Temperature Dependent Current Transport Mechanism in Graphene/Germanium Schottky Barrier Diode

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Abstract—We have investigated electrical properties of graphene/Ge Schottky barrier diode (SBD) fabricated on Ge film epitaxially grown on Si substrate. When decreasing temperature, barrier height decreased and ideality factor increased, implying their strong temperature dependency. From the conventional Richardson plot, Richardson constant was much less than the theoretical value for n-type Ge. Assuming Gaussian distribution of Schottky barrier height with mean Schottky barrier height and standard deviation, Richardson constant extracted from the modified Richardson plot was comparable to the theoretical value for n-type Ge. Thus, the abnormal temperature dependent Schottky behavior of graphene/Ge SBD could be associated with a considerable deviation from the ideal thermionic emission caused by Schottky barrier inhomogeneities.

Index Terms—Graphene, Ge, Si, Schottky barrier height, ideality factor, Schottky barrier inhomogeneities, Gaussian distribution

I. INTRODUCTION

The scaling limits of Silicon (Si) complementary metal oxide semiconductor (CMOS) devices has led to search for an alternative semiconductor material. Germanium (Ge) has been considered as an alternative material for next generation CMOS devices and Si monolithic integration due to its symmetric high speed of electron and holes, low cost, and high absorption coefficient. The main challenge in the realization of high performance Ge-based CMOS devices is posed by the effect of strong Fermi-level pinning close to the valence band of Ge [1-3]. This makes it difficult to modulate the barrier heights (BHs) of metal/Ge junctions by the selection of the metals with different work functions.

To date, two reported causes of Fermi-level pinning observable are: 1) surface states such as dangling bond or vacancy defect and 2) metal induced gap states affected by electron wave function tailoring into Ge [4]. However, some control techniques of BH for metal/Ge contacts were proposed such as plasma treatment [5], segregation [6] and insertion of a thin insulator layer between the metal and Ge [7], the exact mechanism of these techniques not fully understood and still requires further understanding of the interface layer. In recent years, graphene has been considered as a valuable material in both fundamental science and technology because it offers flexibility, mechanical robustness and chemical inertness combined with excellent electrical and optical properties. Khurelbaatar et al. [8] observed that graphene is effective in depinning the Fermi level in Ge. Zheng et al. [9] reported the fabrication of infrared photodetector based on graphene and bulk Ge Schottky junction, where monolayer...
graphene used as transparent electrode. Although, produced graphene/Ge junction shows the typical rectifying behavior which can be described by the thermionic-emission theory, bulk Ge substrate is not compatible with future CMOS application and Si photonic integration. In this context, an attempt to fabricate device on Si based substrate is necessary with heteroepitaxial growth of pure Ge as an active material on Si substrate. On the other words, Ge growth on Si (Ge-on-Si) is more compatible with CMOS circuitry and Si based monolithic integration on a same chip because of its relatively straightforward fabrication technique when compared with free-standing bulk Ge substrate [10-13]. However, the reports on the detailed electrical transport characteristics using temperature dependent I-V characteristics of the graphene/Ge junctions that reveals the nature of the interface are quiet scarce. Moreover, analysis of the electrical characteristics of metal semiconductor structures only at room temperature cannot provide us with detailed information regarding their current conduction mechanisms or the nature of barrier formation at the metal/semiconductor interface [14].

In this work, we have fabricated the graphene/Ge Schottky barrier diode (SBD) using Ge-on-Si substrate and investigated its electrical characteristics in the temperature range of 200-400 K with a temperature step of 40 K. The Schottky barrier height ($\Phi_B$), ideality factor ($n$), and saturation current ($I_0$) of graphene/Ge SBD are extracted at different temperatures. Temperature dependent barrier characteristics of the graphene/Ge SBD are also interpreted based on the existence of the Gaussian distribution of the BHs.

II. EXPERIMENT

Fig. 1 shows a schematic of the fabrication process of the graphene/Ge SBD. The Ge epitaxial layers were grown on phosphorus doped n-type Si (100) wafers with resistivity in the range of 5-15 Ω-cm by using a rapid thermal chemical vapor deposition (RTCVD) method Fig. 1(a). Prior to Ge growth, the Si wafers were piranha-cleaned with H$_2$O$_2$+H$_2$SO$_4$ (1:2) solution and rinsed in deionized water. Native oxides were etched in diluted HF solution for 15 sec, blow dried in nitrogen. Then, Ge buffer layers of 110 nm were grown at 380°C under a process pressure of 20 Torr. GeH$_4$ (20% in H$_2$) source gas was used at 30 sccm with 20 slm of H$_2$ as a carrier gas. Subsequently, phosphorus-doped n-type Ge layers with a thickness of 1.5 μm were grown at 520°C using 100 ppm phosphine (PH$_3$) in H$_2$ as a dopant source under same gas flow rate in the epitaxial growth of Ge buffer layer. The carrier concentration of n-type Ge epilayer, extracted from Hall measurement, was found to be 9.3 × 10$^{16}$ cm$^{-2}$. The cross-sectional transmission electron microscope (TEM) image combined with electron diffraction pattern revealed that epitaxial Ge layer with highly uniform interface and surface morphologies was formed on Si (100) wafers (Fig. 1(d)). After that, the epitaxial grown substrate were cleaned by solvents, a 300 nm thick SiO$_2$ layers was deposited on the substrate using plasma enhanced chemical vapor deposition (PECVD) to isolate the metal contact from the Ge epitaxial layer Fig. 1(b) and windows were opened in the oxide layer on top of the Ge layer.

Monolayer of graphene was synthesized by using low pressure chemical vapor deposition (LPCVD). A polycrystalline copper (Cu) foil (Nippon Mining, 0.035 mm) were used as a metal catalyst and then was loaded into a vacuum quartz tube. Subsequently, the sample was heated up to 1050°C and maintained for 45 minutes for hydrogen annealing that leads to reduction of oxidized surface and large copper grains. The hydrogen (H$_2$) annealing was performed with a H$_2$ pressure of 67 mtorr and flow rate of 5 sccm. After the annealing process,
graphene was grown under ~200 mtorr for 13 min with a gas flow of 20 sccm of methane (CH₄) in conjunction with 5 sccm of H₂. Finally, the grown graphene on Cu foils was rapidly cooled down to room temperature under a 5 sccm flow rate of H₂. In order to transfer the grown graphene onto other substrates, the graphene/Cu was coated with poly methyl methacrylate (PMMA) at 4200 rpm for 50 seconds. Subsequently, the Cu foil was etched away in ammonium persulfate (NH₄)₂S₂O₈ solution, and then the PMMA/graphene film was rinsed with deionized water. Finally, the PMMA backed graphene was transferred onto the prepared substrate. Graphene/Ge Schottky junctions with the contact area of 0.00785 cm² fabricated on Ge-on-Si substrate. The Raman spectrum (not shown here) taken from graphene transferred onto Ge substrate measured and typical monolayer feature of CVD-grown graphene, i.e., a 2D-to-G intensity ratio of > 2 [15, 16]. Finally, for ease of electrical probing, a 10 nm Ti and 90 nm Au metal contacts were patterned on the G areas lying on SiO₂ using photolithography, e-beam evaporation, and subsequent lift-off Fig. 1(c). Fig. 1(d) shows the optical image of fabricated graphene/Ge SBD. The electrical I-V characteristic of the graphene/Ge SBD were evaluated by semiconductor parameter analyzer (Agilent technologies, HP4155A) over the temperature range of 200-400 K in steps of 40 K under dark condition.

III. RESULTS AND DISCUSSIONS

Temperature dependent I-V characteristics of graphene/Ge SBD were characterized in order to extract transport properties. Temperature dependent I-V measurement would enable determination of barrier height without any assumptions of the electrically active area or the presence of any interfacial layer. Fig. 2 shows the forward and reverse bias semi-logarithmic I-V characteristics of the graphene/Ge SBD measured over a temperatures ranging from 200 to 400 K in a step of 40 K. As shown in Fig. 2, all the I-V curves depict rectification behavior with a nonlinear behavior at low voltage and the current increases exponentially with the increasing voltage due to the Schottky nature of the junction between graphene and Ge. It is noted that the leakage currents of graphene/Ge SBD increases with an increase in temperature and is in the range 7.39×10⁻⁹ A (at 200 K) to 8.87×10⁻⁶ A (at 400 K) at -1 V. The BHs of such a diode can be calculated given that it is strongly forward biased. According to the thermionic emission theory, the current across an ideal Schottky barrier at forward biased voltage (V≥3 kT/q), neglecting series and shunt resistance, can be expressed as [17, 18];

\[ I = I₀ \exp \left( \frac{qV}{n kT} \right) \left[ 1 - \exp \left( -\frac{qV}{kT} \right) \right] \]  

(1)

where V is the applied bias voltage, q is the electronic charge, k is the Boltzmann constant, T is the temperature in Kelvin, and I₀ is the reverse saturation current derived from the straight line intercept of lnI-V plot at zero bias and can be estimated by:

\[ I₀ = A' A T³ \exp \left( -\frac{qΦ_{B0}}{kT} \right) \]  

(2)

where A is the rectifier contact area, and A’ is the effective Richardson constant. Φ_{B0} is the zero bias barrier height of the graphene/Ge junction and their values were calculated from Eq. (2). In order to evaluate the BH, conventional Richardson plot of the saturation current, taking natural logarithm of Eq. (2) yields:

\[ \ln \left( \frac{I₀}{T²} \right) = \ln \left( A' A T³ \right) - \frac{qΦ_{B0}}{kT} \]  

(3)

When a forward turn-on voltage (Vₜₒ) was applied to the device, a saturation current Iₓ can be obtained, thus the Eq. (3) can transform to followings:
In this equation, the actual barrier height $\Phi_B$ is less than $\Phi_{B0}$ due to image force lowering and other factors, and the term $E_a=q(\Phi_B-V_F)$ is called activation energy [19]. The value of the $\Phi_B$ can be accurately extracted from the slope of the ln($I_0/T^2$) - 1000 / T plot.

Fig. 3 shows the Richardson plot of ln($I_0/T^2$) versus 1000/T. From the linear fit to data, barrier height was 0.42 eV. This value is comparable to barrier height measured from graphene/bulk-Ge junction (0.45 eV) [9]. Moreover, the Richardson constant, extracted from y-axis intercept of fitted line, was calculated to be $3.16 \times 10^{-4}$ A/cm$^2$K$^{-2}$, of which value was much lower than theoretical value for n-type Ge (50 A/cm$^2$ K$^{-2}$) [20]. Such a large discrepancy between the experimental and theoretical values of Richardson constant could be attributed to the potential fluctuations at the Schottky interface caused by the presence of low and high barrier patches [21, 22]. In addition, structural defects, wrinkles of the graphene and fabrication process induced contaminations could be a main cause of Schottky barrier inhomogeneity [23-26].

The non-linearity of the ln($I_0/T^2$) - 1000 / T plot implies a strong temperature dependence of barrier height and ideality factor. From Eq. (1), ideality factor $n$ can be written as:

$$n = \frac{q}{kT} \left( \frac{dV}{d\ln I} \right)$$

(5)

The experimental values of $\Phi_{B0}$ and $n$ for the graphene/Ge SBDs at different temperatures, determined from Eqs. (2, 5) respectively, were summarized in Fig. 4. As seen in Table 1, the values of $\Phi_{B0}$ and $n$ for the 0.92 eV and 1.1 (at 400 K) to 0.56 eV and 2.38 (at 200 K), respectively. The obtained values of $n$ and $\Phi_{B0}$ are depicted as a function of temperature in Fig. 4. It revealed that both parameters exhibit strong temperature dependence that is the zero bias $\Phi_{B0}$ decreases and $n$ increases with decrease in temperature. Since current transport through metal-semiconductor interface is a temperature activated process, electrons at low temperatures are able to surmount the lower barriers and therefore current transport will be dominated by current flowing through the patches of lower $\Phi_{B0}$ and large $n$. As temperature increases, more electrons have sufficient energy to surmount the higher barrier. As a result, the $\Phi_{B0}$ will increase with the temperature and bias voltage [20].

The abnormal deviations of I-V characteristics of the graphene/Ge SBD from the thermionic emission theory can be explained by adopting the lateral distribution of barrier height with the Gaussian distribution. The Gaussian distribution of the BH with a mean value

![Fig. 3. The Richardson plots of the ln($I_0/T^2$) versus 1000 / T for graphene/Ge SBD in range of 200-400 K.](image)

![Fig. 4. Temperature dependence of the BHs and ideality factor for the graphene/Ge SBD.](image)

**Table 1.** Extracted temperature dependent Schottky barrier parameters

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$I_0$(A)</th>
<th>$n$</th>
<th>$\Phi_{B0}$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>$3.06 \times 10^{-10}$</td>
<td>2.38</td>
<td>0.56</td>
</tr>
<tr>
<td>240</td>
<td>$1.38 \times 10^{-9}$</td>
<td>1.59</td>
<td>0.65</td>
</tr>
<tr>
<td>280</td>
<td>$4.98 \times 10^{-9}$</td>
<td>1.30</td>
<td>0.75</td>
</tr>
<tr>
<td>320</td>
<td>$2.87 \times 10^{-8}$</td>
<td>1.23</td>
<td>0.81</td>
</tr>
<tr>
<td>360</td>
<td>$3.42 \times 10^{-7}$</td>
<td>1.12</td>
<td>0.85</td>
</tr>
<tr>
<td>400</td>
<td>$9.11 \times 10^{-7}$</td>
<td>1.10</td>
<td>0.92</td>
</tr>
</tbody>
</table>
Schottky barrier height ($\Phi_{bo}$) and a standard deviation ($\sigma_0$) can be described by following equations [27]:

$$\Phi_{ap} = \Phi_{bo}(T=0) - \frac{q\sigma_0^2}{2kT}, \quad (6)$$

where $\Phi_{ap}$ and $\sigma_0$ are apparent Schottky barrier height and standard deviation the $\Phi_b$ distribution, respectively.

The observed variation of ideality factor with temperature in the model is given by [28]:

$$\left(1 - \frac{1}{n_{ap}}\right) = \rho_2 - \frac{q\rho_3}{2kT}, \quad (7)$$

where $n_{ap}$ is the apparent ideality factor, $\rho_2$ and $\rho_3$ are voltage coefficients used to quantify the voltage deformation coefficients of the $\Phi_b$ distribution. As shown in Fig. 5, $\Phi_{bo}$ and $\sigma_0$, which correspond to the y-axis intercept and the slope of the linear fits to the plots of $\Phi_{ap}$ as a function of 1/2kT, and values are estimated to be 1.25 eV and 0.02 eV, respectively. The value of $\sigma_0$ is a general measure of the homogeneity of the Schottky barrier. The lower the value of $\sigma_0$ corresponds to a more homogeneous $\Phi_b$. Nevertheless, this inhomogeneity and potential fluctuation dramatically affect low temperature I-V characteristics. As compared to $\Phi_{bo}(T=0)=1.25$ eV, the $\sigma_0=0.02$ eV is not small, implying the existence of Schottky barrier inhomogeneity in the studied SBD. As stated in references [29-33], barrier inhomogeneities may occur as a result of inhomogeneities in the composition of the interfacial layer, non-uniformity of interfacial charges and interfacial layer thickness and charge puddles. Therefore, low temperature I-V characteristics are affected by this inhomogeneity and potential fluctuation. Moreover, the Fig. 5 shows the plot of $(n^{-1}-1)$ versus 1/2kT for graphene/Ge SBD. According to Eq. (7), this plot should be a straight line that gives the voltage coefficients $\rho_2$ and $\rho_3$ from the intercept and slope, respectively. The values of $\rho_2=0.431$ V and $\rho_3=-0.033$ V are obtained from the experimental data. The linear behavior of the plot shows that the ideality factor $n$ expresses the voltage deformation of the Gaussian distribution of the SBD. If the value of $\rho_2$ is negative, the $\Phi_b$ should decrease with increasing forward bias, which is in the opposite sense to image force lowering. The value of $\rho_3$ is indeed negative and thus the $\Phi_b$ increase with increasing forward bias. This bias dependent of $\Phi_b$ in the distribution through mean $\Phi_b$ and standard deviations leads to the temperature dependent ideality factor $n$ in inhomogeneous SBD [33, 34]. As mentioned above, the conventional Richardson $\ln(I_0/T^2)$ versus 1000/T plot deviates from linearity due the barrier inhomogeneity, it can be modified by combining Eqs. (2, 6), which yields:

$$\ln\left(\frac{I_0}{T^2}\right) - \left(\frac{q^2\sigma_0^2}{2k^2T^2}\right) = \ln\left(AA^*\right) - \frac{q\Phi_{bo}}{kT}, \quad (8)$$

Fig. 6 shows the modified Richardson plot for graphene/Ge SBD. The modified Richardson plot gives $\Phi_{bo}(T=0)=1.29$ eV and modified Richardson constant, $A^*=12.98 \text{Acm}^{-2}\text{K}^{-2}$. The $\Phi_{bo}(T=0)$ calculated from the modified Richardson plot is almost the same as the
\( \Phi_{th}(T=0) \) obtained from \( \Phi_{th} \) versus 1/2kT plot (Fig. 5). Furthermore, the modified Richardson constant \( A' \) is comparable to theoretical value of n-type Ge [19]. This implies the barrier inhomogeneities in the interface of graphene/Ge SBD.

V. CONCLUSIONS

We have fabricated monolayer graphene/Ge SBD fabricated on Ge film epitaxial grown on Si substrate. The I-V characteristics of this SBD in the temperature range of 200-300 K have been analyzed using standard thermionic emission theory with assuming a Gaussian distribution of the BHs. The value of \( \Phi_{th} \) increased and the \( n \) decreased with increasing temperature. From the conventional Richardson plot, \( A' \) was calculated to be \( 3.16 \times 10^4 \) Acm\(^{-2}\)K\(^{-2}\), respectively. On the other hand, a modified Richardson plot based on a Gaussian distribution of BH yielded \( A' \) of \( 12.98 \) Acm\(^{-2}\)K\(^{-2}\), of which value was comparable to the theoretical value for n-type Ge. Therefore, the abnormal temperature dependent I–V behavior of graphene/Ge SBD could be associated with the inhomogeneity in the BH.

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