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RESEARCH ARTICLE

# Effects of Carbon Incorporation on Electrical Characteristics and Thermal Stability of Ti/TiO$_2$/*n*-Ge MIS Contact

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**ABSTRACT** The effects of carbon incorporation on the thermal stability of the interfacial TiO$_2$ layer and the electrical characteristics of Ti/TiO$_2$/*n*-Ge contacts were investigated. The improved thermal stability and contact characteristics of Ti/TiO$_2$/*n*-Ge contacts were characterized in terms of Schottky barrier height (SBH) and specific contact resistivity ($\rho_c$) using the Schottky diode and circular transmission line model (CTLM). The values of SBH and $\rho_c$ increased after the rapid thermal annealing (RTA) above 550 °C. The current density–bias voltage ($J - V$) curves of the Schottky diode showed a change of contact characteristics from Ohmic-like behavior to rectifying. This thermal instability was mainly caused by the decomposition of the interfacial TiO$_2$ layer after high-temperature annealing. The structural degradation was confirmed by transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) analyses. When carbon ions were incorporated into the interfacial TiO$_2$ layer, the SBH and $\rho_c$ values showed relatively stable characteristics as the RTA temperature increased up to 600 °C. The EELS mapping showed that the diffusion of oxygen from the interfacial TiO$_2$ layer was effectively suppressed thanks to the incorporation of carbon. Thus, the carbon incorporation can improve the thermal stability of the interfacial TiO$_2$ layer and the metal–insulator–semiconductor contact characteristics for Ge-based device applications.

**INDEX TERMS** Germanium, metal−insulator−semiconductor, thermal stability, Schottky barrier height, Fermi-level pinning, contact resistivity.

## I. INTRODUCTION

Germanium (Ge) has been introduced as a promising replacement for silicon (Si) as a channel material in future complementary metal–oxide–semiconductor (CMOS) devices owing to its high carrier mobility and high compatibility with the advanced Si device fabrication technology [1], [2], [3]. However, the formation of source and drain (S/D) contact with a low contact resistance is a major bottleneck in the commercialization of Ge-based devices. This is mainly attributed to the solid solubility and diffusivity issues of *n*-type dopants in Ge and the Fermi-level pinning (FLP) effect [4], [5], [6]. The FLP effect originates from the metal-induced gap states (MIGS) in the vicinity of a metal/Ge interface. Because it causes near the valence band ($E_v$) of Ge, it increases Schottky barrier height (SBH) to above 0.5 eV regardless of the metal work function [7], [8], [9].

In recent years, metal–insulator–semiconductor (MIS) contact has been proposed to mitigate the FLP effect. As an ultrathin insulator is inserted between metal and

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semiconductor as an interfacial layer, the penetration of the electron wave function from a metal into a semiconductor could be reduced; this suppresses the FLP effect [10], [11]. Among several high-$k$ dielectrics, titanium dioxide ($TiO_2$) is a promising candidate as an interfacial layer of MIS contact because of its negligible conduction band offset (CBO) on an $n$-Ge (100) substrate and its relatively high conductivity, which contributes to the low tunneling resistance of MIS contacts [12], [13], [14]. However, considering that the high thermal budget process after the formation of S/D contact such as conventional back-end-of-line (BEOL) processes, the thermal stability of MIS contacts in the $n$-Ge device must be guaranteed above 400 °C to achieve the low S/D contact resistance.

Several manners have been reported to improve the thermal stability of MIS contacts, for instance, nitrogen plasma treatment and hydrogen annealing [15], [16], [17]. Also, carbon implantation (C-imp) has been utilized to achieve low specific contact resistivity ($\rho_c$) values and to improve the thermal stability of alloying metal–semiconductor (MS) contacts such as silicide and germanide. Besides, C-imp could enhance dopant segregation and reduce FLP in Ti/Ge contacts [18].

In this work, we investigated the effects of carbon incorporation on the thermal stability of the interfacial $TiO_2$ layer of MIS contact and the electrical characteristics of Ti/$TiO_2$/$n$-Ge contacts at thermal annealing temperatures of 450–600 °C. The structural characterization of the interfacial $TiO_2$ layer was analyzed using transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS). Schottky diodes and a circular transmission line model (CTLM) were used to characterize the contact characteristics and thermal stability of Ti/$TiO_2$/$n$-Ge contacts with carbon incorporated $TiO_2$ layer.

## II. EXPERIMENTAL METHODS

Schottky diodes and CTLM test structures were fabricated on $n$-type Ge substrate to analyze the contact characteristics of Ti/$TiO_2$/$n$-Ge such as SBH and $\rho_c$, respectively. The detailed fabrication flow has been described as follows: moderately doped $n$-type 4-inch Ge (100) wafers ($\sim 10^{18}$ cm$^{-3}$) were used as starting materials. The wafers were cleaned with acetone and rinsed with deionized (D.I.) water. And then, the wafers were dipped in 2% diluted hydrofluoric acid (dHF, HF: $H_2O$ = 1:50 ml: ml) in order to remove native oxides and rinsed with D.I. water. First, a 100-nm-thick $SiO_2$ layer was deposited using plasma-enhanced chemical vapor deposition (PECVD) to isolate the contact holes where the pressure, RF power, and temperature were 8 mTorr, 600W, and 300 °C. Subsequently, the Schottky diode and CTLM test structure were patterned using photolithography for micron patterns and an i-line stepper for the sub-micron patterns, respectively. Sequentially, the patterned PECVD oxide was etched using a dry etcher, and the interfacial $TiO_2$ layers were deposited using atomic layer deposition (ALD) to create an MIS structure. The precursors for the ALD $TiO_2$ layer were tetrakis(dimethylamido)titanium (TDMA-Ti) and $H_2O$. The atomic deposition of $TiO_2$ layers was performed with 50 cycles at 200 °C atmospheres to form a 2-nm-thick layer.

Next, carbon ions were implanted into the interfacial $TiO_2$ layer in order to form a diffusion barrier of oxygen ions and to amorphize the surface using an ion implanter (Nissin Ion, Impheat). And the ion implantation condition is as follows: An implantation dose of $10^{15}$ cm$^{-2}$, implantation energy of 10 keV, and a tilt angle of 7°. The optimal ion implantation condition has been established considering the series resistances of Ti/$TiO_2$/$n$-Ge contacts. Then, Ti (5 nm)/TiN (5 nm) layers were deposited using a DC sputtering system. Thereafter, heat treatment was carried out in $N_2$ ambient for 60 s at 450–600 °C using RTA.

After the fabrication of Schottky diodes and CTLM test structures, the electrical characteristics were analyzed using *Keithley 4200-SCS*. The current density–bias voltage ($J-V$) curves of Schottky diodes were measured, and the values of SBH were calculated using the current-temperature (*I-T*) method. Also, the $\rho_c$ values of Ti/$TiO_2$/$n$-Ge contacts were extracted using the transfer length
method (TLM).

Preparing the specimens for the TEM and EELS analyses was performed using a dual-beam focused ion beam (Dual-FIB) with $Ga^+$ ion beam milling and thinning at 30 kV acceleration voltage. Then, conventional TEM images and EELS maps of Ti/$TiO_2$/$n$-Ge contacts with and without C-imp were obtained using a JEOL JEM 2200FS with an image Cs-corrector.

## III. RESULTS AND DISCUSSION

Fig. 1 shows the reverse current density ($J_{OFF}$), which is measured under bias condition: V = −2.0V, of the Ti/$TiO_2$/$n$-Ge Schottky diode with and without C-imp as a function of the annealing temperature. The insets show the $J-V$ characteristics of Ti/$TiO_2$/$n$-Ge diode with and without C-imp. The $J_{OFF}$ values with and without C-imp after RTA at 450 °C show an Ohmic behavior due to alleviation of FLP by inserting the interfacial $TiO_2$ layer. However, as the annealing temperature increases, $J_{OFF}$ without C-imp decreases significantly, but the $J_{OFF}$ with C-imp was almost consistent. In other words, the Ti/$TiO_2$/$n$-Ge Schottky diode with C-imp shows stable Ohmic characteristics after high-temperature annealing. On the other hand, the Ti/$TiO_2$/$n$-Ge Schottky diode without C-imp shows the non-linear characteristic, which is attributed to the poor thermal stability of $TiO_2$ mainly due to the out-diffusion of oxygen [19], [20], [21].

The SBH values have been extracted from the current–temperature (*I-T*) curves of Ti/$TiO_2$/$n$-Ge Schottky diodes with and without C-imp for 27–105 °C. The *I-V* relationship for fabricated Schottky diodes is represented by [22]

$$I = AA^{*}e^{-q\emptyset_B/kT}\left(e^{qV/nkT}-1\right) = I_s\left(e^{qV/nkT}-1\right) \quad (1)$$

where $I_s$ is the saturation current, $A$ is the diode area, $A^{*} = 4\pi qk^2m^{*}/h^3 = 120\,(m^{*}/m)$ A/cm$^2$-K$^2$ is Richardson's constant, $\Phi_B$ is the barrier height, and $n$ is the ideality factor.

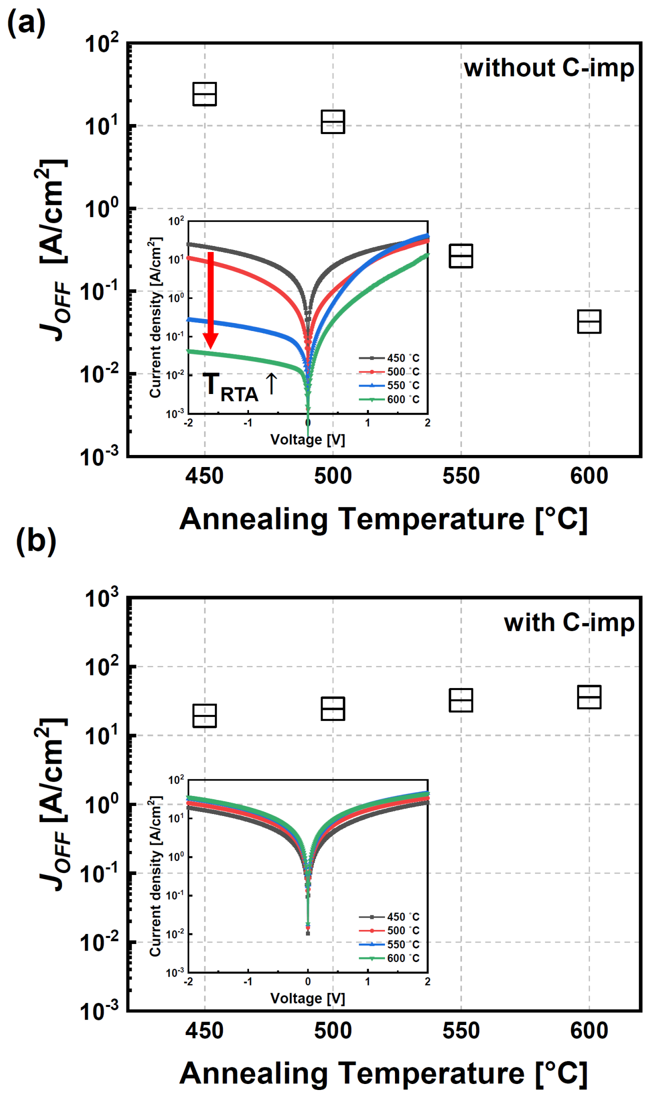

FIGURE 1. $J_{OFF}$ of Ti/TiO$_2$/*n*-Ge contacts (a) without and (b) with C-imp after RTA at 450–600 °C for 60 s in $N_2$ ambient. Inset: corresponding *J-V* curves at various RTA temperatures.

For V≫kT/q, equation (1) can be written as follows:

$$\ln\left(I/T^2\right) = \ln\left(AA^*\right) - q\left(\emptyset_B - V/n\right)/kT \qquad (2)$$

$$\begin{aligned}\emptyset_B &= \frac{V}{n} - \frac{k}{q}\frac{d\left[\ln\left(I/T^2\right)\right]}{d(1/T)}\\ &= \frac{V}{n} - \frac{2.3\,k}{q}\frac{d\left[\log\left(I/T^2\right)\right]}{d(1/T)}\end{aligned} \qquad (3)$$

The barrier height is calculated from the slope $\left(d\left[\ln\left(I/T^2\right)\right]/d\left(1/T\right)\right)$ using bandgap energy $(E_g)$ of 0.66 and an electron affinity $(\chi)$ of 4.0 eV for Ge at 300 K.

Fig. 2 shows the calculated SBH of Ti/TiO$_2$/*n*-Ge after RTA. Without C-imp, the SBH is constant at ∼ 0.35 eV below 500 °C. Above 550 °C, the SBH increases and enters into the FLP regime. Such SBH degradation is attributed to the decomposition of the TiO$_2$ interlayer at the MS interfaces. With C-imp, the SBH is constant up to 600 °C. This suggests that FLP is suppressed in the MIS structure even after RTA temperatures above 550 °C.

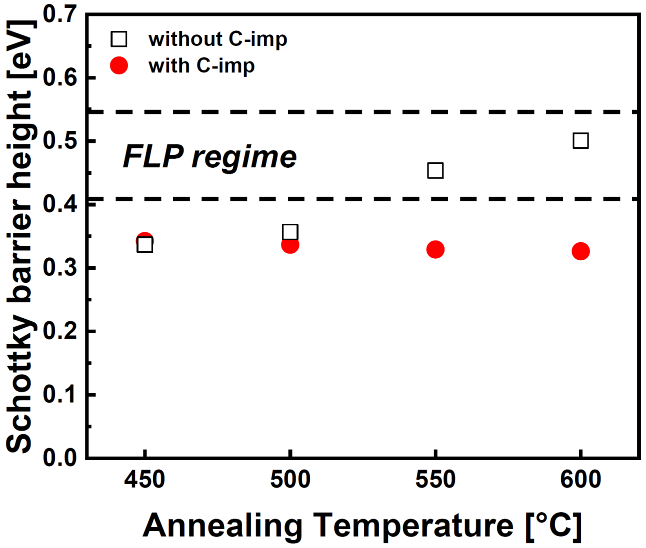

FIGURE 2. SBH of the Ti/TiO$_2$/*n*-Ge contacts without (black rectangle) and with (red circle) C-imp after RTA at 450–600 °C.

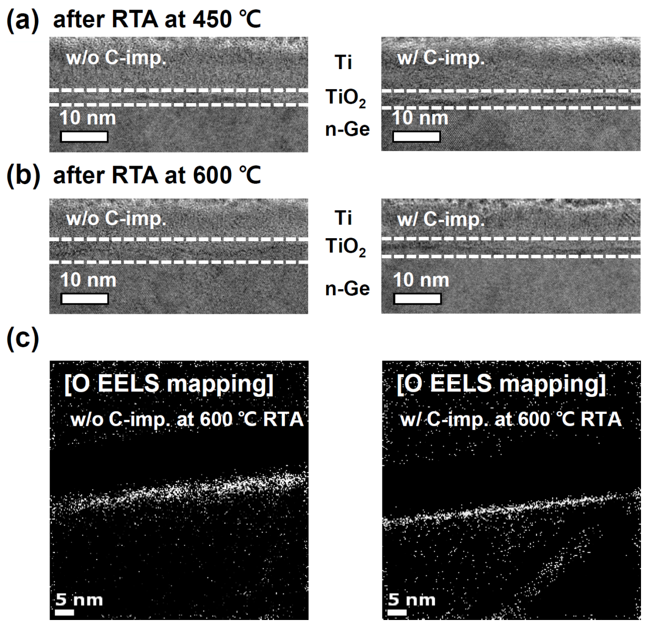

FIGURE 3. Cross-sectional TEM images of the Ti/TiO$_2$/*n*-Ge contacts without and with C-imp after RTA at (a) 450 and (b) 600 °C, and (c) the corresponding EELS maps for oxygen after RTA at 600 °C.

Cross-sectional TEM images and EELS maps were used to understand the effect of the RTA temperature on the *J*–*V* and SBH behaviors. After RTA at 450 °C, there is no deformation of TiO$_2$ layer irrespective of C-imp, as shown in Fig. 3(a). However, after RTA at 600 °C, the TiO$_2$ layer without C-imp becomes faint because of decomposition. This can be suppressed with C-imp, as shown in Fig. 3(b). Fig. 3(c) shows the EELS maps of oxygen for the Ti/TiO$_2$/*n*-Ge structures. The bright regions represent the areas with abundant oxygen.

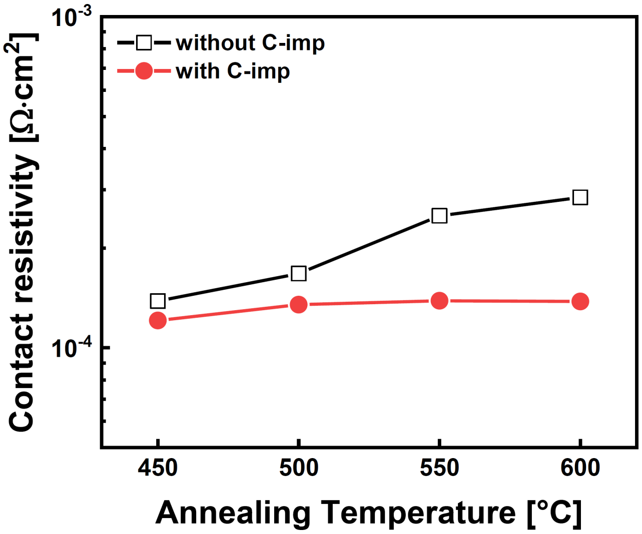

**FIGURE 4.** $\rho_c$ of Ti/TiO$_2$/*n*-Ge contacts without (black curve) and with (red curve) C-imp as a function of RTA temperature.

The TiO$_2$ layer in Ti/TiO$_2$/*n*-Ge without C-imp is thicker than that in Ti/TiO$_2$/*n*-Ge with C-imp. This indicates that C-imp effectively reduces the out-diffusion of oxygen from the TiO$_2$ layer up to an RTA temperature of 600 °C.

Fig. 4 shows the $\rho_c$ values obtained using the CTLM test structure versus the RTA temperature. At 600 °C, the $\rho_c$ value of the sample without C-imp is similar to that of the Ti/*n*-Ge MS contact. This suggests that the TiO$_2$ layer collapses and the MIS structure changes to an MS-like structure. The $\rho_c$ value of the Ti/TiO$_2$/*n*-Ge contact with C-imp is constant ($\sim 1.3 \times 10^{-4}\Omega\cdot\text{cm}^2$) up to 600 °C.

Thus, carbon incorporation effectively improves the thermal stability of the TiO$_2$ layer, thereby enhancing the electrical characteristics of the Ti/TiO$_2$/*n*-Ge contact.

## IV. CONCLUSION

We experimentally demonstrated the effects of carbon incorporation on the electrical characteristics and thermal stability of the TiO$_2$ interfacial layer for Ti/TiO$_2$/*n*-Ge contacts. The MIS contact degraded at an RTA temperature above 550 °C. This degradation was caused by the deformation of TiO$_2$, which was confirmed through TEM images and EELS maps. Carbon incorporation effectively improved the thermal stability of TiO$_2$ with RTA. With C-imp, the SBH and $\rho_c$ were relatively constant up to an RTA temperature of 600 °C. Thus, carbon incorporation effectively improves the thermal stability of MIS contacts, which can help develop high-performance Ge-based devices.

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