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Novel Sn-assisted Nitridation of Ge/HfO_2 Interface and Improved Electrical Properties of This MOS Capacitor

Mei Zhao[1], Renrong Liang[1], Jing Wang[1] and Jun Xu[1]

[1] Tsinghua Univ.
Tsinghua National Laboratory for Information Science and Technology,
Institute of Microelectronics, Tsinghua University, Beijing 100084, China
Phone: +86-010-6279-1272 E-mail: wintersweet.zhao@gmail.com

Abstract

The electrical properties of a Ge/HfO_2 MOS capacitor with an ultrathin GeSnON interlayer were investigated. The GeSn layer was fabricated by a unique processing method: a thick Sn layer was deposited on cleaned Ge substrates, and then the top Sn layer was removed using diluted HCl solution, leaving an approximately 1-nm-thick GeSn layer. The high-quality GeSnON interlayer was formed by annealing a thin GeSn layer in NH_3 ambient at 400℃. The electrical measurement results show that improved capacitance-voltage and leakage current density characteristics were obtained for the Ge/GeSnON/HfO_2 MOS capacitor, with a reduction of interface trap density down to 4.6×10^{11} $cm^{-2}eV^{-1}$. These results indicate effective passivation of the Ge/HfO_2 interface with the implementation of the GeSnON interlayer formed by this original technique.

1. Introduction

Proper passivation of the Ge interface is one of the most challenging issues to be resolved before Ge can be used as a channel material [1]. The nitridation of Ge surfaces prior to high-k film deposition is one of the best-known solutions because it leads to improved performance of Ge-based devices [2-9]. Annealing in NH_3 ambient is widely used for Ge surface nitridation and formation of the GeON interface layer [4-8]. But these methods for introducing nitrogen element always involve high-temperature treatment above 550℃. Recently, GeSnO layer was demonstrated to be a possible passivation interface layer between Ge and high-k layer [10]. Considering the characteristic of GeSnO and especially the higher chemical activity of Sn than Ge, we implement an ultrathin GeSn layer on Ge surface to reduce the temperature for Ge surface nitridation. It is found that the nitridation of Ge/HfO_2 interface was realized at low temperature. The effect of nitridation of Ge/HfO_2 interface by the method was investigated in this study.

2. Experimental

MOS capacitors were fabricated on (100) oriented n-type Ge wafers with a resistivity of 0.09 Ω·cm. After cyclic cleaning between 1:10 HF and DI water, a Sn (~16nm) layer was sputtered on the Ge substrates through magnetron sputtering. The top thick Sn layer was removed by dipping the Ge wafers into diluted HCl (10%) for 3 minutes, leaving an ultrathin GeSn layer on the Ge surface. Then the samples were immediately loaded into an ALD chamber. Prior to high-k deposition, in situ NH_3 annealing was performed at 400℃ for 30 minutes. 5.5-nm-thick HfO_2 was deposited by ALD using TEMAHf precursor and H_2O. Finally, aluminum electrodes were evaporated, patterned, and then etched to form MOS capacitors. Physical characterization of the GeSn oxynitride was performed using X-ray photoelectron spectroscopy (XPS) and cross-sectional high-resolution transmission electron microscopy (HRTEM). Capacitance-voltage (C-V) and leakage current density-voltage (J-V) characteristics were measured at room temperature using an Agilent B1500A Semiconductor Device Analyzer.

3. Results and discussion

As shown in Fig. 1(a), a slight increase in the intensity of the Ge 3d peak at 32.3 eV on both the Ge and GeSn surfaces is caused by the partial oxidation of Ge during annealing [11]. Moreover, the Ge 3d spectrum of the Ge surface with the GeSn layer exhibits a small peak around 26.5 eV due to the presence of Sn 4d. Fig. 1(b) shows the Sn 3d spectrum of the two samples. The Sn peak, which is not visible in the spectrum of the bare Ge samples, can be observed at 497.5 eV for the Ge/GeSn samples. This indicates that, for the Ge/GeSn samples, there are still Sn atoms on the Ge surface after HCl cleaning. Based on XPS data, the Sn and Ge atom concentrations are estimated to be 5.7% and 40.1%, respectively. The main Sn 3d signal presents at a binding energy of 487.5 eV, which implies that the Sn atoms have a Ge-O-Sn bonding configuration near the interface [12]. This also indicates that the Sn atoms are oxidized during annealing. The N 1s component at a binding energy of 399.5 eV can be detected for the nitrided Ge/GeSn surface; this peak cannot be observed for the bare Ge surface, which is also annealed in NH_3 ambient (Fig.1(c)). The nitridation of the surface at low temperature may be attributed to the fact that the introduced Sn element is more chemically active than Ge.

The cross-sectional HRTEM image of the Ge/Sn/HfO_2 stack, as shown in Fig. 2(a), indicates that an approximately 1-nm-thick GeSn layer is generated between the Sn layer and the Ge substrate. Fig. 2(b) shows the HRTEM image of Ge/Sn after HCl cleaning, annealing in NH_3, and HfO_2 deposition, which clearly reveals that an ultrathin interlayer with a thickness of ~1 nm is formed. Based on the XPS analysis described previously, the material of the interlayer

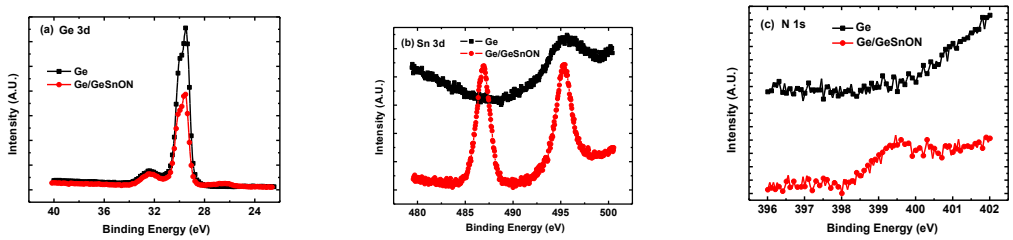

Fig. 1 XPS analyses for Ge and Ge covered with GeSn after HCl cleaning and annealing in NH_3 ambient: (a) Ge 3d spectra; (b) Sn 3d spectra; and (c) N 1s spectra.

is speculated to be GeSnON; this is different from the Ge oxide layer between HfO_2 and Ge, as shown in Fig. 2(c).

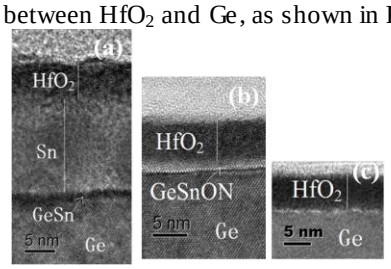

Fig.2 HRTEM images of (a) Ge/Sn/HfO_2/Al gate stack; (b) Ge/GeSnON/HfO_2/Al gate stack; and (c) Ge/HfO_2/Al gate stack.

C-V measurements of Ge/HfO_2/Al (non-nitrided) and Ge/GeSnON/HfO_2/Al (nitrided) MOS capacitors were carried out at 1 MHz at room temperature, as shown in Fig. 3(a). The EOT values increase slightly from about 2.2 nm for the non-nitrided to 2.43 nm for the nitrided capacitors. For the non-nitrided sample, C-V profile is severely distorted in the inversion area. For the nitrided sample, well-shaped C-V curves are obtained without significant frequency dispersion, stretch-out, or bumps near the flat-band voltage. As shown in Fig. 3(b), only slight frequency dispersion is obtained in the range from 1 kHz to 1 MHz, suggesting excellent interface quality at the GeSnON/Ge interface. The densities of the interface states are estimated from conductance measurements to be approximately 1.2×10^{13} $cm^{-2}eV^{-1}$ and 4.6×10^{11} $cm^{-2}eV^{-1}$ for the non-nitrided and nitrided samples, respectively. The D_{it} of the nitrided sample is comparable to those of the GeON/Ge interfaces annealed in NH_3 ambient at high temperature.

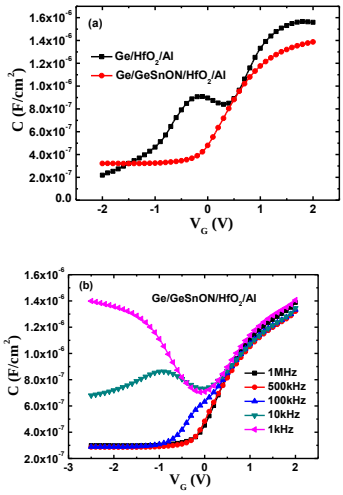

Fig. 3 (a) C-V characteristics measured from Ge/HfO_2/Al and Ge/GeSnON/HfO_2/Al at 1 MHz; (b) multi-frequency gate C-V characteristics measured from Ge/GeSnON/HfO_2/Al capacitors.

As shown in Fig.4, it can be observed that the nitrided gate stack exhibits a leakage current density at least two orders of magnitude lower than the non-nitrided gate stack. The leakage current density of the nitrided sample is lower than 2×10^{-7} A/cm^2 in the voltage range of -1.5 V to 1.5 V. Compared with other surface nitride passivation methods for Ge/HfO_2 MOS devices, the GeSnON layer shows comparable or even better leakage performance. These results indicate that Sn-assisted nitridation of the Ge/HfO_2 interface is an acceptable surface passivation method.

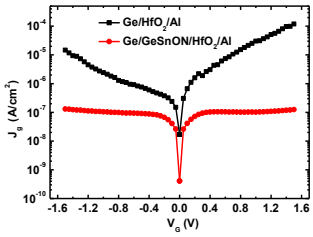

Fig.4 measured J-V characteristics of Ge/HfO_2/Al and Ge/GeSnON/HfO_2/Al capacitors

4. Conclusion

It was demonstrated that a Sn-assisted nitridation approach for the Ge/high-k interface leads to excellent electrical characteristics, with D_{it} reduced to 4.6×10^{11} $cm^{-2}eV^{-1}$. Through XPS and HRTEM analyses, it was confirmed that a thin GeSnON interlayer was formed at the Ge/high-k interface by implementing a thin GeSn layer and subsequent annealing in NH_3 ambient. Electrical measurement results clearly demonstrated that nitridation of the Ge surfaces achieved by this method prior to high-k deposition represents a promising method for improving the interface quality of the gate stacks.

Acknowledgments

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