after 400°C 3 minutes RTA.

Molybdenum work function

Mo work function on germanium oxynitride was obtained by C-V measurement with different dielectric thickness, and was found to be 4.08 eV in our study. This value is lower than the reported Mo vacuum work functions ranging from 4.3 to 4.95 eV. [5]

3. Conclusions

Various metal gate electrodes for germanium oxynitride MOSCAPs were investigated. Mo is found to exhibit excellent thermal stability along with reasonable C-V and I-V characteristics, and is a suitable gate electrode metal for germanium MISFETs.

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