Superior Thermal Dissipation in Graphene Electronic Device through Novel Heat Path by Electron-Phonon Coupling

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Abstract

Interfacial thermal resistance (ITR) plays an important role in thermal dissipation across different materials and it has been widely investigated in recent years. In this work, we measured the relative change of the ITR between metal and aluminum oxide treated with O₂-plasma. Significant reduction of ITR is observed. The measured data shows that plasma treatment induces an order of magnitude decrease of ITR, which is mainly attributed to the direct electron-phonon coupling across the interface. Scanning thermal microscopy technique measurement of graphene electronic devices on aluminum oxide gave direct evidence for heat dissipation applications by tuning the surface charge carries concentration.

Keywords: thermal dissipation; electron-phonon coupling; graphene; metal-nonmetal interface; interfacial thermal resistance

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1. Introduction

In graphene-based electronic devices, the Joule heat is generated in graphene and accumulates between the dielectric layer and graphene film during operations.^[1] Therefore, the interfacial thermal resistance (ITR) at solid-solid interface, especially metal-nonmetal interface, has aroused extensive attention due to its extremely important role in heat dissipation.^[2,3,4,5,6] In general, the thermal energy in metal can be transferred to nonmetal via three channels which can be equivalently derives as a series-parallel thermal network (Fig. 1(a)).^[7] Firstly, the upper and lower limits of interfacial thermal conductance (ITC), which is the inverse of ITR, through phonon-phonon interaction across the interface (Q₃ in Fig. 1) are given by acoustic mismatch model^[8] and diffuse mismatch model,^[5] respectively. Secondly, the electrons transfer thermal energy to the phonons within the metal and then the phonons transfer the energy to the nonmetal side (Q₂

in Fig. 1). Such a channel acts in series with the first channel, which will further increase the value of ITC.^[9] While compared with the measured values across a variety of metal-nonmetal interfaces, such as Pb/Ti/Al/Au (metal) and diamond/sapphire/BaF₂ (nonmetal) interfaces, large underestimations were observed in models considering the above two channels. Thus it's reasonable to take into account the third channel, namely, the direct coupling between electrons from the metal side and phonons from the nonmetal side (Q₁ in Fig. 1).^[10,11,12]

The direct electron-phonon coupling mentioned above has not been experimentally verified yet. Because it is hard to distinguish the direct electron-phonon coupling contribution from other two channels. It has been reported that the ITC across gallium-He II interface at low temperature using the AC technique.^[13] Rotkin *et al.*^[14] demonstrated the dominant role of electron-remote interfacial phonon (RIP) coupling in the heat dissipation across carbon nanotube (CNT)-SiO₂ interface, which was later proved experimentally by Baloch *et al.*^[15] Nevertheless, unlike those in CNT-SiO₂ interfaces, the upper limit of the contribution of RIP scattering in ITC across unbiased graphene-SiO₂ interfaces was found to be < 2% in voltage-modulated thermal reflectance (VMTR) experiments,^[16] letting alone the effect of better conformity of the interface. Therefore, whether the role of direct electron-phonon

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Fig. 1 Schematic illustration of heat conduction from metal to nonmetal across the interface. Q is the total heat current. (a) shows traditional heat path between metal and nonmetal interface and opening a new heat path through electron-phonon coupling at the interface (b).

coupling is important and what the mechanism of direct electron-phonon coupling is across the interface are still under debates. The experimental observation of metal-nonmetal interfacial thermal transport behavior will give us the opportunity to investigate this process.

Here we adopted differential 3ω method to measure the variations in ITR across Au- Al_2O_3 interfaces after treating the Al_2O_3 surface with O_2 -plasma. Comparing the ITR with and without applying the O_2 -plasma, we found that the longer treated time of O_2 -plasma corresponded to smaller ITR. The surface roughness of Al_2O_3 was morphologically tested using atomic force microscope (AFM) to eliminate the effect from surface contamination/roughness. Then we deduced the carrier concentration of Al_2O_3 under different O_2 -plasma treatment time by transfer a single layer graphene and measuring its Hall resistance. These results show that with the increase in treatment time of plasma, the carrier concentration is increased. According to the surface states electron-phonon coupling model proposed by Lu *et al.*,^[17] the increase of the

charge carrier concentration leads to an increase of Fermi level, which leads to a large increase of ITC. In addition, the results of scanning thermal microscopy technique (SThM) measurement based on graphene/ Al_2O_3 devices show a broader space for the application of thermal dissipation.

2. Experiments

2.1 Doping the Interface Between Metal and Nonmetal

The sample fabrication process is summarized in Fig. 2(a). Nearly 200 atomic layer deposition (ALD) cycles were firstly achieved to deposit 30 nm Al_2O_3 in this work. The 30 nm-thickness Al_2O_3 layer was deposited onto silicon dioxide substrate under the temperature of 100 °C by an ALD system in which AlMe_3 and H_2O were used as the precursors of Al and O, respectively. Subsequently, the samples were treated by O_2 -plasma with different times varying from four minutes to ten minutes (marked as S4, S5, S6, S7, S8, S9, S10) (Table 1.) and one sample without any treatment (marked as S0) was regarded as reference. The plasma cleaner machine was used to perform the operation whose power is 10.5 W for medium-power setting. O_2 -plasma treatment can thoroughly clean the organic matter and simultaneously evacuate the pollutants by vacuum to avoid secondary pollution effectively. More importantly, this process will lead to the recombination among the chemical component on the surface of samples and form new surface features. Finally, a narrow Au electrode with 50 nm in thickness, which is suitable for 3ω measurement, was evaporated onto all the samples through a stainless steel mask by standard thermal evaporation method (insert of Fig. 2(b)).^[18] To eliminate sample-to-sample difference, all the electrodes of these samples were evaporated at the same time. This kind of four probe electrode will enable the accurate thermal resistance measurement crossing several interfaces.

2.2 Interfacial thermal resistance measurement

To obtain the interfacial thermal resistance of different samples, the differential 3ω method, which is one of the most common technique to measure the thermal conductivity of

Fig. 2 (a) Fabrication process of metal-nonmetal interface. (b) Temperature changes versus the frequency of AC-current source for sample S0, S5, S8, S10.

Table 1. The thermal resistance variation changes with the treatment time by O₂-plasma at the room temperature.

Sample name	S0	S4	S5	S6	S7	S8	S9	S10
Plasma time (mins)	0	4	5	6	7	8	9	10
$\Delta R_{th}(10^{-8} \text{ m}^2 \text{KW}^{-1})$	/	1.40	2.06	6.41	9.24	8.10	9.94	13.52

bulk material and thin film was employed in this work.^[19] For differential 3ω measurement, a thin metal electrode with specific shape and thickness is firstly deposited onto the sample. The Au electrode pattern is 50 μm across and 1000 μm in length so that it can guarantee the one-dimensional heat flux from sample to substrate when a driven AC-current was applied. There is a linear relationship between its resistance and temperature, following $R = 7.22 + 0.03561T$ between the temperature range of 100 K - 300 K in this experiment. Then a driven AC-current with varying frequency of ω was applied into this metal electrode so that this electrode could act as heater and temperature sensor simultaneously. A spontaneous temperature change with frequency of 2ω ($T_{2\omega}$) will be obtained by detecting the voltage signal with frequency of 3ω ($V_{3\omega}$). Here, the temperature raise of electrode $T_{2\omega}$ can be calculated from^[20]

$$T_{2\omega} = 2 \frac{dT}{dR} \frac{R}{V} V_{3\omega}, \quad (1)$$

where $V_{3\omega}$ is the detected 3ω voltage signal, R is the resistance of electrode and V is the voltage with frequency of 1ω . This temperature raise will decrease with the raise of frequency, which is shown in Fig. 2(b). Then the differences in thermal resistance (ΔR_{th}) between different samples can be obtained by

$$\Delta R_{th} = \frac{S \Delta T_{2\omega}}{P}, \quad (2)$$

where S is the cross-section area of sample below electrode, P is the power of heat source, $\Delta T_{2\omega}$ is temperature difference between samples. The thermal conductivity of silicon wafer from $T = 100$ K to $T = 300$ K can be detected simultaneously during the measurement of ITR. The thermal conductivity of S0 is about $\sim 113 \text{ Wm}^{-1}\text{K}^{-1}$ and $\sim 660 \text{ Wm}^{-1}\text{K}^{-1}$ at $T = 300$ K and $T = 100$ K, respectively. It shows that 3ω measurement in this work is reliable by comparing to the reported result.

3. Results and Discussions

The ITR variations ΔR_{th} of Au-Al₂O₃ interface change as a function of the treatment time with O₂-plasma at room temperature is shown in Fig. 3(a). The thermal resistance variations were obtained from $\Delta R_{th} = R_{th,0} - R_{th,i}$ ($i = 4, 5, 6, 7, 8, 9, 10$ mins), which is listed in Table 1. With the increase of treatment time, the thermal resistances decrease dramatically, but their variations become more remarkably which vary from $\sim 1.40 \times 10^{-8} \text{ W}^{-1}\text{m}^{-1}\text{K}$ to $\sim 13.5 \times 10^{-8} \text{ W}^{-1}\text{m}^{-1}\text{K}$. We also measured the thermal resistance variation at different temperature (Fig. 3(b)). All the three samples show similar temperature dependence tendency that the thermal resistance variation is slightly increased with the improvement of temperature, which

indicates that the treatment time with O₂-plasma significantly change the thermal transport capability through metal-Al₂O₃ interface.

To demonstrate the essential reasons that influenced the ITR, we should ensure the factors that have been affected by O₂-plasma. Firstly, treatment with O₂-plasma may probably breakdown the Al₂O₃ film electrically, thus we measured the electrical resistance of Al₂O₃ after O₂-plasma treatment for ten minutes (inset of Fig. 3(a)). This ultralow electrical conductivity indicates that O₂-plasma did not breakdown the Al₂O₃ film and the electrical thermal conductivity of Al₂O₃ is negligible. Secondly, O₂-plasma treatment with different time may lead to the variation of the surface roughness of Al₂O₃ layer. To verify whether the roughness is the factor that plays an important role in the interface thermal transport in this

Fig. 3 (a) The thermal resistance variation changes as a function of the treatment time with O₂-plasma under the room temperature $\Delta R_{th} = R_{th,0} - R_{th,i}$ ($i = 4, 5, 6, 7, 8, 9, 10$ mins). The black square is sample S8' which was kept in vacuum for two months after O₂-plasma. Insert: electrical resistance of Al₂O₃ after plasma. **(b)** The thermal resistance changes versus the temperature.

work, the AFM image for S0, S8, S10 are shown in Fig. 4. The roughness value of Al_2O_3 films keep within 0.3 nm-0.37 nm, which provides specific evidence to support that the treatment of O_2 -plasma did not make obvious influence to the roughness of Al_2O_3 film. Thirdly, surface chemical bonds introduced by O_2 -plasma will also affect the ITR,^[21] which however will decay with time. To eliminate the effect the chemical bonds, we measured another sample (S8'), whose electrode was evaporated two months (kept in a high vacuum chamber with vacuum level better than 1×10^{-5} pa) after 8-minutes O_2 -plasma (Fig. 3(a)). The result indicate that chemical bond could not explain the huge reduction in ITR. Finally, we focus on the carrier concentration, which could be obviously changed by the treatment of O_2 -plasma.

The O_2 -plasma treatment is believed to change the carrier concentration of Al_2O_3 on the surface and will open a new heat path: the electrons on metal transfer thermal energy to the electrons on surface state of nonmetal, which will then transfer the energy to phonons of nonmetal through direct electron-phonon coupling (Fig. 1(b)). This new and strong electron-phonon coupling will open a new heat path between metal and nonmetal.^[17]

To testify the contribution of electron-phonon coupling to ITR in this work, we measured the Hall resistance of graphene samples which were transferred onto the surfaces of different O_2 -plasma treated Al_2O_3 layers. The insert of Fig. 5(a) shows the schematic diagram for Hall measurement. The sample fabrication steps are same as Fig. 2(a). Subsequently, single layer graphene synthesized through chemical vapor deposition (CVD)^[19] were transferred onto Al_2O_3 films (including S0, S5, S8, S10).^[22] Then the standard E-beam lithography, thermal

evaporation method and lift-off process were used to make suitable electrodes for hall measurement. We swept the magnetic field from -5T to 5T at room temperature. The hall resistance R_{xy} versus different magnetic field of S0 is plotted in Fig. 5(a). The carrier concentration of graphene samples onto different treated Al_2O_3 layers can be easily obtained by analyzing the slopes of hall resistance. According to the varied carrier concentration of graphene (Fig. 5(b)), it could be inferred that the carrier concentration of Al_2O_3 films have been changed by O_2 -plasma treatment. Note the measured carrier concentration of graphene is not the same with that in Al_2O_3 , it only reflects the fact that carrier concentration on surface of Al_2O_3 changes. With the increase of O_2 -plasma treatment time, the carrier concentration of graphene is higher. So the higher carrier concentration of aluminum oxide will enhance the electron-phonon coupling through the metal-nonmetal interface (Fig. 1(b)), leading to the reduction of interfacial thermal resistance.

To further prove that O_2 -plasma treated devices has lower ITR and promising prospect on the application of heat dissipating devices, we reintroduce scanning thermal microscopy technique (SThM), a novel method, which could obtain the surface topography and temperature distribution simultaneously based on the atomic force microscopy. Fig. 6(a) shows the topographic image of a part of the graphene device, whose graphene sample was transferred onto sample S10. The non-treated graphene sample S0 is regarded as reference in this work. With the same DC-current applied onto the graphene films, this self-heating process will generate joule heating and lead to higher temperature near the center region (dashed square in Fig. 6(a)). Figs. 6(b-c) shows the temperature image

Fig. 4 The surface roughness of Al_2O_3 (S0, S8, S10) measured by Atomic Force Microscope.

Fig. 5 (a) Hall resistance R_{xy} versus magnetic field. The insert is the schematic diagram for hall measurement. (b) The carrier concentration of graphene under different O_2 -plasma treatment time.

of the graphene device S0 and S10 at the same high temperature region corresponded to power density of 1340 W/cm^2 and 2700 W/cm^2 , respectively. The temperature variation of reference device is much higher than that of S10 (Fig. 6(e)), which directly illustrate that O_2 -plasma treatment effectively enhance the heat dissipation effect of metal-nonmetal device.

4. Conclusions

In summary, we treated the surface of ALD-grown Al_2O_3 with O_2 -plasma with different time ranging from 4 to 10 minutes. We used differential 3ω method to measure the changes in the interfacial thermal resistance across Au- Al_2O_3 interfaces. Results show that the change in interfacial thermal resistance increases with the plasma treatment time. The carrier concentration was extracted by measuring the Hall effect of graphene which was transferred onto the surface of Al_2O_3 . We found a significant increase in the carrier concentration with the increase of plasma treatment time, which could induce a change in the relative Fermi level. Finally, we measured the temperature distribution of graphene- Al_2O_3 devices utilizing SThM technique, the better heat dissipation of O_2 -plasma treated sample indicating the promising prospect on the improvement of electronic devices.

Fig. 6 AFM and SThM image of graphene device used. (a) AFM topological image of device, where bright parts are the electrodes. (b) Thermal image of graphene device (S0) heated at $I = 5 \text{ mA}$, represent square region in (a). (c) Thermal image of graphene device (S10) heated at $I = 5 \text{ mA}$, represent square region in (a). (d) The temperature profile of S0 and S10 of the dash line in (b) & (c). (e) The relationship between temperature changes and power density. The slope of S0 is larger than S10, indicating better heat dissipation in S10.

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Supporting information

Not applicable

Conflict of interest

There are no conflicts to declare.

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