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Fermi level depinning by a C-containing layer in a metal/Ge structure by using a chemical bath*

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Abstract: Insertion of a C-containing layer in a metal/Ge structure, using a chemical bath, enabled the Schottky barrier height (SBH) to be modulated. Chemical baths with 1-octadecene, 1-hexadecene, 1-tetradecene, and 1-dodecene were used separately with Ge substrates. An ultrathin C-containing layer stops the penetration of free electron wave functions from the metal to the Ge. Metal-induced gap states are alleviated and the pinned Fermi level is released. The SBH is lowered to 0.17 eV. This new formation method is much less complex than traditional ones, and the result is very good.

Key words: Schottky barrier; Fermi level pinning; chemical bath; blocking layer

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1. Introduction

Materials with high carrier mobilities, such as Ge, are promising as substitutes for Si. Ge gives twice the electron mobility and four times the hole mobility of Si, and is also compatible with most traditional Si processes[1]. In the scaling down of metal–oxide–semiconductor field-effect transistors (MOSFETs), significant degradation of performance occurs as a result of short channel effects and ultrashallow source and drain junctions are needed in order to suppress them. In Ge n-MOSFETs, traditional dopants such as P, As, and Sb have low solid solubility, increased diffusion, and are difficult to activate, so traditional source/drain (S/D) processes are difficult to apply to Ge[2, 3]. Metal S/D and Schottky contacts could help to avoid large S/D resistances, but these also cause problems. The crystal lattice and the electronic wave functions in the semiconductor are not ideal and unlimited, which indicates that some energy levels in the semiconductor surface area are taken up, even though they should not be in an ideal case. A similar situation happens in the metal. When the metal contacts the semiconductor directly, the electrons in the taken level and their wave functions will couple each other because of the non-ideal characters, which generate gap states. These states are known as metal-induced gap states (MIGS)[4, 5]. They cause strong Fermi-level pinning just above the valence band edge of Ge, near the charge neutrality level. Connelly *et al.* studied this situation for Si and suggested the insertion of an SiN layer to lower the Schottky barrier height (SBH)[6, 7]. Kobayashi *et al.* also tried this with Ge[8]. By inserting an insulator layer, the penetration of metal wave functions was blocked. Much fewer metal wave functions can couple with those in the semiconductor by passing through the layer and the current transportation was significantly changed. The layer thickness is quite critical, but is hard to control using traditional methods[9]. Based on decoupling the wave functions and reducing MIGS, we researched the Fermi-level de-pinning of a metal/Ge contact by inserting a layer between the metal and Ge.

2. Experiment and results

A C-containing monolayer as the blocking layer was formed by applying a chemical bath to the Ge substrate in the study. The effective barrier height ($\phi_{\mathrm{b,\,eff}}$) can be modulated as a result of wave function blocking and Fermi-level depinning. The chemical bath was applied to n-type (Sb-doped) (100) Ge wafers with resistivities of 24.5–27.5 Ω·cm. The non-thermionic emission part of the current could be greatly suppressed during the tests by using a low-doped substrate. Surface cleaning was carried out as shown in the flow-chart in Fig. 1. After Ge–H bond formation on the surface, the substrates were immersed in the chemical baths. 1-octadecene, 1-hexadecene, 1-tetradecene, and 1-dodecene were used individually in the baths. Chemical baths were applied at 180 ℃ for 2 h. Other experiments with conditions of 80 ℃ and 1 h were also performed for comparison. After removal from the baths, the samples were rinsed with alcohol and de-ionized water for three cycles. For measuring purposes, Al was deposited on the blocking layer to form an electrode. Samples without a blocking layer and with native oxide were also prepared. All conditions and corresponding sample indexes are listed in Table 1.

Unsaturated alkenes accept electrons during the reaction, which is similar to hydrogermylation[10]. The Ge–C bonding energy is 100% higher than that of Ge–H. The unsaturated bonds receive electrons from Ge–H, and form Ge–C bonds on the substrate surface[11].

Representative X-ray photoelectron spectroscopy (XPS) data obtained from these samples are shown in Figs. 2 and 3. Figure 2 shows that the C1s spectra of samples 1 and 2 have ob-

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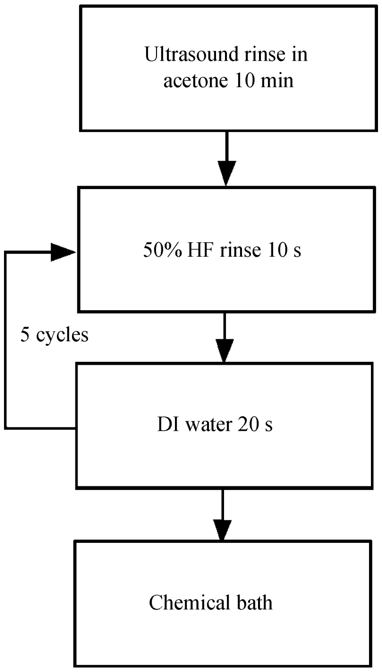

Fig. 1. Substrate-cleaning process. A clean surface with Ge-H bonds is critical for use in the chemical bath.

Table 1. Conditions for different experiments. Sample 7 was cleaned, but a chemical bath was not applied. Sample 8 was as-received 3.7-nm oxide.

Sample	Environment	Bath time (h)	Temperature (℃)
1	1-octadecene	2	160
2	1-octadecene	2	80
3	1-octadecene	1	80
4	1-hexadecene	2	160
5	1-tetradecene	2	160
6	1-dodecene	2	160
7	Clean, no layer	N/A	N/A
8	Native oxide	N/A	N/A

vious peaks at 283.4 eV; these are below the main C–C peaks and are ascribable to Ge–C surface bonds. Sample 2 has a third peak at 286.3 eV, which indicates that the surface may not be fully covered by the C-containing layer. The peaks at 30.2 eV in the Ge3d spectra in Fig. 3 prove the presence of Ge–C. In Fig. 3(b), there is a Ge–O peak at 33 eV which is not obvious in Fig. 3(a). This is the result of the oxidation of unreacted Ge–H bonds at a later stage in the process[12]. Higher temperatures ensure increased coverage of the surface by the blocking layer and lead to better results.

The monolayer thickness can be calculated using a substrate-overlayer model[13, 14]. The thickness of the overlayer can be determined by using Eq. (1):

$$d_{\rm ov} = \lambda \sin\theta \times \ln\left[1 + ({\rm SF_{Ge}}/{\rm SF_{ov}})\,(I_{\rm ov}/I_{\rm Ge})\,(\rho_{\rm Ge}/\rho_{\rm ov})\right], \tag{1}$$

in which SF is the sensitivity factor, I is the raw intensity, ρ is the density of the layer, λ is the escape depth through the overlayer for electrons, and θ is the takeoff angle from the horizontal used in collection of the XPS data (35°). If the Ge3d and C1s data are used to solve Eq. (1)[15], the results indicate that the thickness is about 2.4 nm. Figure 4(a) is a cross-sectional transmission electron microscopy (TEM) image of sample 1. The blocking layer has a thickness of about 2.2 nm, which agrees well with the calculated value. The layer thickness of sample 6 can also be obtained from Fig. 4(b), which is 1.3 nm.

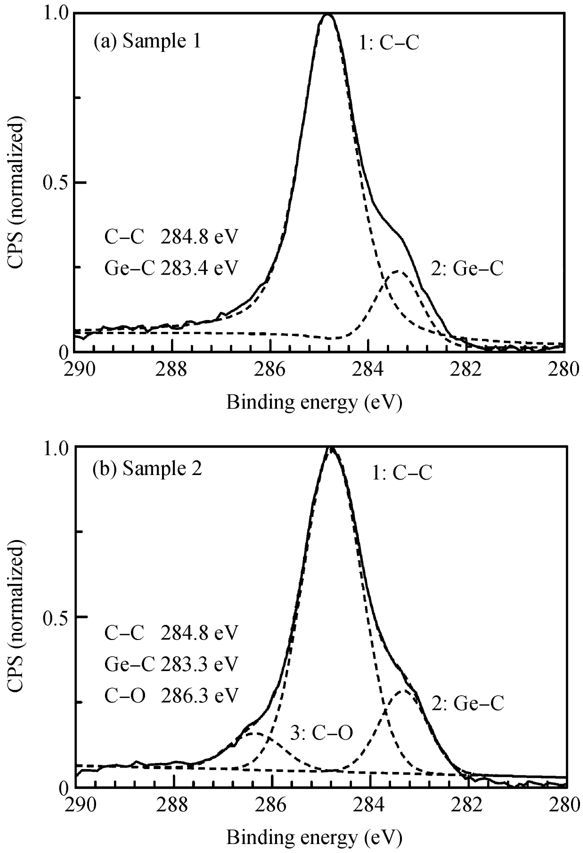

Fig. 2. Detailed XPS spectra of C1s. (a) Sample 1 was in the bath for a longer time and at higher temperature. The peak at the binding energy lower than that of C–C represents electrons shifting to C, which suggests a Ge–C bond. (b) The third peak indicates a C–O bond, as a result of the lower temperature and short bath time. The surface was not completely covered.

The SBH and the pinning factor were obtained by using the electronic properties of the samples. A three-terminal measuring method was used to reduce the effective substrate resistance and avoid the parasitic effects of the probes[6, 16]. The current density versus voltage (J–V) characteristics measured for monolayers bathed in 1-octadecene under different conditions (samples 1, 2, 3, and 7) are shown in Fig. 5(a). There is strong pinning for the sample without a blocking layer (sample 7). The obvious rectification characteristic indicates that there is a high barrier in the reverse voltage bias if there is no interface between the Ge substrate and the metal. After inserting the blocking layer, the pinning was released. The current density of both the forward and reverse biases increased due to the reduction of MIGS. The differences of current density between samples 1–3 are larger in low positive bias than in large positive bias, which indicates the presence of different SBH. Figure 5(b) shows the J–V characteristics of the samples bathed in different environments below 180 ℃ for 2 h (samples 1, 4, 5, and 6). All the samples show good ohmic characteristics. The Fermi-level pinning was released in the reverse voltage bias

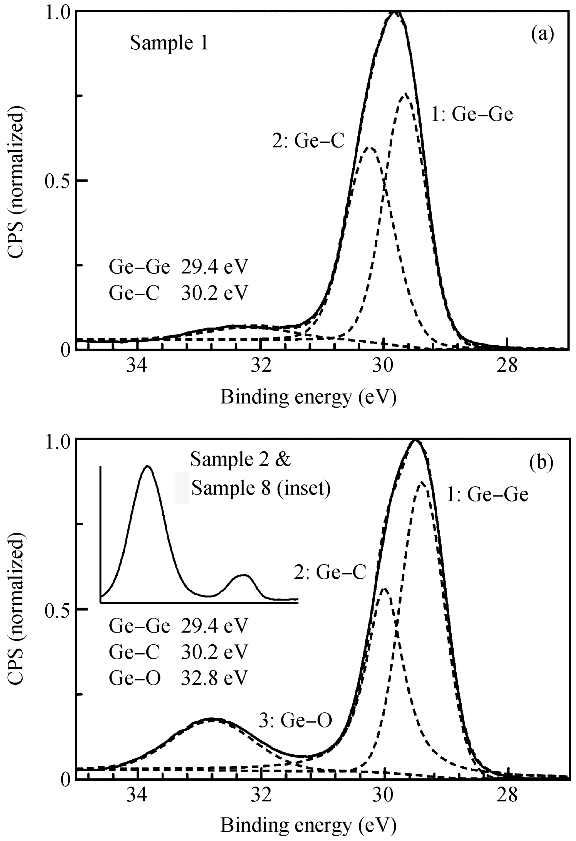

Fig. 3. Detailed XPS spectra of Ge3d. (a) For sample 1, the higher binding energy peak at 30.2 eV is assigned to Ge–C. (b) There is an obvious Ge–O peak for sample 2.

region when the temperature was high enough and the bathing time long enough, compared to the samples treated at 80 ℃ and 1 h. The blocking-layer effects were related to the C-chain lengths. None of the samples behaved anomalously, unlike the case of previous research on Si gate insulators[17].

The current densities of the different samples at $V = 1$ V with increasing thickness of the blocking layer[18] are shown in Fig. 6. Although the current density of samples 5 (C_{14}) and 6 (C_{12}) were significantly increased in the reverse bias region, they are smaller than that of the sample without a blocking layer, at high positive voltages. In samples 5 and 6, the blocking layers only prevent MIGS to a small extent, as a result of the lack of layer thickness, and little control of the wave function penetration, while introducing new tunneling barriers to the junction. When the layers get thicker, the current density increases significantly as seen in samples 1–4 due to low SBH. However, in sample 8, the 3.7-nm native oxide layer seems to be too thick for blocking purposes, without introducing a large tunneling barrier. The maximum current density is at an optimal point where the heights of these two barriers are both acceptable.

For a metal/very thin insulator/Ge structure, the commonly used transport mechanism is mainly thermionic emission mixed with tunneling[19, 20], as described by Eq. (2):

$$J = A^* T^2 \exp\left(-\phi_{\mathrm{b,eff}}/k_{\mathrm{B}}T\right) \exp\left(eV/nk_{\mathrm{B}}T\right) \times \left[1-\exp\left(-eV/k_{\mathrm{B}}T\right)\right], \tag{2}$$

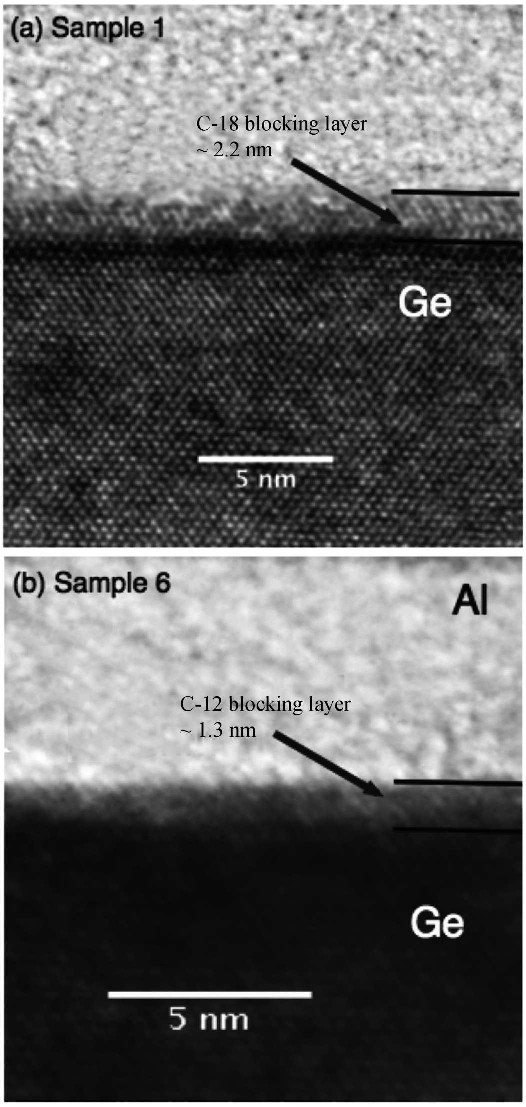

Fig. 4. Cross-sectional TEM result for (a) sample 1 (a blocking layer of thickness about 2.2 nm is formed) and (b) sample 6 (The blocking layer is about 1.3 nm).

where A^* is the Richardson constant and is 143 A/(cm^2·K^2) for n-type Ge[21]; $\phi_{\mathrm{b,eff}}$ is related to the Schottky barrier and the tunneling barrier as described in Eq. (3):

$$q\phi_{\mathrm{b,eff}} = q\phi_{\mathrm{b}} + kT\beta l, \tag{3}$$

in which β is a structure-dependent attenuation factor that depends on the tunneling mechanism and l is the tunneling thickness. The $\phi_{\mathrm{b,eff}}$ can be extracted from the J–V characteristics[22]. The sample without the blocking layer has a pure SBH of 0.62 eV, which suggests that the Fermi level is pinned just above 0.04 V from the top of the Ge valence band[5]. The best result is given by sample 1; the high temperature and long bath time leads to good coverage by the blocking layer, providing enough blocking and introducing an acceptable tunneling barrier. The $\phi_{\mathrm{b,eff}}$ is at about 0.46 eV. Considering that in a typical tunneling mechanism of an alkyl monolayer, the attenuation factor β is 0.63 per CH_2[23], the SBH of sample 1 is as low as 0.17 eV, which is 73% lower than the original value. Figure 7 shows the extracted results for some samples.

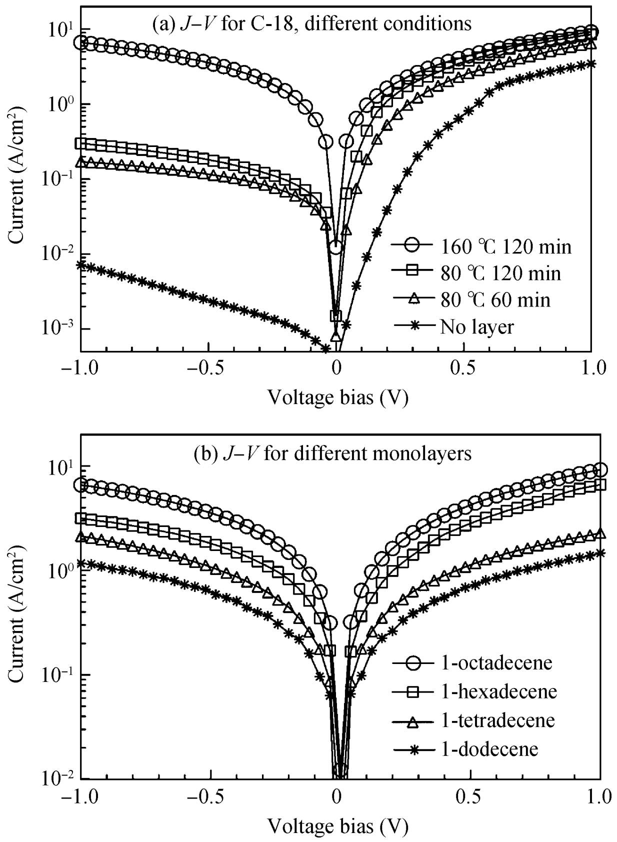

Fig. 5. (a) J–V results for samples prepared in 1-octadecene with different temperatures and durations. The results for the sample without a blocking layer show a rectification characteristic. All the other results show significant increases in both biases. (b) J–V results for the same conditions (160 ℃ and 120 min) but different bath environments.

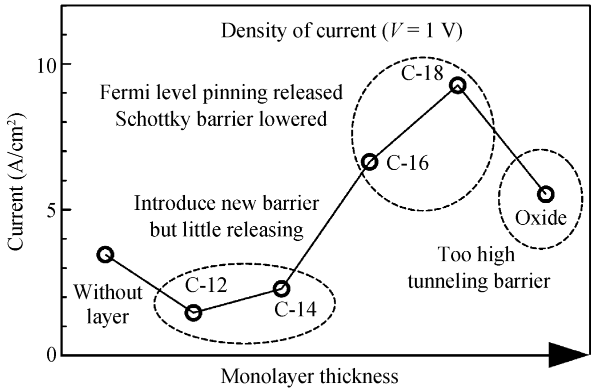

Fig. 6. Current density changes with layer thickness at high positive voltage biases. The results for the C-12 and C-14 samples are even worse than those for the clean (without a blocking layer) sample at 1 V, but are a little better in reverse bias; this suggests the existence of a tunneling barrier. The sample with the thickest layer gave a poor result because of the high tunneling barrier.

3. Conclusion

In summary, chemical baths consisting of different liquid alkenes were applied to ⟨100⟩ Ge substrates under various conditions. Alkyl monolayers were formed on the surface; these layers blocked MIGS penetration to the substrates and released the Fermi-level pinning. The derived $\phi_{\mathrm{b,eff}}$ is about 0.46 eV and the SBH is 0.17 eV. Compared with other blocking-layer formation methods, this is a very easy and promising way of forming layers to lower the effective barrier height.

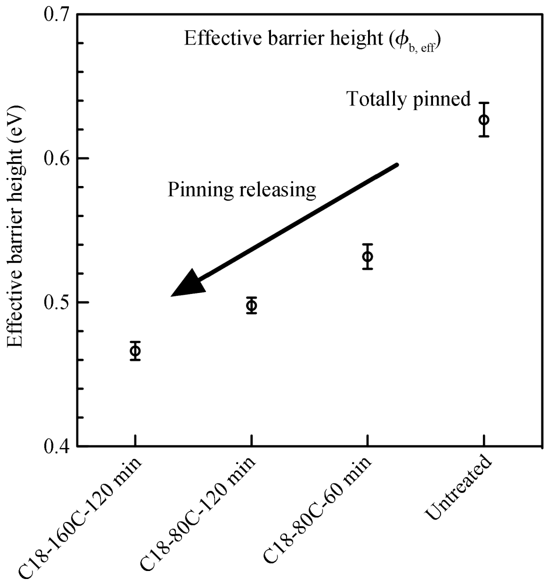

Fig. 7. Extracted $\phi_{\mathrm{b,eff}}$ values for some samples. These effective barrier heights consist of SBHs and tunneling barrier heights. The best result is 0.46 eV, and the corresponding SBH is about 0.17 eV.

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