Germanium Negative Capacitance Field Effect Transistors: Impacts of Zr Composition in Hf$_{1-x}$Zr$_x$O$_2$

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Abstract

Germanium (Ge) negative capacitance field-effect transistors (NCFETs) with various Zr compositions in Hf$_{1-x}$Zr$_x$O$_2$ ($x = 0.33$, 0.48, and 0.67) are fabricated and characterized. For each Zr composition, the NCFET exhibits the sudden drop in some points of subthreshold swing (SS), which is induced by the NC effect. Drive current $I_{DS}$ increases with the increase of annealing temperature, which should be due to the reduced source/drain resistance and improved carrier mobility. The steep SS points are repeatable and stable through multiple DC sweeping measurement proving that they are induced by the NC effect. The values of gate voltage $V_{GS}$ corresponding to steep SS are consistent and clockwise $I_{DS}-V_{GS}$ are maintained through the multiple DC sweeps. At fixed annealing temperature, NC device with Hf$_{0.52}$Zr$_{0.48}$O$_2$ achieves the higher $I_{DS}$ but larger hysteresis compared to the other compositions. NCFET with Hf$_{0.67}$Zr$_{0.33}$O$_2$ can obtain the excellent performance with hysteresis-free curves and high $I_{DS}$.

Keywords: Ferroelectric, Negative capacitance, Hysteresis, Subthreshold swing, FET

Background

The ferroelectric negative capacitance field-effect transistor (NCFET) with a ferroelectric film inserted into gate stack is a promising candidate for the low-power dissipation applications owing to its ability to overcome the fundamental limitation in subthreshold swing (SS) for the conventional metal-oxide-semiconductor field-effect transistor (MOSFET) [1]. The negative capacitance (NC) phenomena in NCFETs have been extensively studied in different channel materials, including silicon (Si) [2, 3], germanium (Ge) [4], germanium-tin (GeSn) [5], III–V [6], and 2D materials [7]. Also, the NC characteristics have been demonstrated in NCFETs with various ferroelectrics, such as BiFeO$_3$ [8], PbZrTiO$_3$ (PZT) [9], PVDF [10], and Hf$_{1-x}$Zr$_x$O$_2$ [11]. Compared to other ferroelectrics, Hf$_{1-x}$Zr$_x$O$_2$ has the advantage of being compatible with CMOS integration. Experimental studies have shown that the electrical performance of NCFETs can be optimized by varying the thickness and area of Hf$_{1-x}$Zr$_x$O$_2$, which affects the matching between MOS capacitance ($C_{MOS}$) and ferroelectric capacitance ($C_{FE}$) [12, 13]. It is expected that the Zr composition in Hf$_{1-x}$Zr$_x$O$_2$ also has a great impact on the performance of NCFETs, because it determines the ferroelectric properties of Hf$_{1-x}$Zr$_x$O$_2$. However, there is still a lack of a detailed study on the impacts of Zr composition on the electrical characteristics of NCFETs.

In this paper, we comprehensively study the influences of the annealing temperature and the Zr composition on the performance of Ge NCFET.

Methods

Key process steps for fabricating Ge p-channel NCFETs with the different Zr compositions in Hf$_{1-x}$Zr$_x$O$_2$ are shown in Fig. 1(a). After the pregate cleaning, n-Ge (001) substrates were loaded into the atom layer deposition (ALD) chamber. A thin Al$_2$O$_3$ (25 cycles) film was deposited, which was followed by the O$_3$ passivation. Then, the Hf$_{1-x}$Zr$_x$O$_2$ films ($x = 0.33$, 0.48 and 0.67) were...
deposited in the same ALD chamber using [(CH$_3$)$_2$N]$_4$Hf (TDMAHf), [(CH$_3$)$_2$N]$_4$Zr (TDMAZr) and H$_2$O as the Hf, Zr, and O precursors, respectively. After that, the TaN metal gate was deposited using the reactive sputtering. After gate patterning and etching, boron ions (B$^+$) were implanted into source/drain (S/D) regions at an energy of 20 keV and a dose of $1 \times 10^{15}$ cm$^{-2}$. Non-self-aligned S/D metals were formed by lift-off process. Finally, rapid thermal annealing (RTA) was carried out at various temperatures for dopant activation, S/D metallization, and crystallization of Hf$_{1-x}$Zr$_x$O$_2$ film. Ge control pMOSFETs with the Al$_2$O$_3$/HfO$_2$ stack was also fabricated.

Figure 1(b) shows the schematic of the fabricated NC transistor. (c) TEM image of the gate stack of NC device illustrating the 7 nm Hf$_{0.52}$Zr$_{0.48}$O$_2$ layer and 2 nm Al$_2$O$_3$ layer.

To confirm the stoichiometries of Hf$_{1-x}$Zr$_x$O$_2$, the X-ray photoelectron spectroscopy (XPS) measurement was carried out. Figure 2(a) and (b) show the Hf 4f and Zr 3d photoelectron core level spectra, respectively, for the Hf$_{0.67}$Zr$_{0.33}$O$_2$, Hf$_{0.52}$Zr$_{0.48}$O$_2$, and Hf$_{0.33}$Zr$_{0.67}$O$_2$ films. The material compositions were calculated based on the area ratio of the peaks and the corresponding sensitivity factors. The two peaks of Zr 3d$_{5/2}$ and Zr 3d$_{3/2}$ have a spin-orbital splitting of 2.4 eV, which is consisted with Refs. [14, 15]. With the increment of Zr composition in Hf$_{1-x}$Zr$_x$O$_2$, Zr 3d, and Hf 4f peaks shift to the lower energy direction. The ferroelectric properties of the Hf$_{1-x}$Zr$_x$O$_2$ films (x = 0.33, 0.48, and 0.66) were characterized by the polarization $P$ vs. drive voltage $V$ hysteresis loops.
measurement. \(P-V\) loops were recorded on the pristine devices. Figure 3 shows the curves of \(P\) vs. \(V\) for TaN/Hf\(_{1-x}\)Zr\(_x\)O\(_2\)(10 nm)/TaN samples in a series of drive voltages. With the post-annealing temperature increases from 500 to 550 °C, the \(P-V\) curves of the Hf\(_{1-x}\)Zr\(_x\)O\(_2\) tend to be saturated in a sub-loop state. As the Zr composition increases, the remnant polarization of the film is obviously improved, and the thinning of the hysteresis loop at zero bias is observed, which can be phenomenologically best described as superimposed antiferroelectric-like characteristics [16, 17].

**Results and Discussion**

Figure 4(a) shows the measured transfer characteristics of Ge NCFETs with Hf\(_{0.52}\)Zr\(_{0.48}\)O\(_2\) ferroelectrics with different annealing temperatures and control device with Al\(_2\)O\(_3\)/HfO\(_2\) stack dielectric. The control device was annealed at 500 °C. All the devices have a gate length \(L_G\) of 2 μm. The forward and reverse sweeping are indicated by the open and solid symbols, respectively. The NCFETs have a much higher drive current compared to the control device. It is seen that, with the annealing temperature increasing from 450 to 550 °C, the threshold voltage \(V_{TH}\) of the NC devices shift to the positive \(V_{GS}\) direction. The NCFETs exhibit a small hysteresis, which becomes negligible with the increasing of RTA temperature. The trapping effect also leads to the hysteresis, but that produces the counterclockwise \(I_{DS}-V_{GS}\) loop, opposite to the results induced by ferroelectric switching [18]. Point SS vs. \(I_{DS}\) curves in Fig. 4(b) show that the NC transistor exhibits the sudden drop in some points of SS, corresponding to the abrupt change of \(I_{DS}\) induced by the NC effect [19]. It is observed that NCFETs achieve the improved SS characteristics compared to the control device. We found that the sudden drop points of the devices are consistent at the different annealing temperatures. The measured \(I_{DS}-V_{DS}\) curves of the NCFETs with Hf\(_{0.52}\)Zr\(_{0.48}\)O\(_2\) ferroelectric annealed at different temperatures are shown in Fig. 4(c). \(I_{DS}-V_{DS}\) curves of the NC transistor show the obvious NDR phenomenon, which is a typical characteristic of NC transistors [20–23]. Figure 4(d) is the plots of the \(I_{DS}\) of the Ge NCFETs with the Hf\(_{0.52}\)Zr\(_{0.48}\)O\(_2\) ferroelectric layer annealed at...
450, 500, and 550 °C, respectively, at $V_{DS} = -0.05$ V and $-0.5$ V, and $|V_{GS} - V_{TH}| = 1.0$ V. Here, the $V_{TH}$ is defined as the $V_{GS}$ at $I_{DS}$ of $10^{-7}$ A/μm. $I_{DS}$ increases with the increasing of RTA temperature, which is due to the reduced source/drain resistance and improved carrier mobility at the higher annealing temperature.

In addition to the Hf$_{0.52}$Zr$_{0.48}$O$_2$ ferroelectric transistor, we also investigate the electrical characteristics of Ge NC transistors with the Hf$_{0.33}$Zr$_{0.67}$O$_2$ ferroelectric. Figure 5(a) presents the $I_{DS}$-$V_{GS}$ characteristics of the devices with Hf$_{0.33}$Zr$_{0.67}$O$_2$ with the different annealing temperatures at $V_{DS} = -0.05$ V and $-0.5$ V. Compared to the Hf$_{0.52}$Zr$_{0.48}$O$_2$ NC transistors, even smaller hysteresis is obtained. Similar to the Hf$_{0.52}$Zr$_{0.48}$O$_2$ NC transistors, as the annealing temperature increases from 450 to 550 °C, $V_{TH}$ of the device increases from $-0.63$ V to $0.51$ V in the forward sweeping at $V_{DS} = -0.05$ V. Point SS as a function of $I_{DS}$ characteristics for the Hf$_{0.33}$Zr$_{0.67}$O$_2$ ferroelectric NCFETs are depicted in Fig. 5(b). In addition, devices with 450 °C and 500 °C annealing temperature obtains the more obvious sudden drop in SS in comparison with the 550 °C annealed transistor. The sudden drop points in different annealing temperatures occur at the same gate voltage. Figure 5(c) exhibits forward and reverse $I_{DS}$ of the Hf$_{0.33}$Zr$_{0.67}$O$_2$ NCFETs at $V_{DS} = -0.05$ V and $-0.5$ V, and $|V_{GS} - V_{TH}| = 1.0$ V. Whether for the forward or reverse sweeping, the $I_{DS}$ increases with the annealing temperature, which is consistent with the characteristic of the Hf$_{0.52}$Zr$_{0.48}$O$_2$ device.

We also investigate the electrical performance of Ge NCFET with the smaller Zr composition. The transfer characteristics of the Hf$_{0.67}$Zr$_{0.33}$O$_2$ NCFETs annealed at different annealing temperatures are presented in

![Fig. 4](image-url)

(a) Measured $I_{DS}$-$V_{GS}$ curves for NCFETs with Hf$_{0.52}$Zr$_{0.48}$O$_2$ ferroelectric and control device. (b) Point SS vs. $I_{DS}$ curves showing that NCFETs have the steeper SS compared to control MOSFET. (c) $I_{DS}$-$V_{GS}$ curves for the NCFETs demonstrating the typical NDR phenomena. (d) Comparison of the $I_{DS}$ for the NCFETs annealed at various temperatures at a gate overdrive of 1 V.
Fig. 6(a). No hysteresis phenomenon is observed. Compared to Hf$_{0.33}$Zr$_{0.67}$O$_2$ and Hf$_{0.52}$Zr$_{0.48}$O$_2$ devices, the $V_{TH}$ shift induced by varying annealing temperature is less pronounced in Hf$_{0.67}$Zr$_{0.33}$O$_2$ NCFETs. Point SS vs. $I_{DS}$ curves in Fig. 6(b) show that the Hf$_{0.67}$Zr$_{0.33}$O$_2$ NC transistor exhibits the sudden drop in some points of SS of NC transistor at $V_{DS} = -0.05$ V. Figure 6(c) presents the $I_{DS}$ of Hf$_{0.67}$Zr$_{0.33}$O$_2$ Ge NCFETs annealed at 450 °C, 500 °C, and 550 °C, at $V_{DS} = -0.05$ V and $-0.5$ V, and $|V_{GS} - V_{TH}| = 1.0$ V. Likewise, $I_{DS}$ enhances as the RTA temperature increases. The stability of the NC effect induced by the ferroelectric layer of the Hf$_{0.52}$Zr$_{0.48}$O$_2$ NCFET was
verified by multiple DC sweeping measurements. The measured $I_{DS}$-$V_{GS}$ curves over 100 cycles of DC sweeping are shown in Fig. 7(a). It can be seen that the values of $V_{GS}$ corresponding to steep SS are consistent. In addition, the clockwise I-V loops are maintained through the multiple DC sweeps. The steep SS points are repeatable and stable through multiple DC sweeps, which further proves that they are induced by the NC effect. Figure 7(b) presents the best point SS and drive current across the number of sweeping cycles. Figure 7(c) shows the hysteresis characteristics as a function of the number of DC sweeping cycles. Stable I-V hysteresis window of ~82 mV are seen.

We summarize the hysteresis and drive current characteristics of Ge NCFETs with different Zr compositions in Hf$_{1-x}$Zr$_x$O$_2$ in Fig. 8. As shown in Fig. 8(a), the hysteresis values are 70, 148, and 106 mV for devices with $x = 0.33$, 0.48, and 0.67, respectively, at a $V_{DS} = -0.5$ V. As the composition increases from 0.33 to 0.48, the hysteresis of the NC device increases significantly. With the further increasing of Zr composition, the hysteresis decreases rapidly. The $I_{DS}$ of NCFETs annealed at 450 °C is plotted in Fig. 8(b), at $V_{DS} = -0.5$ V and $V_{GS} - V_{TH} = -1.0$ V. Open and solid represent the forward and reverse sweeping, respectively. The NC device with Hf$_{0.52}$Zr$_{0.48}$O$_2$ achieves the highest $I_{DS}$, but its hysteresis is serious. NCFET with Hf$_{0.67}$Zr$_{0.33}$O$_2$ can obtain excellent performance with hysteresis-free curves and high $I_{DS}$. As Zr composition increases, the ferroelectric capacitance $C_{fe} = (0.3849\times P_r)/(E_{c}\times t_{fe})$ [24]) increases with the increasing of $P_r$ and meanwhile, the MOS capacitance ($C_{MOS}$) rises as well due to the growing permittivity of the HZO film. The $I_{DS}$ and hysteresis are determined by $|C_{fe}|$ and $C_{MOS}$ of the transistor. With Zr composition increasing from 0.33 to 0.48, the increase of $|C_{fe}|$ is speculated to be slower than does the $C_{MOS}$, leading to the widening of the hysteresis. Nevertheless, the larger $C_{MOS}$ produces a higher $I_{DS}$. With the further increase of Zr composition, the increase of $|C_{fe}|$ is faster than $C_{MOS}$, which might provide $|C_{fe}| \geq C_{MOS}$, reducing the hysteresis of NCFET.

**Conclusions**

The impacts of the annealing temperature and Zr composition in Hf$_{1-x}$Zr$_x$O$_2$ on the electrical performance of the Ge NCFETs are experimentally studied. The stoichiometries and ferroelectric properties of Hf$_{1-x}$Zr$_x$O$_2$ were confirmed by XPS and P-V measurements, respectively. NCFETs demonstrate the steep point SS and improved $I_{DS}$ compared to the control device, due to the NC effect.
The $V_{TH}$ and $I_{DS}$ of the Hf$_{1-x}$Zr$_x$O$_2$ NCFET are greatly affected by the annealing temperature. Multiple DC sweeping measurements show that the stability of the NC effect induced by the ferroelectric layer is achieved in NCFET. Hf$_{0.67}$Zr$_{0.33}$O$_2$ NCFET can more easily achieve the hysteresis-free characteristics than the devices with higher Zr composition.

**Abbreviations**

Al$_2$O$_3$: Aluminum oxide; ALD: Atomic layer deposition; BF$_2$+: Boron fluoride ion; DC: Direct current; Ge: Germanium; GeO$_x$: Germanium oxide; HF: Hydrofluoric acid; HfO$_2$: Hafnium dioxide; HRTEM: High-resolution transmission electron microscope; MOSFETs: Metal-oxide-semiconductor field-effect transistors; NC: Negative capacitance; Ni: Nickel; SS: Subthreshold swing; TaN: Tantalum nitride; TDMAHf: Tetrakis (dimethylamido) hafnium; TDMAZr: Tetrakis (dimethylamido) zirconium

**Acknowledgements**

Not applicable.

**Funding**

The authors acknowledge support from the National Natural Science Foundation of China under Grant No. 61534004, 61604112, 61622405 and 61874081, and 61851406. This work was also supported by the 111 Project (B12026).

**Availability of Data and Materials**

The datasets supporting the conclusions of this article are included within the article.

**Authors’ Contributions**

YP carried out the experiments and drafted the manuscript. YP and GQH designed the experiments. GQH and YL helped to revise the manuscript. JCZ and YH supported the study. All the authors read and approved the final manuscript.

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**Competing Interests**

The authors declare that they have no competing interests.

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Received: 19 December 2018 Accepted: 6 March 2019
Published online: 04 April 2019

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