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Study of Fermi Level Pinning at Metal/Semiconductor Interface through Re-investigation of Interfacial Alloy Interaction

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1. Introduction

It has been well known that an interface between metal and narrow gap semiconductor shows the strong Fermi level pinning (FLP) (ex. Ge [1]). Furthermore, we successfully demonstrated the FLP alleviation by inserting ultra-thin (1~2 nm-thick) oxide (UTO) between metal and Ge [2]. This effect has also been confirmed by several groups [3-5]. Although the dominant FLP mechanism has been discussed including these results, it is still unclear.

Whereas, Hiraki et al. have reported the alloy interaction between metal (ex. Au) and semiconductor with narrow band gap [6]. In the case of Au/Si stack, SiO_2 is formed on the Au surface even at room temperature (below the eutectic point) in air as shown in **Fig. 1(a)**. It was also confirmed the alloy interaction was suppressed by inserting SiO_2 between Au and Si [7]. Then, the alloy interaction seems to be related to FLP as they have also mentioned.

The objective of this work is to re-investigate the alloying interaction reported by Hiraki et al. with and without UTO and to discuss the Schottky barrier height (SBH) formation mechanism.

2. Experimental

Three kinds of semiconductors such as Ge (100), Si (100) and 4H-SiC (0001), (000$\bar{1}$) substrates were prepared by HF-last process. 20 nm-thick Au was thermally evaporated on substrates in a vacuum chamber. The alloy interaction was performed by heating the samples at 75-140°C. The thickness and bonding state of oxides grown on Au were characterized by X-ray photoemission spectroscopy (XPS).

3. Results and Discussion

3.1 Oxide growth and semiconductor consumption

As reported in ref. 6, in the present study, oxides were observed over the top of Au on Si and Ge, whereas oxide was never on SiC. **Fig. 1(b)** shows the XPS spectra of Si 2p of Au/Si stacks annealed at 75°C. The intensity of Si 2p peak assigned to SiO_2 increases with increasing annealing time. The SiO_2 thickness grown on Au was estimated by XPS spectra as shown in **Fig. 1(c)**.

On the other hand, in the case of Ge, GeO_x was immediately formed on as-deposited Au film as shown in **Fig. 2(a)**. Furthermore, the intensity of Ge 3d peak little increased by thermal annealing in contrast to case of Si. **Figure 2(b)** shows the thickness of GeO_x as a function of annealing time. It was almost saturated below a few nm. This fact indicates that the rate-limiting process of GeO_x growth seems to be different from that of SiO_2 one.

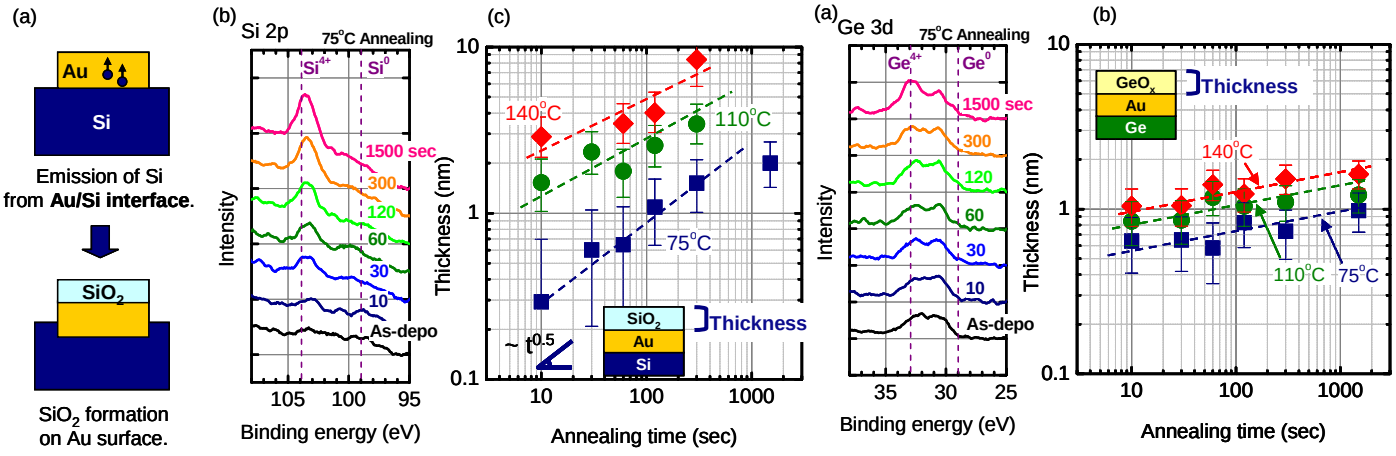

Fig. 1 (a) Schematic diagram of alloy interaction of Au/Si stacks reported by Hiraki et al. [6] By removing reacted Au and grown SiO_2, we can observe a trench formed by the alloy interaction. **(b)** XPS spectra of Si 2p of 20-nm thick Au/Si stack annealed at 75°C for various time. A peak intensity of Si 2p deriving from SiO_2 on Au was gradually increased. **(c)** SiO_2 thickness grown by thermal annealing at various temperatures estimated by XPS. SiO_2 thickness on Au is roughly proportional to $t^{0.5}$, which implies that a diffusion process in the SiO_2 limits the SiO_2 growth [8].

Fig. 2 (a). XPS spectra of Ge 3d of 20-nm thick Au/Ge stack annealed at 75°C for various time. GeO_x has already grown on Au before annealing. With increasing annealing time, the intensity of Ge 3d slightly increased. **(c)** GeO_x thickness grown by thermal annealing at various temperatures.

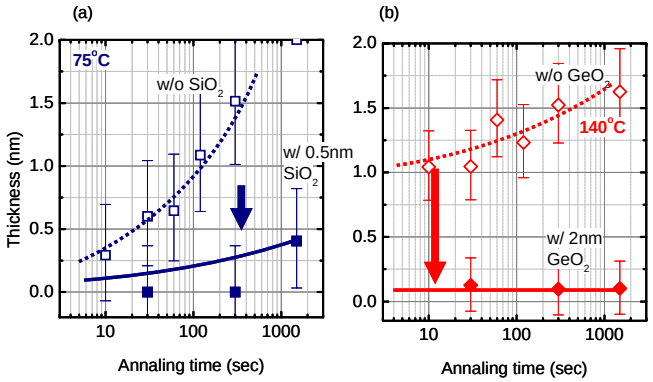

Fig. 3 (a) The SiO_2 thickness grown on Au/SiO_2(0.5 nm)/Si (solid line) and Au/Si (broken line) grown by annealing at 75°C. **(b)** The GeO_x thickness Au/GeO_2(2 nm)/Ge and Au/Ge grown by annealing at 140°C. Even at 140°C, GeO_x is hardly grown on Au/GeO_2/Ge, which suggests that the interface GeO_2 significantly suppresses the GeO_x growth on Au.

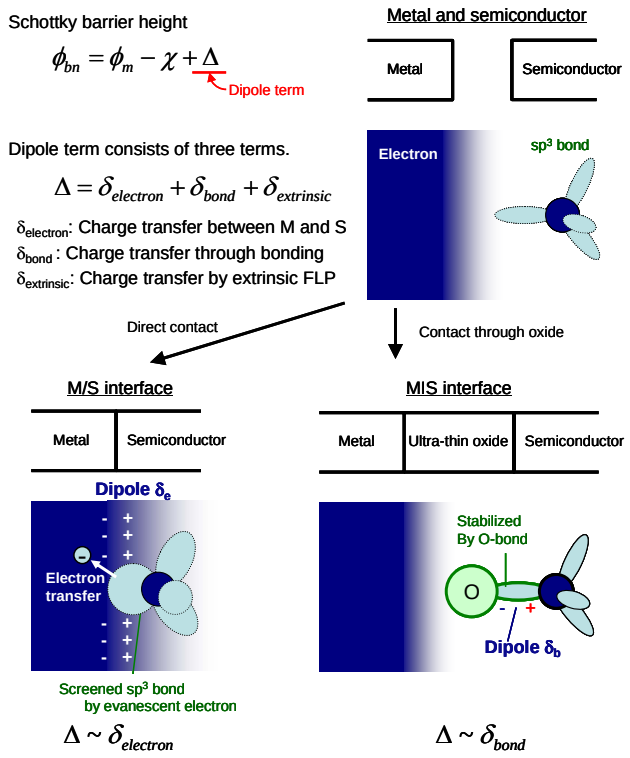

Fig. 4 Schematic diagrams of charge transfer mechanisms. FLP is described as the dipole of Δ in the equation. The Δ consists of three terms of charge transfer between metal and semiconductor: $\delta_{electron}$, charge transfer through the interfacing bond: δ_{bond} and extrinsic charge transfer: $\delta_{extrinsic}$. (The $\delta_{electron}$ term is direct electron transfer between metal and semiconductor. The δ_{bond} term is dipole formed by chemical bonding.) Then, at direct M/S interface, the $\delta_{electron}$ is dominantly effective due to the strong screening. However, at M/UTO/S interface, the δ_{bond} is also effective due to O-S bonding. With increasing the UTO thickness, $\delta_{electron}$, is weakened due to the reduction of the screening effect, and δ_{bond} turn to be more dominant.

3.2 An impact of interfacial oxide at Au/Ge interface

0.5 nm-thick SiO_2 on Si and 2 nm-thick GeO_2 on Ge were formed by H_2SO_4+H_2O_2 solution and by thermal annealing at 400°C, respectively. **Figure 3** shows the thickness of oxide grown on the Au by alloy interaction. The interfacial SiO_2 at the interface effectively suppressed SiO_2 growth on Au. Furthermore, the interfacial GeO_2 almost inhibits GeO_x growth on the Au even at 140°C.

Based on the present and previously obtained results in our study, we propose the FLP mechanism of metal/semiconductor (M/S) interface. The essential point is that the FLP is not determined by single origin but multiple ones. We should consider both dipole shift and defect-induced states at the interface as shown in **Fig. 4**. Furthermore, the dipole shift comes from two origins. One is the charge-transfer between metal and semiconductor and the level to be charge-transferred is determined by the semiconductor side. This is the case of M/S interface. The other is the charge-transfer through the interfacing bonds in the case of M/UTO/S interface.

As Hiraki et al. mentioned, at direct M/S interface, sp^3 hybrid bonds are screened by the metal, of which electrons may weaken the semiconductor bonding [6]. Whereas, we have confirmed that 2 nm-thick oxide can perfectly suppress the alloy interaction. Namely, the screening of sp^3 hybrid bonds should be well suppressed. However, there can still be the dipole shift due to the charge-transfer through the interfacing bond. In fact, it has been recently reported that the epitaxially grown metal/Ge interface is not pinned at the valence band edge of Ge [9]. This fact is simply understandable from the viewpoint of the charge-transfer through the interfacing bond.

Furthermore, even though the UTO film is inserted, the FLP is still observable (S<1). This might be due to the additional extrinsic FLP mechanism (ex. defects at oxide/semiconductor interface), which disappears under the stronger pinning origin in case of narrower band gap semiconductors.

4. Conclusion

Interfacial reaction between Au and group IV semiconductors was re-investigated. SiO_2 and GeO_x are grown on Au/Si and Au/Ge, respectively, but not on SiC. Furthermore, the interface oxide suppresses the alloying interaction. From the FLP behavior and the alloy interaction at direct M/S interface and at M/UTO/S one, it is reasonably understandable that the SBH at M/S interface is determined by both charge transfer between metal and semiconductor and that through the interfacing bond.

References

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