High-mobility germanium p-MOSFETs by using HCl and $(NH_4)_2S$ surface passivation*

Xue Bai-Qing(薛百清), Wang Sheng-Kai(王盛凯)†, Han Le(韩 乐), Chang Hu-Dong(常虎东), Sun Bing(孙 兵), Zhao Wei(赵 威), and Liu Hong-Gang(刘洪刚)‡

Microwave Device and IC Department, Institute of Microelectronics, Chinese Academy of Sciences, Beijing 100029, *China*

(Received 26 March 2013; revised manuscript received 6 May 2013)

To achieve a high-quality high-κ/Ge interfaces for high hole mobility Ge p-MOSFET applications, a simple chemical cleaning and surface passivation scheme is introduced, and Ge p-MOSFETs with effective channel hole mobility up to 665 $cm^2/V{\cdot}s$ are demonstrated on a Ge (111) substrate. Moreover, a physical model is proposed to explain the dipole layer formation at the metal–oxide–semiconductor (MOS) interface by analyzing the electrical characteristics of HCl- and $(NH_4)_2S$-passivated samples.

Keywords: Ge, MOSFET, high-*k* dielectric, mobility

PACS: 73.40.Qv, 71.55.Eq, 77.55.D– **DOI:** 10.1088/1674-1056/22/10/107302

1. Introduction

Germanium is a promising candidate for advanced metal–oxide–semiconductor field effect transistors (MOSFETs) because of its superior carrier mobility compared with silicon. However, the presence of undesirable native oxides is one of the major obstacles to the heterogeneous integration of Ge MOSFETs with Si integrated circuits.[1] Completely removing the defective native oxide from the Ge surface is essential to realizing high-performance Ge MOSFETs. Many attempts have been made to apply Si-cleaning processes for the treatment of Ge surfaces, but the results have been poor. Sun *et al.*[2] showed that the use of conventional hydrogen fluorine (HF) solutions does not effectively remove the GeO_x from the Ge surface, but instead, made its surface rougher. Using hydrogen chloride (HCl) and hydrogen bromine (HBr)[2,3] were investigated to remove the GeO_x, however the cleaned Ge surfaces were easily reoxidized in the air. Therefore, a subsequent surface passivation step may improve the interface performance of high-κ dielectric and Ge. Several Ge passivation techniques including surface or interfacial nitridation,[4] S-passivation,[5–7] Si-passivation,[8] and F-passivation,[9] have been applied to improve the stability of high-κ/Ge systems. However, these passivation methods are carried out in the HF-last process. Chemical passivation followed by HCl cleaning has rarely been reported. Moreover, from the aspect of substrate orientation engineering, which is known to be effective for the mobility enhancement of Ge MOSFETs, Ge (110) p-MOSFETs have been confirmed as having the highest hole mobility[10] of all orientations, such as Ge (100) and Ge (111). However, the impacts of surface chemical passivation on Ge substrate with orientations have not been systematically investigated so far.

In this paper, we introduce a simple chemical cleaning and surface passivation scheme using HCl and $(NH_4)_2S$ to achieve a high-quality high-κ/Ge interface for high mobility Ge p-MOSFETs application. Effective channel hole-mobility up to 665 $cm^2/V{\cdot}s$ has been achieved on a Ge (111) substrate. To reveal the effects of chemical passivation, *C*–*V* and *I*–*V* characterizations were performed, and the mobility scattering mechanism on Ge (100), (110), and (111) substrates is discussed. Moreover, a physical model is proposed to explain the dipole layer formation at the MOS interface by analyzing the electrical characteristics of HCl and $(NH_4)_2S$ passivated samples.

2. Device fabrication

The n-type Ge wafers used in this work have a resistivity of approximately 0.01 Ω·cm–0.1 Ω·cm. These Ge wafers were pre-cleaned in acetone and alcohol for 5 min, respectively, and rinsed in deionized water (DIW) to dissolve any surface solvent. To remove the surface native oxide (GeO_x), the Ge wafers were immersed in a diluted HCl (30% v/v) solution for 60 s, then rinsed in DIW. After the cleaning process, some wafers were soaked in HCl (30% v/v) solution for 10 min, while others were treated in $(NH_4)_2S$ solution for 10 minutes, followed by DIW rinsing and N_2 drying. The treated samples were immediately transferred into the load-lock chamber of an atomic layer deposition (ALD) system (Beneq TFS200). Then, 10-nm-thick Al_2O_3 films were deposited on the as-passivated substrates at 300 °C, using trimethylaluminium

*Project supported by the National Basic Research Program of China (Grant Nos. 2011CBA00605 and 2010CB327501), the National Natural Science Foundation of China (Grant No. 61106095), and the National Science and Technology Major Project of the Ministry of Science and Technology of China (Grant No. 2011ZX02708-003).

†Corresponding author. E-mail: wangshengkai@ime.ac.cn

‡Corresponding author. E-mail: liuhonggang@ime.ac.cn

© 2013 Chinese Physical Society and IOP Publishing Ltd

(TMA) and water as precursors. After high-κ dielectric deposition, a standard "gate-first" process flow was applied for Ge MOSFETs fabrication, including Ti/Au (20 nm/200 nm) gate electrodes deposition on the surface of the Al_2O_3 films, B^+ ion implantation (30 keV, 10^{15} cm^{-2}), and RTA annealing (30 s at 400 °C). To form source and drain, Ni/Au was evaporated as the source/drain contact.

3. Results and discussion

XPS measurements are performed on the HCl- and $(NH_4)_2S$-passivated samples, as shown in Fig. 1, to examine the effects of the surface passivation by comparing the Ge 3d core-levels. Compared with the original wafer surface (the inset of Fig. 1(a)), no obvious sub-oxide peaks exist in the XPS spectra, indicating that the HCl cleaning is more effective than HF cleaning for removing Ge surface oxides.[2] However, the main peak in Figs. 1(a) and 1(b) clearly shifts to a higher binding energy. The reason for this shift is still unclear, but we infer that this shift results from interfacial reactions during chemical surface passivation. Figures 1(a) and 1(b) show the Ge 3d peak deconvolution results after the HCl and $(NH_4)_2S$ passivation for the Ge (100) surface. Two peaks of Fig. 1(a) are used to fit the Ge 3d spectra; the peak with the lowest binding energy is the Ge bulk peak, and the other peak shows a chemical shift of 0.57 eV toward higher binding energies, possibly due to Ge–S bond formation.[5] For the HCl-passivated case, a similar chemical shift of 0.59 eV is found, this may be caused by Ge–Cl bond formation.[2] The inset of Fig. 1(b) shows the root-mean-square (RMS) roughness of chemical passivated Ge wafers, measured by AFM. The RMS for the HCl cleaning surface is only 0.24 nm, significantly lower than the RMS values for the original and HF cleaning samples, and the HCl-cleaned surface presents a superior surface morphology. The improvement of the surface roughness may be attributed to the differences in the etching mechanisms of the Ge surface using HF and HCl.[2]

Ge pMOSFETs are fabricated on Ge (100), (110), and (111) substrates, with a 10-nm ALD-Al_2O_3 gate oxide grown on the HCl- and $(NH_4)_2S$-passivated Ge surfaces. Figures 1(c) and 1(d) show the Ge (110) I_d–V_d characteristics of the 24-μm gate length p-MOSFETs with HCl- and $(NH_4)_2S$-passivated, respectively. The maximum drain current reaches 16 mA/mm for the HCl-passivated sample and 13 mA/mm for the $(NH_4)_2S$-passivated sample at V_G–V_T = 2.3 V, and similar characteristics are shown in the (100) and (111) samples.

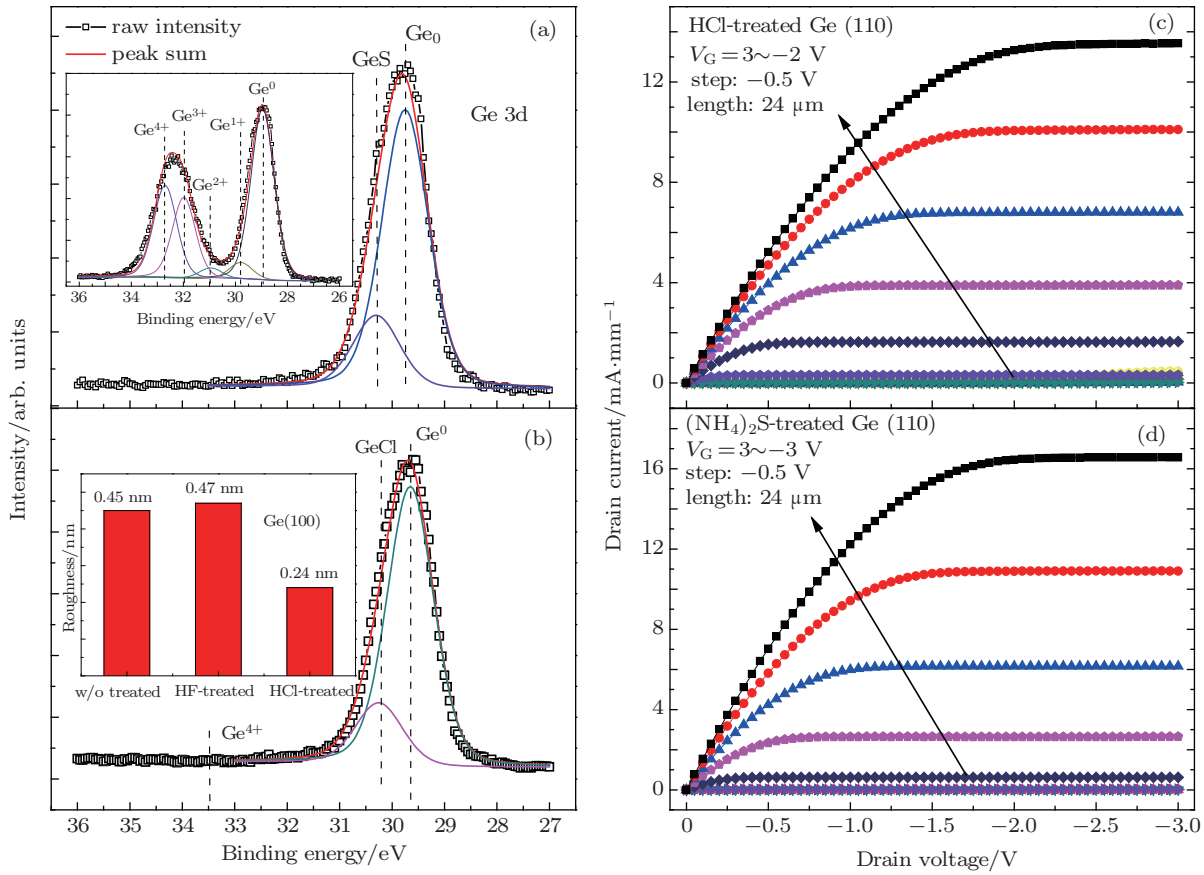


Fig. 1. (color online) Ge 3d XPS spectra from Ge (100) surface, (a) with $(NH_4)_2S$ passivation, where the inset shows the spectrum of the sample without any chemical passivation; (b) with HCl passivation, and the inset shows the RMS roughness value under different chemical surface cleaning; the I_d–V_d characteristics of Ge p-MOSFETs on a (110)-orientation substrate, for (c) HCl-passivated sample, and (d) $(NH_4)_2S$-passivated sample.

To determine the inversion layer hole-mobility, a split *C–V* method is applied. The frequency dispersion free *C–V* curves on Ge (110) are shown in Fig. 2 in the 1 kHz–100 kHz range, suggesting both HCl- and $(NH_4)_2S$-passivation are effective in improving the Al_2O_3/Ge interface quality. The inset in Fig. 2 displays the p-MOSFET structure. Similar results are obtained in Ge (100) and Ge (111) cases (data not shown here). After correction by deducting the S/D resistance, the hole-mobilities of HCl-passivated samples for the Ge (100), (110), and (111) substrates are shown as a function of surface carrier density (N_s) in Fig. 3(a). The peak hole-mobilities are 394, 544, and 665 $cm^2/V{\cdot}s$ for Ge (100), (110), and (111) samples, respectively. A 3.5× hole-mobility enhancement is achieved in the Ge (111) device, compared with the Si universal hole-mobility, with a substrate impurity concentration (N_{sub}) of 5.8×10^{15} cm^{-3}. For the $(NH_4)_2S$-passivated samples, the hole-mobilities of the Ge (100), (110), and (111) devices reach 210, 556, and 525 $cm^2/V{\cdot}s$, respectively.

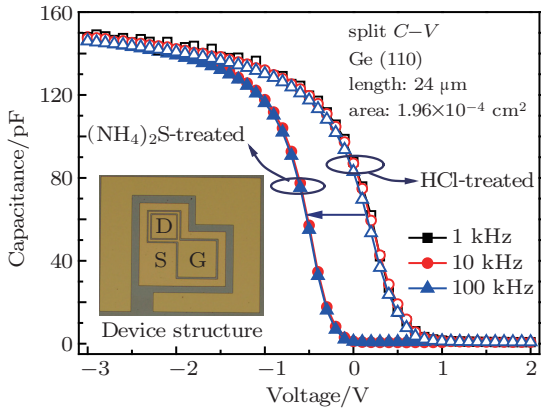


Fig. 2. (color online) Split *C–V* curves for Ge (110) p-MOSFETs after HCl- and $(NH_4)_2S$-passivation, where the inset shows the device structure.

According to our results (as shown in Fig. 3(a)), the mobility of Ge (111) is higher than that of Ge (110), which seems to conflict with the reports that the Ge (110) orientation has the highest hole mobility.[10,11] To explain this result, we would ascribe it to the difference in Coulomb scattering and surface roughness. Under Matthiessen's rule, the inversion layer mobility is given by $1/\mu = 1/\mu_c + 1/\mu_{ph} + 1/\mu_{sr}$. Here, μ, μ_c, μ_{ph}, and μ_{sr} represent the total mobility, the mobility limited by Coulomb scattering, phonon scattering, and surface roughness scattering, respectively.[12] In this work, since the fabrication processes and substrate doping density are identical for the devices with different substrate orientations, the difference of phonon scattering could thus be eliminated. However, in low electric field region, the hole mobility is mainly dominated by the Coulomb scattering.[12] Compared with Ge (111), the density of the surface dangling bonds of Ge (110) is higher. For the Cl-passivated case, each surface dangling bond is terminated by a Cl atom; therefore, the surface Cl- terminus density for Ge (110) is higher than that of Ge (111). We infer, due to the difference of surface Cl-termination density, the Coulomb scattering is stronger for the Ge (110) case. Besides the Coulomb scattering, the surface roughness also affects the hole mobility, especially at high field, but not only limited at high field. Therefore, we measured the surface roughness of the three HCl-passivated samples with substrate orientations of (100), (110), and (111) using AFM, and we find the surface roughness after HCl passivation follows the trend: RMS (110) > RMS (100) > RMS (111). This trend is consistent with the result shown in Fig. 3.

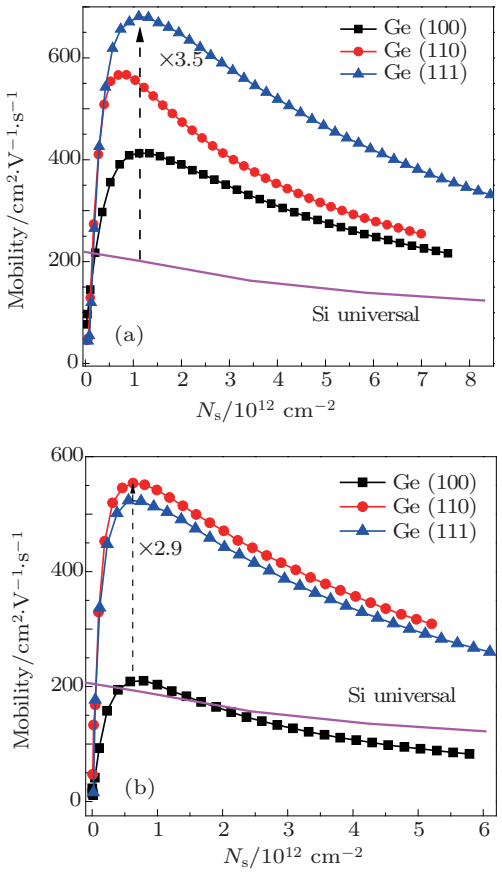


Fig. 3. (color online) Hole mobilities of p-MOSFETs on Ge (100), (110), and (111) substrates; (a) passivated using HCl solution, and (b) passivated using $(NH_4)_2S$ solution.

Figure 4 shows the I_d–V_G characteristic of HCl-passivated and $(NH_4)_2S$-passivated p-MOSFETs on Ge (110) substrates, respectively. Both samples show an I_{on}/I_{off} ratio of over 10^4 at $V_{DS} = -50$ mV, indicating a good on–off characteristic. However, our HCl-passivated Ge MOSFET functions under the depletion mode, and is not pinched off at zero gate bias, while the $(NH_4)_2S$-passivated device is an enhancement mode MOSFET, in which the transistor is pinched off at zero gate bias. The threshold voltage (V_T) of the $(NH_4)_2S$-passivated device is −0.2 V, while the HCl-passivated device is a depletion-mode transistor with a V_T of 0.8 V. A similar sub-threshold slope (SS) of about 130 mV/dec is extracted from the I_d–V_G curves for the HCl- and the $(NH_4)_2S$-passivated ones on Ge

(110) substrate. Moreover, both HCl-passivated and $(NH_4)_2S$-passivated MOSFETs show similar SS factor of 200 mV/dec on Ge (100) and 180 mV/dec on Ge (111).

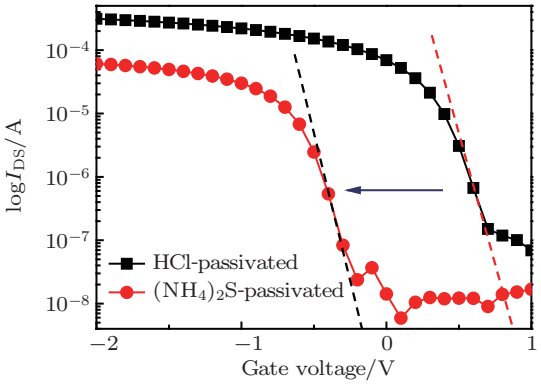


Fig. 4. (color online) The I_d-V_G curves of Ge p-MOSFETs on a (110)-orientation substrate, for HCl- and $(NH_4)_2S$-passivated samples.

Concerning the difference in electrical characteristics between the Ge MOS devices passivated by HCl and $(NH_4)_2S$, a discussion about dipole formation[13,14] is helpful in understanding the difference between the phenomena that take place at the interface of Ge p-MOSFETs. Compared with the $(NH_4)_2S$-passivated sample, the flat-band (V_{fb}) of the split C–V for the HCl-passivated case shifts significantly toward positive values, as shown in Fig. 2. This shift of split C–V curves is consistent with the V_T shift for the HCl-passivated and $(NH_4)_2S$-passivated samples, shown in Fig. 4. Those demonstrate the obvious difference between the HCl and $(NH_4)_2S$ surface passivation. For the MOSFETs we fabricated, all processes were identical except for the surface passivation methods (HCl-passivation and $(NH_4)_2S$-passivation). To explain the difference between the two surface passivation methods, a physical model is proposed by considering the interfacial dipole formation, as shown in Fig. 5. For the HCl-passivated sample, the HCl cleaning surface was passivated using HCl to form a Cl-terminated layer. Since the Pauling electronegativity of Cl is stronger than that of Ge (Ge-2.01, Cl-3.16), the shared electrons would be closer to the Cl atom. When Al_2O_3 is deposited on the as-passivated surface, a dipole layer is formed at the interface, due to the large difference in the Pauling scale between Ge and Cl; the formation process is illustrated in Fig. 5(a). Because the dipole layer determines the interfacial characteristics, the V_{fb}, V_T, and depletion characteristics of the HCl-passivated devices are obviously different from those of the $(NH_4)_2S$-passivated devices. For the $(NH_4)_2S$-passivated cases, as depicted in Fig. 5(b), the sharing electrons would be located in the middle between the two atoms, due to the lower Pauling electronegativity disparity between Ge and S (Ge-2.01, S-2.58), compared with Ge and Cl; therefore, the dipole layer does not form easily.

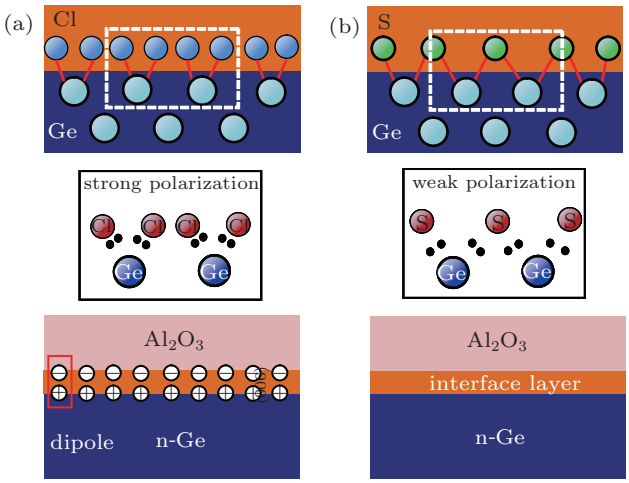


Fig. 5. (color online) Schematics of a physical model explaining the dipole formation at the Al_2O_3/Ge (110) interface, based on the difference between the surface passivation methods: (a) the dipole formation for HCl-passivated surface, and (b) the dipole formation for $(NH_4)_2S$-passivated surface.

4. Conclusions

In summary, a novel chemical cleaning and surface passivation scheme to achieve a high-quality high-κ/Ge interface for high mobility Ge p-MOSFET applications were introduced in this paper, and effective channel hole-mobility was up to 665 $cm^2/V{\cdot}s$ on a Ge (111) substrate. Moreover, a physical model was proposed to explain the dipole layer formation at MOS interface by analyzing the electrical characteristics of HCl- and $(NH_4)_2S$-passivated samples.

References

[1] Prabhakaran K, Maeda F, Watanabe Y and Ogino T 2000 *Appl. Phys. Lett.* **76** 2244
[2] Sun S Y, Sun Y, Liu Z, Lee D L, Peterson S and Pianetta P 2006 *Appl. Phys. Lett.* **88** 88
[3] Frank M M, Koester S J, Copel M, Ott J A and Loesing R 2006 *Appl. Phys. Lett.* **89** 112905
[4] Xu J P, Lai P T, Li C X, Zou X and Chan C L 2006 *IEEE Electron Dev. Lett.* **27** 439
[5] Xue B Q, Chang H D, Sun B, Wang S K and Liu H G 2012 *Chin. Phys. Lett.* **29** 046801
[6] Chang H D, Sun B, Zhao W, Wang W X and Liu H G 2012 *Acta Phys. Sin.* **61** 217304 (in Chinese)
[7] Chang H D, Liu G M, Sun B, Zhao W and Liu H G 2013 *Chin. Phys. Lett.* **30** 037303
[8] Aktag A, Yimaz E, Mogaddam N A P, Aygun G, Cantas A and Turan R 2010 *Nucl. Instrum. Method B* **268** 3417
[9] Li C X, Leung C H, Lai T P and Xu J P 2010 *Solid State Electron* **54** 675
[10] Zhang R, Iwasaki T, Taoka N, Takenaka M and Takagi S 2011 in *VLSI* 56
[11] Lee C H, Nishimura T, Tabata T, Wang S K, Nagashio K, Kita K and Toriumi A 2010 in *IEDM* 18.1
[12] Takagi S, Toriumi A, Iwase M and Tanago H 1994 *IEEE Trans. Electron Dev.* **41** 2357
[13] Kita K and Toriumi A 2009 *Appl. Phys. Lett.* **94** 132902
[14] Krisch P D, Sivasubramani P, Huang J, Young C D, Quevedo-Lopez M A, Wen H C, Alshareef H, Choi K, *et al.* 2008 *Appl. Phys. Lett.* **92** 092901