Two-Dimensional Materials Inserted at the Metal/Semiconductor Interface: Attractive Candidates for Semiconductor Device Contacts

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Supporting Information

ABSTRACT: Metal–semiconductor junctions are indispensable in semiconductor devices, but they have recently become a major limiting factor precluding device performance improvement. Here, we report the modification of a metal/n-type Si Schottky contact barrier by the introduction of two-dimensional (2D) materials of either graphene or hexagonal boron nitride (h-BN) at the interface. We realized the lowest specific contact resistivities ($\rho_c$) of 3.30 nΩ cm$^2$ (lightly doped n-type Si, $\sim 10^{15}$/cm$^3$) and 1.47 nΩ cm$^2$ (heavily doped n-type Si, $\sim 10^{21}$/cm$^3$) via 2D material insertion are approaching the theoretical limit of 1.3 nΩ cm$^2$. We demonstrated the role of the 2D materials at the interface in achieving a low $\rho_c$ value by the following mechanisms: (a) 2D materials effectively form dipoles at the metal–2D material (M/2D) interface, thereby reducing the metal work function and changing the pinning point, and (b) the fully metalized M/2D system shifts the pinning point toward the Si conduction band, thus decreasing the Schottky barrier. As a result, the fully metalized M/2D system using atomically thin and well-defined 2D materials shows a significantly reduced $\rho_c$. The proposed 2D material insertion technique can be used to obtain extremely low contact resistivities in metal/n-type Si systems and will help to achieve major performance improvements in semiconductor technologies.

KEYWORDS: 2D material-inserted contact, work function modulation, pinning effect, specific contact resistivity, graphene, hexagonal boron nitride

The downscaling of complementary metal–oxide–semiconductor (CMOS) devices is necessary to achieve optimal packing densities and device performances. With much research effort and the development of various strategies, such as high-k/metal gates and fin-type field-effect transistor (FinFET) structures, current CMOS technology utilizes channel lengths of 10 nm and allows the manufacture of 4.5 GHz processor chips and 512 GB NAND memory chips. However, progress in downsizing CMOS technology has recently slowed, as the technology faces critical challenges.

One of the major challenges in the further downsizing of CMOS chips is the metal–semiconductor interfacial contact resistance, which deteriorates the device performance by inducing high operating voltages, high power dissipation, and low device operating speed. Ultimate, according to the International Technology Roadmap for Semiconductors (ITRS), sub-nΩ cm$^2$ specific contact resistivities ($\rho_c$) is required for sub-10 nm nodes.

The $\rho_c$ between a metal and Si can be determined by various charge-carrier transport mechanisms, which are critically influenced by the barrier width and height. Regarding the barrier width, the depletion thickness can be controlled by increasing the dopant concentration in the semiconductor, thereby reducing the $\rho_c$. However, further reduction of the $\rho_c$ is limited by intrinsic doping limits, difficulties in finely controlling the dopant profile, and high leakage currents. As for the barrier height, the energy difference between the work function of the metal and the electron affinity of Si in the contact, known as the Schottky barrier height (SBH), is the main cause of high $\rho_c$ values; the SBH can be modulated by matching the metal work function to the electron affinity of Si. However,  experimental evidence over the years has demonstrated that, regardless of the metal work function, the SBH tends toward a constant value because of Fermi-level pinning. In particular, pinning points near the valence bands of the most commonly used semiconductors such as Si, $\rho_c$...
The contact performance of the M/2D/Si structures is demonstrated using a nanoscale contact device with a contact size of 60 nm. The contact resistance of the M/2D/Si structures has yet been performed regarding the interfacial behaviors between the low-work-function metal and n-type Si. However, the insulating barrier decreases the tunneling current through the barrier or the thermionic field emission current over the barrier, thereby impeding reduction of the contact resistance. Furthermore, the optimized insulator thickness of less than 1 nm is technically challenging to achieve because of the native oxide of Si and the roughness caused by the nucleation growth mode of film growth. In addition, it is difficult to maintain the interface and composition of the ultrathin insulator because of the thermal budget in the standard manufactoring of integrated circuits. As another approach, the formation of various silicides between the metal and Si has been studied infrequently with controversial results. The inserted insulator alleviates Fermi-level pinning; thus, a low $\rho_c$ can be achieved in a metal–insulator–semiconductor (MIS) structure by tuning the SBH between the low-work-function metal and n-type Si. However, the insulating barrier decreases the tunneling current through the barrier or the thermionic field emission current over the barrier, thereby impeding reduction of the contact resistance. Furthermore, the optimized insulator thickness of less than 1 nm is technically challenging to achieve because of the native oxide of Si and the roughness caused by the nucleation–growth mode of film growth. In addition, it is difficult to maintain the interface and composition of the ultrathin insulator because of the thermal budget in the standard manufacturing of integrated circuits. As another approach, the formation of various silicides between the metal and Si interface has been studied. However, the silicide applied to the process has a relatively high barrier of $\sim 0.5$ eV. Current Si technologies use combined technologies with both highly doped semiconductors and silicides; no winning solution yet exists, and technological limitations remain in overcoming the contact resistance issue.

Meanwhile, two-dimensional (2D) materials such as graphene and hexagonal boron nitride (h-BN) have emerged as good candidates for interfacial layers because they have crystalline structures, single-atom thickness ($\sim 0.34$ nm), and high thermal stability ($>800^\circ$C). The interfacial behaviors of binary contacts such as metal/2D material or semiconductor/2D material structures have been studied in different electric and optical devices. However, most experiments on binary contacts have focused on specific phenomena, such as the modulation of the work function or the depinning effect. Further, ternary contact interfaces such as metal/2D material/semiconductor structures have been studied infrequently with controversial results. No systematic investigations on the $\rho_c$ of metal/2D material/Si (M/2D/Si) systems have yet been performed regarding the 2D material/Si junctions.

In this study, we suggest a method to reduce the $\rho_c$ of a metal–semiconductor junction by the insertion of the 2D materials of graphene and h-BN. We systematically analyze the behavior of the 2D materials at the metal/Si interface and investigate the major factors affecting $\rho_c$, i.e., the work function, SBH, and pinning effect in the M/2D/Si structures. The contact performance of the M/2D/Si structures is demonstrated using a nanoscale contact device with a contact size of 60 nm–100 μm over a wide range of doping concentrations (n-type, 1015 to 1021/cm3) using a CMOS-compatible process at the wafer scale. Finally, we achieve $\rho_c$ values of 3.30 and 1.47 Ω·cm2 with lightly doped n-type Si (1015/cm3) and heavily doped n-type Si (1021/cm3), respectively; these approach the theoretical limit predicted for $\rho_c$. Only monolayer 2D materials decrease the SBH by effectively changing the work function of the metal and the pinning point of Si by forming dipoles at the M/2D interface. This method is a suitable approach for achieving a low $\rho_c$ and can potentially lead to a $\rho_c$ of sub-nΩ·cm2.

Graphene and h-BN, which can be controllably grown as a monolayer with a thickness of 0.34 nm, were chosen as
semimetallic and insulating insertion materials, respectively. The devices for contact analysis were fabricated on a 6 in. n-type Si wafer (Figure 1a) based on the transverse line method (TLM)\textsuperscript{28} with 0.5–10 $\mu$m separation. Three-point measurements\textsuperscript{29} were performed on contact areas from 400 nm\textsuperscript{2} to 100 $\mu$m\textsuperscript{2} with a few-micrometer channel lengths to extract $\rho_c$ over multiple scales (Figure 1b). In particular, three-point measurements were used as a direct method for extracting low $\rho_c$ at the level of $\sim$1–10 n$\Omega$ cm\textsuperscript{2} in field-effect transistor (FET) devices using the relationship:

$$\rho_c = A(V_0 - V_m)/I_0$$

where $A$ is the area of the contact, $I_0$ is the applied current, and $V_0$ and $V_m$ are the measured voltages at the current source electrode and voltage measurement electrode, respectively. The fabrication process and analysis method are described in detail in Supporting Information 1, Figures S1 and S2. Briefly, M/2D/Si contacts were fabricated by the dry transfer of the 2D materials onto n-type Si wafers. After that, metal was evaporated onto the 2D material, and the TLM structure was fabricated by conventional e-beam lithography. The 2D materials are highly compatible with conventional CMOS integration processes, such as lithography and reactive ion etching (RIE); the devices were successfully fabricated on 6 in. wafers, as shown in Figure 1a.

A clean M/Si interface is necessary to accurately evaluate the electrical properties of the contact. In particular, native oxides are easily formed on the Si surface during the 2D transfer and device fabrication, which can cause many changes in characteristics.\textsuperscript{30} In the presence of native oxides, a low SBH and high $\bar{n}_c$ are observed, as shown in Supporting Information 2 and Figure S3. Figure 1c shows the clean interfaces of Ti/Si and Ti/graphene or h-BN/Si, obtained by high-resolution transmission electron microscopy (HR-TEM). The $\rho_c$ of these interfacially clean structures was characterized on Si with a 1018/cm\textsuperscript{3} doping concentration (Figure 1d). Highly processable metals widely used in CMOS devices were selected. The $\rho_c$ of the M/2D/Si structure is decreased dramatically compared to that of M/Si without the inserted 2D material. Regardless of the type of metal, the $\rho_c$ of M/graphene/Si is decreased by 3–4 orders of magnitude, and that of M/h-BN/Si is decreased by 1–3 orders compared to that of M/Si. The lowest $\rho_c$ value in M/2D/Si is achieved with Ti metal and graphene and/or h-BN. The $\rho_c$ of junctions obtained by conventional techniques such as silicide,\textsuperscript{17} MIS,\textsuperscript{12,14} and the 2D insertion technique are compared according to Si doping concentrations ranging from $10^{18}$/cm\textsuperscript{3} to $10^{21}$/cm\textsuperscript{3}, as shown in Figure 1e. For the junction obtained by the silicide technique, $\rho_c$ changes exponentially as a function of the doping concentration. The $\rho_c$ for the junction obtained by the MIS technique is less affected by the doping, and the $\rho_c$ difference for equivalent doping is determined by the type and thickness

Figure 2. (a) Work functions (W_F) of M/2D structures calculated via ab initio simulations as a function of the distance between the metal and 2D material. Arrows indicate the optimal distance of M/2D. (b) Work functions of M/2D structures with various metals calculated by ab initio simulations. (c) UPS spectra of M/2D structures. The work function was determined by the difference between the energy of the UV photons (21.22 eV) and the energy of the secondary edge. (d) Work functions of M/2D structures measured using UPS.
interface in achieving a low $\rho_c$ drain regions.

used in CMOS devices requiring high doping in their source/

functions of the M/2D system are predicted (Figure 2b).

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optimal distance is less than the sum of the van der Waals radii

and the variation in the work function depend on the

2D material to the metal. The number of electrons transferred

M/2D system is reduced by the transfer of electrons from the

result suggests that the M/2D/Si contact can be e

Nano Letters

Nano Lett. XXXX, XXX, XXX

Figure 3. Schottky barrier height (SBH) of M/2D/Si. (a) SBH of M/Si (black), M/h-BN/Si (blue), and M/graphene/Si (red) junctions with various metals. (b) SBH of M/Si without any 2D material (black squares), with h-BN (blue triangles), and with graphene (red circles) as a function of the work function of the metal or M/2D. (c) Calculated SBH of an M/graphene/Si structure with/without H termination of the Si surface and the corresponding atomic models (inset).

of the insulating material. In both cases, the $\rho_c$ in the $10^{20}/cm^3$ region is limited at $\sim 2$ n$\Omega$ cm$^2$. However, both graphene and h-BN materials in structures fabricated by the 2D insertion technique induce low $\rho_c$ values in the M/2D/Si structures from $\sim 1.4$ to $\sim 7.0$ n$\Omega$ cm$^2$ at all Si doping concentrations from $10^{17}/cm^3$ to $10^{19}/cm^3$. In particular, the $\rho_c$ of the 2D material-inserted structure at a low doping level of $10^{19}/cm^3$ is 1000 times lower than those of the silicide and MIS structures. This indicates that the lowering of $\rho_c$ by 2D material insertion is observed more clearly at lower doping concentrations compared to that observed for the junctions fabricated by conventional technology. The improved $\rho_c$ at low Si doping concentrations in the M/2D/Si structure can be applied to next-generation FETs such as junction-less FETs and tunnel FETs. 31−33 Furthermore, the $\rho_c$ of M/2D/Si at the Si doping level of $10^{20}/cm^2$ reached the lowest value of 1.4 n$\Omega$ cm$^2$, approaching the theoretical limit of 1.3 n$\Omega$ cm$^2$ at Si-doping of $S \times 10^{20}/cm^2$ predicted for $\rho_c$ by atomistic modeling. 41 This result suggests that the M/2D/Si contact can be effectively used in CMOS devices requiring high doping in their source/drain regions.

To understand the role of 2D materials at the metal/Si interface in achieving a low $\rho_c$ value, we conducted a systematic analysis of the major factors affecting $\rho_c$, i.e., the work function, SBH, and pinning effect in the M/2D/Si structures. First, we investigated the modulation of the work function of the M/2D structures with various metals. Figure 2a shows the work function computed through ab initio simulations as a function of the bonding distance between Ti and the 2D materials (graphene and h-BN). 35−37 As the distance between the 2D materials and Ti decreases, the work function of M/2D decreases substantially. The optimal distance between the 2D material and metal is determined by the highest adsorption energy of the system, as represented by the arrow in Figure 2a. In addition, the work function of the M/2D system is reduced by the transfer of electrons from the 2D material to the metal. The number of electrons transferred and the variation in the work function depend on the adsorption distance between the 2D material and metal. The optimal distance is less than the sum of the van der Waals radii of the 2D materials and the metal, and the 2D material is fully metalized. This result implies that the M/2D system acts as a new single material, rather than as a structure with two independent layers. Based on this simulation, the work functions of the M/2D system are predicted (Figure 2b).

The work functions of the M/2D systems are lower by 0.3−1.5 eV than those of the metals themselves. The work functions of Ti and Ni, which bond strongly with the 2D materials, show particularly dramatic reductions by 0.9−1.5 eV. The effect of the lowering of the work function by h-BN is greater for most of the metals than that by graphene, owing to the higher electron transfer.

The work functions of the M/2D systems were experimentally determined by ultraviolet photoelectron spectroscopy (UPS) analysis (Figure 2c, Supporting Information 3). The work functions were extracted by the difference between the energy of the UV photons (21.22 eV for He I radiation) and the binding energy of the secondary edge measured by UPS analysis. Figure 2d shows the experimental work functions of the M/2D systems. Although the variations in the experimental work functions are relatively smaller than those predicted by the simulations, the results otherwise show good agreement. Furthermore, in Al, Ti, and Cr metals with low-work functions after 2D interaction, a low $\rho_c$ is expected after contact with n-type Si by forming low SBHs below $\sim 0.2$ eV, if the 2D inserted contact is in a fully depinned state. Figure 3a shows the SBH of M/Si and M/2D/Si systems. The SBH was extracted by investigating the temperature dependence of the M/Si contact in the reverse-bias saturation regime (Supporting Information 4, Figure S4). The M/Si contacts of most of the metals have high SBHs of 0.4 eV or more; however, the M/h-BN/Si contact has a relatively low SBH of 0.3 eV. In particular, the M/graphene/Si contact has a low SBH below 0.2 eV with most metals, which is consistent with the low $\rho_c$ of M/graphene/Si (Figure 1a). This means that the SBH reduction between M/2D and Si arises from the decreased work function of M/2D, which in turn lowers the $\rho_c$ of the M/2D/Si junction.

We also examined another important factor of the $\rho_c$ of the M/Si contact, the pinning effect. Simply, we can guess that the insertion of an ultrathin 2D material between the metal and Si creates a depinning state at the Si interface, similar to insulator insertion behaviors in MIS structures. The pinning factor, S, extracted from the slope of the SBH vs metal work function, has a value between 1 (representing the Schottky limit) for perfect depinning and 0 (representing the Bardeen limit) for full pinning. Figure 3b shows the measured SBH of M/Si or M/2D/Si as a function of the work function of the metal or the M/2D system. The M/Si systems show high pinning states with the pinning factor of 0.32, and the SBH of M/Si does not
change significantly with changing metal work functions. In contrast, the M/2D/Si systems with h-BN and graphene have almost equal SBHs, irrespective of the work function of M/2D. Contrary to our expectations, the pinning factor of M/2D/Si is almost 0, that is, full pinning occurs, which is quite different from the depinning results of binary 2D/Si contacts. This also implies that the low-work function of M/2D does not directly lower the $\rho_c$. Fully metalized graphene has a density of states (DOS) similar to that of a metal, unlike intrinsic graphene (Supporting Information 5, Figure S5a). We discovered that the fully metalized 2D materials on metal lose the inherent depinning effect of 2D materials in the ternary M/2D/Si contacts because the contact acts as a new single material. However, despite the strong pinning of the interface between M/2D and Si, the pinning point is near the conduction band of Si. Therefore, the SBH at the interface between M/2D and Si is reduced. The pinning points of the M/graphene/Si and M/h-BN/Si systems are respectively 4.15 and 4.27 eV, lower than the original Si pinning point of 4.5 eV. The change in the SBH due to the inserted 2D material as a function of the work function difference agrees with the equation S2 in Supporting Information 6. The SBH appears to be constant with varying metal work functions, as shown in Figure 3b. In other words, although the contact between the M/2D and Si surface is pinned at a new position by its metalized state, the $\rho_c$ is decreased by the decrease in the SBH. The pinning effect is strongly related to the surface state of Si. In general, the state of the Si surface is known to be unstable owing to many defects, dangling bonds, rearrangement, and so on. Furthermore, the surface passivation of Si with H is also unstable, maintained for only a few minutes in general conditions or during processing. However, it is important to understand the relationship between pinning and the surface properties. To confirm the surface state effects on pinning, we calculated the pinning effect of two different Si surfaces, H-terminated Si and Si without H-termination. As shown in Figure 3c, when Ti/graphene is in contact with H-terminated Si, the pinning factor is computed as $\sim 0.37$. On the contrary, full pinning ($S = 0$) is predicted when Ti/graphene makes contact with Si without H-termination. The behavior of Ti/h-BN on the two different Si surfaces also shows similar results (Supporting Information 7, Figure S7). To control the pinning effect perfectly, research on stable surface control remains necessary in Si technology.

Figure 4 shows the atomic structure and the expected band structure when the number of layers of graphene is changed from 1 to 3. Figure 4a shows the change in the SBH and $\rho_c$ according to the number of layers of graphene (Supporting Information 8, Figure S8). When monolayer graphene is inserted into M/Si, SBH and $\rho_c$ decrease significantly relative to those of the original M/Si. For monolayer graphene, M/graphene in contact with Si is similar to a unified material because it is fully metalized. However, bilayer graphene is hardly metalized, and trilayer graphene is expected to exist as a pristine graphene layer affected a little by the metal. This property can be confirmed by the change in the DOS of the metal/multilayer graphene (Supporting Information 5, Figure S5b). For this reason, the work function of M/graphene is increased by increasing the number of graphene layers, which increases the SBH and $\rho_c$ of the M/graphene/Si system, as shown in Figure 4b. Moreover, for bilayer graphene, $\rho_c$ is slightly higher than that for monolayer graphene, because of the limited current flow by the increased electron tunneling length. As a result, a uniform and monolayer 2D material of 0.34 nm in thickness can significantly reduce the $\rho_c$ to a level equivalent to the ideal value.

Figure 5a summarizes the relationship between $\rho_c$ and SBH in the M/Si contact, according to the type of 2D material. For
M/Si and M/2D/Si, a low $\rho_c$ is observed at low SBH; these show a nearly exponential relationship. Figure 5b shows the expected band structures of the M/Si, M/graphene/Si, and M/h-BN/Si contacts. Carrier transport in the contact between the metal and semiconductor is simply classified as thermionic emission, thermionic field emission, or tunneling. The currents of thermionic emission and thermionic field emission are strongly dependent on the SBH, and the tunneling current is significantly influenced by the thickness of 2D materials. Therefore, the M/2D/Si system with a lower SBH can increase the current level to exceed that in M/Si. In addition, despite the additional layer inserted in the contact system, the atomically thin and well-defined 2D materials do not affect the reduction of the current level, unlike MIS systems. Therefore, low $\rho_c$ values are achieved.

In conclusion, we achieved the lowest $\rho_c$ of 1.47 nΩ cm$^2$ using monolayer graphene insertion at the Ti/n-type Si interface; this value approaches the theoretical $\rho_c$ limit of 1.3 nΩ cm$^2$. To understand the role of the 2D materials of graphene and h-BN at the interface in achieving a low $\rho_c$ value, we systematically confirmed that 2D materials could lower the work function of the metal by forming dipoles at the M/2D interface. However, the low-work function of M/2D did not directly lower the SBH; instead, the pinning points shift because of the dipole effect. The modiﬁed pinning points of the M/graphene/Si and M/h-BN/Si systems are determined as 4.15 and 4.27 eV, respectively, which are much lower than the original Si pinning point of 4.5 eV. As a result, the SBH at the interface between M/2D and Si can be reduced because the pinning points are near the conduction band of Si; thereby, the lowest $\rho_c$ could be achieved. The proposed 2D material insertion technique can be used to obtain sub-nΩ cm$^2$ contacts for metal/n-Si, thus dramatically improving CMOS performance.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.8b01509.

Experimental details of fabrication, measurement methods for specific contact resistivity, work function, and Schottky barrier height, analysis of multilayered graphene by transfer, and effect of a few-nanometer-thick native oxide in M/Si contact (PDF)

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The Letter was written through contributions of all authors. All authors have given approval to the final version of the Letter.

Notes

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**REFERENCES**


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